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RESEARCH ARTICLE

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Chemical, Thermal and Electrical Destabilization Methods of Crude Oil Emulsions: A Review

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Abstract:

In crude oil industry, highly stable water-in-oil (w/o) emulsions are inevitably formed during extraction process due to multiple water and oil contact. These emulsions are stabilized by the indigenous surface active species ubiquitously present in the crude oil. The recovery of crude oil through emulsion breakdown and subsequent separation (demulsification) is of a significant importance in order to avoid costly pumping and cooling of emulsion which enhances emulsion stability. This review paper has discussed chemical, thermal and electrical demulsification techniques demonstrating their theoretical aspects and practical applications highlighting the mechanism(s) by which these methods proceed in the demulsification task. Of these techniques, chemical treatment is not sufficient enough to demulsify w/o emulsions; besides, it is costly. Thermal procedures on their own have been found energy-intensive and might cause loss of valuable light components naturally found in the crude. If coupled with chemical methods in which a chemical demulsifier is used, thermal methods, in which heat is a must, may result in the deterioration of the performance of that demulsifier. Likewise, use of electricity to demulsify w/o emulsions suffers from some obstacles. Unless a costly high voltage is applied, coalescence of demulsified droplets into larger droplets might occur. Furthermore, due to space limitations in offshore crude oil fields, use of electricity to breakdown w/o emulsions is not a practical approach.

***Keywords*:** Crude oil, emulsion, stability, coalescence, demulsification.

1. Introduction:

Emulsions formation is an inevitable phenomenon in crude oil industry due to multiple water and oil contact during oil processing [1]. Elsewhere, it was elucidated that existence of surface-active compounds such as asphaltenes, resins, etc. is with enormous problematic influence on the oil industry through production and refinery stages through emulsion stabilization [1-12]. Emulsion stability level is proportional with crude content of these emulsifiers and their interactions; higher content of these compounds; of-course, grants the emulsion a higher stability extent. Therefore, in order to meet pipeline and exportation specifications; demulsifying of these emulsions (i.e. reversible flocculation/coagulation followed by irreversible coalescence of the dispersed phase droplets and eventually creating two distinctive layers of oil phase on top and water/aqueous phase at the bottom [10,11-19] is an important but has been a difficult process in petroleum industry [1,20-25] as otherwise severe processing problems will arise. These generally include pipes and equipment corrosion, catalyst poisoning and difficulties in transportation.

In order to effectively meanwhile economically demulsify water in oil (w/o) emulsions, it is crucial to understand how they have been stabilized. This requires knowledge of asphaltenes and resins properties and interactions as they have been considered as the main emulsion stabilizers. Other stabilizers such as wax, acids and solids are also of considerable importance due to their strong tendency to interact with asphaltenes and/or resins [3,8-9,16,20-22,26-45].

Although, Kenneth J back in 1988 concluded that no much work was reported about demulsification of emulsions for reasons that the basic work was already done and that no more work to be done, most of the work was commercially conducted; thus, cannot be published unless patented and also due to a difficulty of the area of emulsions [19]. Currently, there has been a progress; chemical, thermal and electrical demulsification works are underway. Chemical treatment through the use of chemical demulsifiers (surface active agents) have been the main methods used to separate these problematic emulsions, heating/ microwave demulsification and electro-demulsification have also been in use. Combination of two techniques, in order to enhance demulsification efficiency, was also reported [1,8,12,14,16,20-22,46-52]. Microfiltration has also been used to breakdown w/o emulsions. It is worth observing that there has been no universal method that can be applied for all emulsions, i.e., methods are very application/crude specific, with the trial and error principle has been the basis to decide on the applied method for a given emulsion [56-61]. This is simply due the diversity of crude oils as well as brines and hence resultant emulsions [16].

Due to the wealth of details of the subject of microfiltration of such emulsions for the purpose of w/o demulsification, it has been decided not to include this subject into the contents of this review paper to avoid a lengthy manuscript. Accordingly, this review shall try to give a summary of only chemical, thermal and electrical demulsification techniques demonstrating their theoretical aspects and practical applications highlighting the mechanism(s) by which these methods proceed in the demulsification task.

2. Demulsification Methods:

2.1 Chemical Demulsification Methods:

Various chemicals (chemical cocktails) which are of different surface-active characteristics have been widely implemented to destabilize w/o emulsions such as acids, bases, fatty acids and their derivatives, alcohols, amines, acetone, copolymers of ethylene oxide, polyoxyethylene, polypropylene or polyester and propylene oxide, etc., and some other commercial demulsifiers [1,11,22,32,38,44,62-66]. Owing to their surface active character, demulsifier molecules consist of hydrophilic and hydrophobic groups. At an interface, hydrophilic groups will orient toward the polar phase (water) while hydrophobic groups will choose the oleic phase to orient toward [63]. For further information on the various employed chemical demulsifiers a rather comprehensive list is available [54,68].

Demulsifiers according to their molecular weight are classified into two grades; these are low molecular weight (LMW) demulsifiers, typically below 3000 Da, and high molecular weight (HMW) demulsifiers, usually above 10,000 Da. The latter demulsifiers due to their higher molecular weight diffuse slower than the former ones [22]. For petroleum emulsions (w/o) the latter type is mostly used in comparison to the former one. In addition to high molecular weight, these demulsifiers should be highly branched and with a great affinity towards water droplets [48]. Generally, demulsifiers of the first class are some types of oil-soluble surfactants such as pure paraffinic hydrocarbons, aromatic hydrocarbons, alcohols and diols and they function through increasing the interfacial activity (suppression of the interfacial tension) and changing the wettability of surface active components, respectively. HMW demulsifiers represent polyelectrolytes and various types of oil-soluble polymers and macromolecules like block copolymers. These demulsifiers influence the interfacial film via their ability to penetrate through this film modifying the rheological properties inducing film drainage which has the sequence of droplet coalescence and subsequently phase separation [22,38,68].

