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TÍTULO DO TRABALHO:

EMULSION FORMATION, CHARACTERIZATION, AND DEMULSIFICATION TECHNIQUES - A REVIEW

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RESUMO

Emulsões de água em óleo são geradas durante atividades de exploração e refino de petróleo bruto. Eles representam riscos operacionais para as instalações devido à corrosão e exigem maior