Prior to the addition of a demulsifier to an emulsion, surface active components maintain a high interfacial tension within the interfacial film [43] and a low interfacial tension elsewhere away from the film within the emulsion. This set-up is reversed once a demulsifier has been added, owing to its strong surface-active properties, and that binding forces between water and oil droplets are reduced and the film is drained , i.e. the emulsion becomes unstable and therefore water droplets are flocculated and then coalesced [48,63,69]. Therefore, it can be inferred that the main contribution of a chemical demulsifier to reduce the stability of an emulsion (speed up droplet coalescence) is its ability to improve film drainage by suppressing the tension gradient (Gibbs-Marangoni effect) [23,49,51,54,66,71]. Interfacial tension measurements have been widely used to relate the adsorption of a demulsifier at the oil/water interface so that demulsifier/interface based-interactions (demulsifier functionality) can be studied [17,39].

The structure of the demulsifier, its ability to distribute throughout the bulk of emulsion, speed of agitation, its partitioning character between the phases at the interface, ambient temperature, stability of the emulsion and pH and salinity of the water phase are all factors influence the demulsifier performance [18,40,48,71]. Concentration of the demulsifier is also an important factor as it was suggested that too high demulsifier concentration, that’s too higher than critical micelle concentration (CMC), weakens the demulsifier action through asphaltene solubilization. In fact, demulsifier(s) should be dosed carefully. Too little demulsifier will not be beneficial in term of emulsion breakdown, too much demulsifier(s); on the other hand, may further complicate the emulsion stability [16,44]. Too high demulsifier(s) concentration(s) may result in increased emulsion stability, perhaps as a result of a new stabilizing film around emulsion droplets by the demulsifier(s) [22]. Experimental evidence shows that the rate of demulsification was increased with surfactant concentration until a threshold of surfactant aggregation is reached at which lower demulsification rates were obtained or the rate of demulsification became independent on the demulsifier concentration [54,71].

In addition, there are some properties a good chemical demulsifier should possess. A good demulsifier in the first instance should be a poor emulsifier with a high molecular weight and amphiphile character with a tendency to thoroughly mix through the emulsion to speed up water-oil separation [52-53,66,68,73]. Also, equal partitioning between both phases at the interface (water and oil) was considered as an important factor for swift demulsifier adsorption at the interface to reduce interfacial tension gradient and therefore it increases the demulsifier performance [12,23,38,48,52-53,66,71]. Its interfacial tension has to be notably lower than that of the indigenous surfactants of the crude so that demulsifier molecules can absorb at the interface so as to can displace emulsifier molecules [38,45,53-54,62,64]. Furthermore, a successful demulsifier should have a high diffusivity and activity through the interfacial film so that it functions to reduce interfacial film elasticity and dynamic film tension [16,18,38,48,53,70].

Upon the successfulness of demulsifier(s) to demulsify emulsion, there are two different water resolution profiles. One is the immediate water resolution profile which occurs when the demulsifier is not mixed with a carrier solvent prior to its addition to the emulsion. The second one is the inductive water resolution profile (not instantaneous) which was demonstrated as a result of mixing the demulsifier with carrier solvent before its usage as a demulsifier. It was stated that the mechanism by which a demulsifier disturbs oil/water interface is dependent on the nature of the demulsifier itself as demulsifiers of alcoholic character act by altering the rigidity of the interfacial layer through diffusion/partitioning process, whereas aminic demulsifiers were reported to increase the hydrophilicity of the interfacial layer through the attachment to the functional groups of the compounds at the interface layer [71].

Mohammed et al., investigated the demulsification of w/o emulsions by using different non-ionic demulsifiers of different HLB numbers as shown in Fig. (1). At first glance, these investigations demonstrated that higher separation efficiency is obtained as the demulsifier concentration increases. Using Unidem120 demulsifier at low concentrations gave a very little separation. Hence, in practical applications this demulsifier is used at lower concentrations but with the assistance of heat and electrical treatment to help resolve the emulsion. However, higher demulsifier concentrations led to demulsification profiles with higher separation efficiencies until a plateau in demulsification efficiency is reached against concentration increment. In addition, the water resolved from this test was murky in its appearance [71].

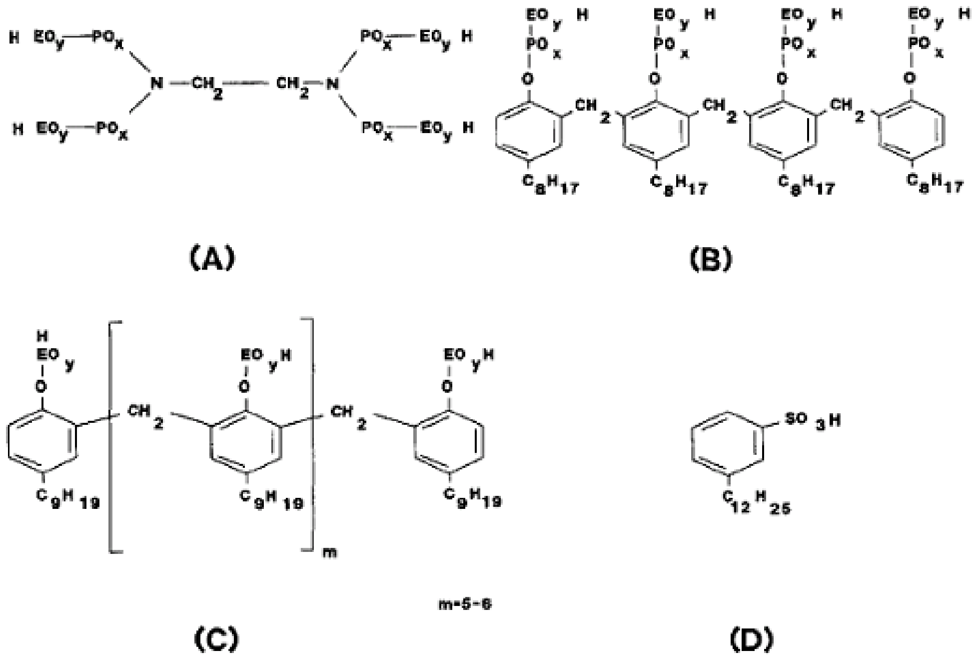

Fig. (1). The structure of the demulsifiers used [71].

Adding T1301 (which displaces the asphaltene from the interface layer), T1302 (which partitions to the water phase due to its high ethylene oxide, EO number), T701 (which partitions to the oil phase due to its low solubility in water due to its small EO number) and T803 (which partitions to the water phase due to its high EO number) to the emulsion increased the percentage of water being resolved. However, with overdosing, the separation efficiency collapsed to a plateau value even at higher concentrations. Different pattern was attained when BJ18 (which lacks enough wetting agent to drag the asphaltic film into the oil) or T150l (which displaces the asphaltene from the interface layer) were used, with higher deterioration to zero water separation. Nevertheless, Adding IL2 (wetting agent) which wets waxes and neutralises basic groups found in the interfacial film increasing its hydrophilicity, DI12 and DW12 demonstrated increased separation efficiency with their concentrations without any drop with increased concentrations. In all these tests water quality was good.

In summary, the variety of the employed demulsifiers apart from IL2 and BJ18 has shown ability to demulsify w/o emulsions by a similar mechanism. They head towards the interface and displace the asphaltic layer around water droplets and reduce the viscosity of the interfacial film [9,38,72]. Water droplets then flocculate and coalesce where larger water droplets are formed. IL2; however, was used to disturb the interface layer to provide places for the other demulsifiers at the interface, whereas BJ18 acted as a film inhibitor.

Sun and others have examined the influence of branch-chain (AE-121) and straight-chain (SP-169) demulsifiers on the interfacial properties of an oil-water interface that possesses surface active fractions from crude oil. They concluded that crude surfactants can be replaced by a chemical demulsifier through its tendency to adsorb at the interface owing to its structure of hydrophilic and hydrophobic (libophilic) ends. In this study, demulsifier adsorption and its capability to substitute the film making components were evidenced by the enlargement of interface film that took place upon the addition of a demulsifier. At the interface, demulsifier molecules in their vacancies can accommodate molecules of surface active components. This can be imagined as a new layer that consists of a mixture of demulsifier and surface active molecules, with mixed interfacial properties of both the emulsifier and demulsifier molecules [58].

The surfactant accommodation is dependent on the size of the surface active molecules; large molecules will find it difficult to enter the demulsifier vacancies, smaller ones would not as demonstrated in Fig. (2). If the surfactant molecules are smaller than the demulsifier vacancies, they can get through the demulsifier vacancies. In this case, the properties of the interface are therefore a mix-adsorption layer. If they are fairly larger than the demulsifier vacancies, they therefore cannot enter the demulsifier vacancies and accordingly the interface layer properties are just of that of the demulsifier. In addition to the size of surface active molecules, the demulsifier structure is also important for the surfactant molecules not to be trapped in between the demulsifier vacancies at the interface and that the interface film is only composed of the demulsifier molecules (unstable interface).

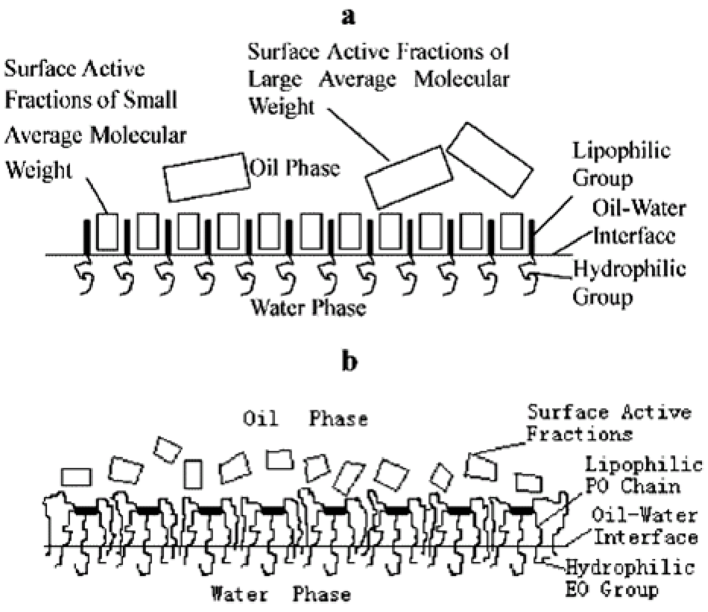

Fig. (2). Schematic diagram for mix-adsorption of demulsifier and surface active fraction molecules. (a) Straight-chain (SP-169) ;(b) Branch-chain (AE-121) [58].

In fact, in this study it has been demonstrated that the structure of the demulsifier plays an important role in the demulsification performance. A branched demulsifier, in comparison to a straight chain demulsifier, demonstrated a higher ability in replacing the surfactant molecules at oil-water interface, i.e. more effective demulsification, irrespective of the surfactant molecules sizes examined. This result was also supported by Zhang and co-workers in their work to demulsify w/o emulsions from Shengli Oilfield in China through the use of amphiphilic denderimer copolymers [63]. The other demulsifier; that's with straight chain structure showed a partial replacement of surfactant molecules from the interface; larger molecules were replaced and could not re-enter the demulsifier vacancies due to their sizes, whereas smaller ones were not replaced. Such a higher ability of branched demulsifiers over straight demulsifiers to replace crude surface active molecules is attributed to the small vacancies due to congested structure of the former type.

There is also another more recent study by Kang and co-workers concerned with the interfacial properties between oil and water in the presence of a demulsifier which offers support to this mechanism. This study aimed to investigate the effect of four different demulsifiers (water/oil soluble) concentrations on film strength, film thinning, emulsion dewatering rate, interfacial tension and interfacial viscosity in a synthetic w/o emulsion. They concluded that high demulsifier concentrations result in more demulsifier adsorbed at the interface film. This in turn leads to film strength reduction and therefore accelerates film thinning which eventually leads to film rupture [59]. The mechanism by which this process can be explained is that upon demulsifier adsorption at the interface, it partially replaces the emulsifiers leading to weakening the interfacial film [11,18]. Dewatering rate is also increased with increasing demulsifier concentration. However, increasing the demulsifier concentration has an opposite effect on both interfacial tension and interfacial viscosity. Indeed, this interfacial tension and interfacial viscosity reduction, as a result of increased demulsifier concentration is a key factor to improve the demulsification efficiency and dewatering rate [52,54]. It was also found that water-soluble demulsifiers such as polyoxyethylene and polyoxyethylene polymers have a higher ability in this regard than oil-soluble demulsifiers such as phenol-formaldehyde resin polyoxyethylene and polyoxyethylene.

2.2 Thermal Demulsification Methods:

The application of heat to an emulsion results in a reduction in the mechanical strength of the interfacial film after which droplet coalescence is likely [53,73]. Both conventional and microwave heating have been extensively implemented to demulsify w/o emulsions. Microwave irradiation technique is considered advantageous over the conventional heating procedures which are laborious and time-consuming [21,27,61,74]. With microwave heating, the heating can be selective, the equipment can be miniaturized, electrical power consumption cost and environmental pollution can be reduced [27]. Historically, first successful patent applications in demulsifying w/o emulsions by means of microwave heating were registered by Klaila in 1983 and Wolf in 1986. Microwave irradiation offers a clean, chemicals-free, inexpensive and convenient method of heating leading to the acceleration of the demulsification task. Microwave heating offers faster heat transfer rates as the energy is delivered to the targeted object directly through molecular interaction with the electromagnetic field in volumetric heating effects. Also, with microwave radiation uniform heating throughout the object volume is possible. It is recognized that the key for microwave heating, which is facilitated by dipole rotation and ionic conduction, is material-wave interactions which lead to thermal effects and selective absorption of microwave energy by polar molecules within the crude [21,27,75-77]. In case of crude oil emulsions in particular, microwaves interact with water molecules, dissolved salts and polar crude compounds such as asphaltenes and resins, leading to phase separation [74]. Water content of an emulsion and its salinity influence the microwave demulsification efficiency. The higher the water content, the larger the heating effect would be. Nevertheless, increased salinity level of water content results in a reduced microwave demulsification efficiency [27]. Although microwave irradiation has been a successful process to demulsify w/o emulsions, the literature on this topic has been scarce.

Xia and his colleagues employed microwave radiation to demulsify an emulsion stabilized by asphaltenes or resins. W/o model emulsions were prepared by dispersing distilled water in jet kerosene in the presence of different amounts of asphaltenes or resins as emulsifiers. They investigated the possibility of demulsifying the resultant emulsions (at low asphaltenes and resins concentrations; lowest of concentrations ranges examined) by means of microwave radiation [61]. The successfulness of this technique for both emulsions stabilized by asphaltenes or resins was demonstrated via 100 % of water separation in a matter of hundreds of seconds. In another study, Nour et al., have used microwave heating instead of conventional heating to demulsify w/o emulsions. Having applied microwave heating to a w/o emulsion, results show that this technique is powerful to demulsify w/o emulsions [75]. Microwave irradiation as a consequence of temperature elevation reduces emulsion viscosity and due to the expansion of the dispersed phase due to increased internal pressure of water droplets reduces the thickness of the interfacial surfactant(s) film and also reduces emulsion stability as a result of breaking hydrogen bonds between surfactant and water molecules [53,75,78].

Due to temperature increase, emulsion viscosity is decreased (decreased fluid flow resistance) and therefore water droplets settling velocity and collision rates, due to increased thermal energy of the droplets, will increase (Stoke’s law) [16,27,48,53,67,75,78]. These new conditions (high temperature and low viscosity) lead to faster coagulation producing droplets of larger size which ultimately leads to phase separation with improved rate of film drainage [53]. In addition, increasing an emulsion temperature results also in an increased density difference between oil and water phases as the density of the oil phase is reduced at a rate that’s faster than that of the aqueous phase. This therefore leads to increased frequency of droplets collision as well as increased settling velocity [48,53]. Solubility of surfactants in both oil and aqueous phases of an emulsion can be increased at higher temperatures [79-80]. Furthermore, when heat and chemical methods are employed synergically to demulsify an emulsion, the former augments the performance of the latter [53]. Microwave heating performance, to a large extent, depends on dielectric properties of emulsion components, emulsion viscosity, density and composition (water content), size and distribution of the dispersed phase within the emulsion, salinity level, pH of the aqueous phase, temperature level and frequency of microwave radiation [21,27]. Effects of such variables were investigated in a patent by Coutinho and co-workers [27].

Also, Rajakovic and Skala have obtained very good results of separating w/o emulsions via coupling freeze/thaw with microwave irradiation method. Freeze/thaw demulsification method has been found to be so successful to remove water from w/o (oily sludges) emulsions with 90 % water removal containing some organic materials. Freezing is used to expel surfactant molecules from ice lattice whereas thawing is to create surfactant micelles. In their work they used microwave radiation to induce the freeze/thaw demulsification efficiency. The benefit of employing the heat in freeze/thaw demulsification experiments is that to selectively utilize the adsorption of radiation energy by surfactant molecules; therefore, these molecules become energized, leading to superheating at which reaction rates are increased [81]. Also, heat is applied in order to reduce the viscosity of oil (continuous) phase and to help rupture the outer oily film around water droplets so that water droplets can coalesce together. In addition, Chen and He used freeze/thaw process to demulsify w/o emulsions. Out of their work, it is concluded that demulsification is dependent on initial water content, freezing temperature and duration, thawing rate and temperature [82-83].

2.3 Electrical Demulsification Methods:

Although various chemical and thermal demulsification methods of w/o emulsions, as demonstrated in previous sections, have been to a large extent successful processes; however, in addition to the high cost of these demulsifiers, emulsion contamination irrespective of the chemical demulsifier used seems inevitable which entails further processing and cost [1,25,51,80,84-88]. With regards to thermal methods, loss of crude oil light components which determine the crude price is highly envisaged. Also, due to temperature increase while heating the crude separation efficiency may decline due to the formation of air bubbles which can absorb the surfactants found within the crude [12,16,89-90]. Furthermore, if thermal treatment is integrated with chemical methods in particular in case of heat-sensitive demulsifiers, heat may deactivate the performance of the demulsifier [53]. Finally, heating a crude may also lead to increased propensity towards scale deposition and an increased risk of corrosion in treating vessels [16].

Therefore, a physical method featured with simplicity of operation, efficiency and affordability and equally important with no chemical waste or moving parts, would clearly be advantageous. A candidate that may possess these features is the electrical demulsification. In petroleum industry during different processing units, electrical destabilization is widely used to break w/o emulsions that may develop throughout crude production and refining. It is a physical process and can be used alone or in conjunction with both chemical and/or thermal demulsification methods in an attempt to augment the performance of these methods [73,91]. Emulsion coalescence can be accelerated when gravity coalescence is coupled with an electrical field [35,80]. Using electrokinetic phenomena in the field of oil industry to disrupt w/o emulsions is advantageous due to simplicity and possibility of attaining good separation efficiencies at low power consumption levels. This therefore has inspired several researchers to further investigate this technique in dealing with w/o emulsions.

Electrical demulsification of w/o emulsions goes back in time to 1911 by Cottrell in the USA [24,92]. In electrical destabilization techniques different currents are applied; of these, are AC and DC fields; continuous or pulsed [12,24,84,89-90,92-96]. AC field is the oldest and the commonest used current to demulsify crude emulsions [8,24] and may be more economic than pulsed electric fields; the latter one; however, in particular in case of emulsions with high water content is characterized with higher droplet coalescence efficiency [24,84,92]. When a DC current is applied throughout an emulsion, which mainly used in the treatment of low water content emulsions [8,24], droplets coalescence is improved via electrophoretic motion of droplets. In AC fields; however, droplets coalescence is improved through the motion in the bulk field; thereby, this type of electrical fields is more suitable for continuous demulsification processes [90,97].

Depending on the placement of the electrodes in the demulsification cell, there are two types of fields may develop. These are uniform and non-uniform electric fields. When both electrodes are positioned in the emulsion, a uniform electrical field is created between these electrodes. Non-uniform electric field is resulted when only one electrode is contained within the emulsion whereas the other one is in an electrolyte solution. With this configuration, short circuiting due to development of water droplets chains is overcome. Electrode insulation with thin coatings of materials that are non-water wetting (hydrophobic) can also serve this purpose in the former setup (uniform field) [8,80,92].

Spontaneous but slow coalescence of droplets of an emulsion is well known to occur according to three consecutive steps: droplets approach each other with their surrounding film, which is mainly composed of asphaltenes and resins, etc.; this process is called flocculation. This step is then followed by film thinning and drainage during which the thickness of interfacial film is reduced. Capillary and disjoining pressures affect the film thinning rate; according to Marangoni effect film thinning rate is delayed in the presence of surfactants. At high shear rates, rate of film thinning is inversely proportional to the square of droplet diameter [65,89-90]. Further film thickness reduction; that’s to a critical thickness, by disturbance effects, leads to film rupture which eventually results in internal phase droplet-droplet coalescence. Coalescence phenomenon is accompanied with an increase of droplets size meanwhile reduced number of droplets [8,14,17,20,30,45,50,90-92].

Applying an electrical field across a flowing or a stationary emulsion to attain an appropriate droplets size, with which phase separation is possible, is evidently known to enhance the demulsification rate through some interactions between water droplets, small ones in particular, and the applied field [8,14,20]. This interaction leads to droplet charging and agglomeration which subsequently lead to droplet-droplet coalescence [24,98]. Generally, emulsion resolution by an electrical field has been to be irreversible; however, low electric fields (that’s not high enough to induce droplet coalescence) have only been found to result in a linear chain-like configuration; these chains are prone to disappear upon switching off the applied field [8,35]. Successfulness of high enough fields to achieve irreversible demulsification is credited to their ability to permanently rupture the protective film around water droplets leading to droplets coalescence that’s by no means can be reversible [35]. Electrical field increases the internal droplets collision (motion energy) due to the oscillation of these droplets under electric field. Water droplets attraction force is proportional to the square of the applied current as shown in the equation below [73,80]. Therefore, large groups of droplets flocks, but with their surfactant film around them are formed. By this droplet-droplet proximity the influence of electrical becomes further pronounced [90]. This film is then stripped by the tearing force by electric field, which also results in charging and agglomeration of water droplets, so that water droplets contained within this film have nothing halt them to combine with each other (coalescence) [14,30,73,90-92].

$$F \propto E^2 r^6 d^{-4}$$

Where F is the attractive force between droplets, E the electric field strength (V/cm), r the droplet radius and d droplet separation [80].

These larger droplets will then settle down into the water phase under the influence of both gravity and electric forces [90,95]. Behaviour of droplets of an emulsion under the influence of an electrical filed is depicted in Fig. (3) [98]. According to this figure, water droplets are initially dispersed everywhere through the emulsion; Fig. (3a). Following applying an electrical field water droplets with the effect of increased conductivity by water ions become polarized as shown in Fig. (3b). Further increase of the field makes water droplets lined up between the two electrodes (chain formation), see Fig. (3c) [98]. Similar representation was also given by Sullivan et al. [99] and Havre and Sjöblom [34].

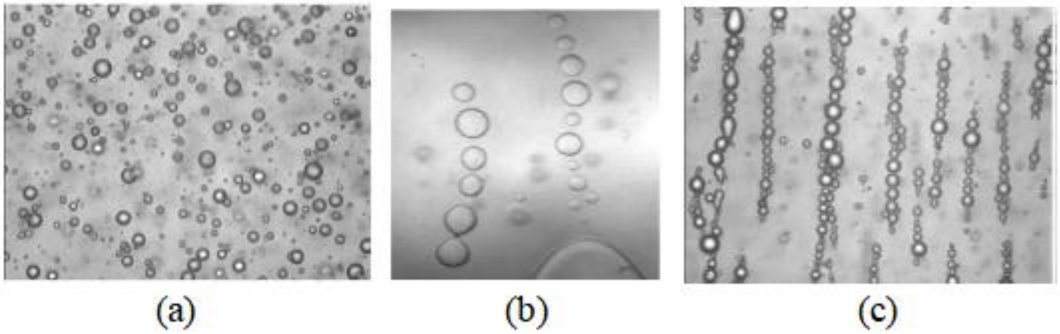

Fig. (3). Emulsion behavior under the influence of an electrical field [6].

Several mechanisms have been proposed to explain the principal effect(s) that may develop during electrocoalescence. Among these are: chain formation of droplets, formation of intermolecular bonds, electrophoresis, dielectrophoresis, dipole coalescence, random collision and electrofining [8,24,48]. A synopsis of these mechanisms along with the most prevailing factors which are with influential effect on separation efficiency is given by Eow and co-workers [8] as shown in Fig. (4). Chain formation occurs due to potential differences, with both AC/DC currents, among emulsion droplets due to their induced charges. Chains of droplets are then created as a result of individual droplets movement. It is worth noting that these chains do not necessarily start/finish at an electrode nor touch neither electrode, also they are arranged in such a way that they are aligned in line with the field intensity direction. Droplet-droplet coalescence through chain formation depends on oil phase viscosity, dispersed phase fraction and intensity of the applied electric field [8,99].

Electrophoresis is concerned with applying an electrical field through a stationary fluid in which a charged particle is encouraged to move through it; particle-neighboured fluid is also susceptible to move. This process is based on charge separation between the particle surface and the fluid that’s immediately adjacent to it. Applying a non-uniform electric field results in the movement of water droplets in w/o emulsion towards the direction of field strength under the influence of polarization; this is known as dielectrophoresis. Practically, dielectrophoresis is less significant in terms of droplets coalescence than electrophoresis since a droplet velocity due to the first phenomenon is somewhat low in comparison to that resulted by electrophoresis; however, dielectrophoresis becomes crucial in case of moderately charged droplets when; for instance, insulated electrodes are used. In dipole coalescence, Brownian motion, sedimentation, flocculation or electrophoresis are required to bring emulsion droplets together. Electrofining involves electrophoresis, dipole coalescence, collision of drops of different charges meanwhile flowing in opposite directions and also collision of drops of different sizes moving in the same direction as the direction of the applied DC current [8,24,80,89,92].

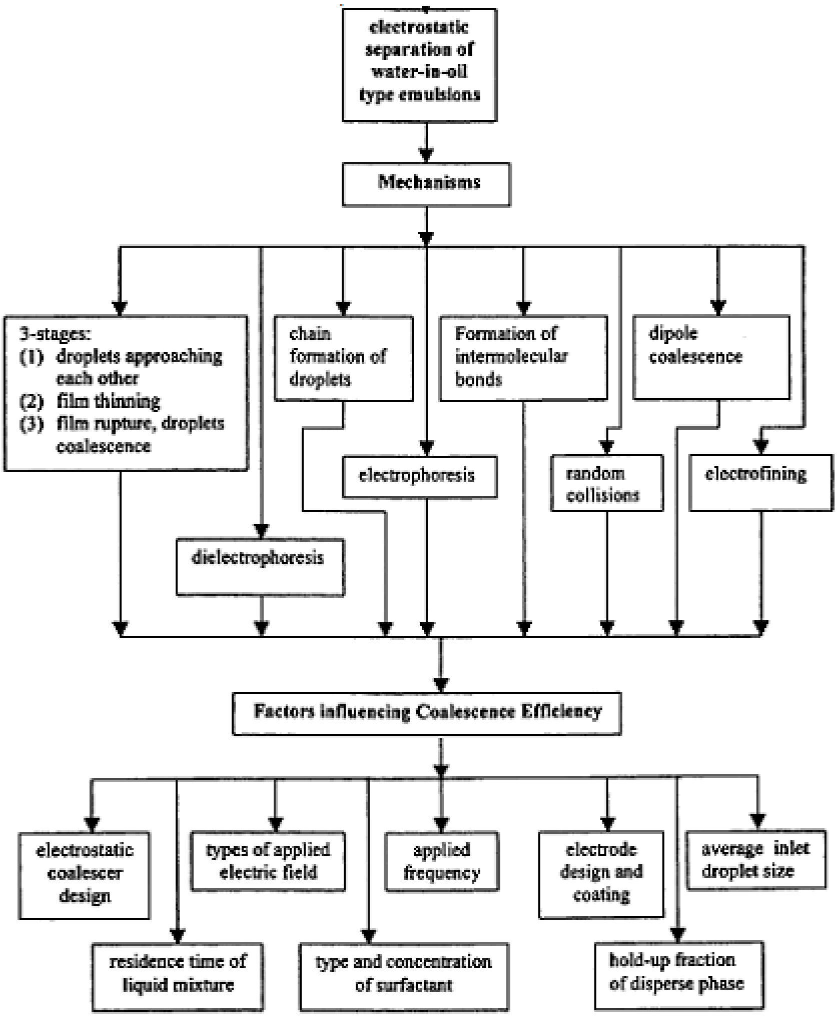

Fig. (4). Mechanisms and factors influencing the coalescence efficiency of electrostatic separation of w/o emulsions. Reproduced from [8].

Electrical demulsification kinetics can be influenced by some factors including: dielectric properties of both dispersed and continuous phase, volume fraction of the dispersed phase along with its droplets size distribution, temperature, emulsion viscosity and density, conductivity, electrode geometry, intensity of the applied electric field and its type (AC/DC), etc. [8,35]. Generally, separation efficiency is increased with voltage intensity [8,84,89,99-101]. However, this was shown not always necessarily to be the case as Kim et al. have showed, in the systems they examined, that although separation efficiency increased as the strength of the applied field increased; however, it decreased when the applied field passed a certain value by which droplet deformation and break-up took place; consequently, separation efficiency is decreased [90]. Furthermore, emulsions with higher water volume fractions give higher separation efficiencies under the effect of electric field due to increased polarization effects [12,43,89]. To this end, it is expected that in crude oil emulsions with high content of oil;

that’s less conductive than water, the separation efficiency may be reduced [8,12,43,102]. Hano et al. in their investigation of kinetics of demulsification of w/o emulsions in an AC electric field, concluded that the viscosity of an emulsion has an important effect on electrostatic demulsification. With decreased emulsion viscosity, the rate of demulsification increases. Also, coalescence and water droplets settling increase as water droplet size is increased [95].

Furthermore, Taylor in his investigations into the electrical and coalescence behaviour of water in three different crude oils emulsions (Kuwait, Ninian and Romashkino crudes) in high voltage gradients noticed that electrical destabilization of w/o emulsions is largely dependent upon the nature of the resultant interfacial film between oil and water. Emulsions based on crudes that contain incompressible interfacial films tend to form chains of water droplets through the emulsion. In these emulsions, water droplet-droplet coalescence was limited, emulsion conductivity was increased. However, in emulsions that possess surfactants at the interfacial film, rapid water droplets coalescence with low emulsion conductivity was demonstrated with no chain formation. This was ascribed to enhanced interfacial film mobility as a result of surfactants presence. A synopsis of these two mechanisms is given in Fig. (5) [73]. A similar conclusion was introduced by Chen and his colleagues in terms of the influence of nature of the interfacial film on coalescence mechanism when they investigated emulsion resolution by the application of an electric field [92].

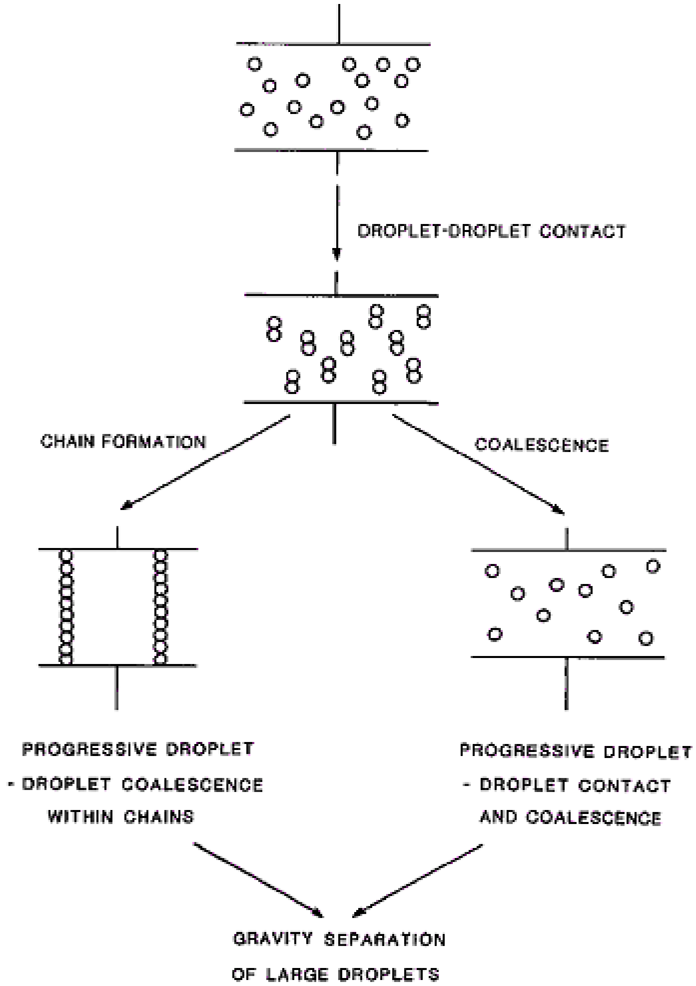

Fig. (5). Schematic representation of the stages of electrical coalescence process of an emulsion [73].

In another work by Eow and Ghadiri, two novel compact electrocoalescer-separators to separate aqueous drops dispersed in flowing viscous oil were developed. One separator was based on coupling gravity forces with electrical potential; where as in the other separator, centrifugal force was coupled with electrical forces. Successful separation results were obtained by using either separator particularly when an optimum electrical field was applied. Optimum field is somewhere between a too low field value and a too high field value, fields at values beyond this optimum field gave reversed results of decreased separation efficiencies due to water droplet deformation and break-up (smaller droplets) [103].

3.Overview of Current Chemical, Thermal and Electrical Destablization Methods:

It seems that currently implemented treatment techniques to demulsify emulsions, mainly due to high stability, have not been efficient enough to effectively and entirely deal with this problem [74]. Chemical treatment requires addition of chemicals (contamination) which in turn brings more complication to the emulsion system as it is required to remove these chemicals, at an additional cost, prior to the next downstream processes. Another obstacle with chemical methods is that for highly viscous w/o emulsions (which is usually the case); it might be difficult to mix the required chemicals with the emulsion [77].

Although thermal demulsification has been useful in the demulsification procedures since following heating up an emulsion its oil phase viscosity will accordingly be reduced; therefore its fluidity will increase and more droplet collision takes place. By increasing the emulsion temperature, solubility of surfactants in both oil and aqueous phases of an emulsion can be increased [80]. Also at elevated temperatures, difference in density of the phases, resulting in the heavier fluid (water) settles down and that the lighter fluid (oil) raises up to build the top layer, is increased [12,72,103]. In addition, due elevated temperatures within a crude wax precipitation is reduced which accordingly by freeze/thaw method is safe, no chemicals are required; hence, no additional treatment is entailed, convenient and effective with demulsification efficiencies up to 90 % [81]. Thermal demulsification methods are; however, energy-intensive processes, heating a crude oil can promote loss of light components which dictate crude price. Also, due to temperature increase while heating the crude separation efficiency declines due to the formation of air bubbles which can adsorb the surfactants found within the crude. Furthermore, if thermal treatment is integrated with chemical methods in particular in case of heat-sensitive demulsifiers, heat may deactivate the performance of that demulsifier [[53,104-105].

Electrical fields, were reported to help enhance demulsification rates through electro-kinetic effects and high internal forces, respectively [56]. However, most of electrococoalescer equipment currently in use are huge and bulky [48,106]. In addition, the need to use extremely high voltages to attain droplet coalescence may limit the use of this method [25,86]. Also, this method is considered ineffective to demulsify emulsions with high water contents [88]. Likewise, electrical resolution of crude oil emulsions with low water contents can be ineffective due to low conductivity [48]. Another problem with this method particularly in offshore fields, where space is usually restricted, is that it is usually coupled with chemical methods to speed up the demulsification task [70,107-108] for which additional hardware would be required.

4 .Conclusions:

Among the routes of demulsification of w/o considered in this review paper are: chemical, thermal and electrical methods. Although they have been able to breakdown w/o emulsions in a way or another, they; however, suffer from some limitations and obstacles. Chemical demulsifier(s) required in the chemical methods result in the contamination of the crude oil. This contamination cannot be resolved, unless separation procedures, at an additional cost, are in place. Also, in highly viscous w/o emulsions, it is difficult to have the demulsifier(s) thoroughly mixed within the emulsion. This has the sequence of a reduced usability of the used demulsifier(s); thus, a reduced demulsification capability. Due to use of heat in thermal demulsification of w/o emulsions, valuable light components that determine the price of the crude which are naturally found in the emulsion of the crude oil, are susceptible to be lost. Heat used has also been responsible on the formation of air bubbles that might impede a good separation of emulsion's surfactants. Furthermore, heat is of a negative effect on the chemical demuldifier(s) if chemical treatment is integrated with thermal treatment for the purpose of boosting the process efficiency. Electrical methods are also not an ideal solution that can be effectively sought in order to breakdown w/o emulsions. Equipment used are bulky, applied voltage is high and demulsification capability is low if w/o emulsion is with a high content of water.

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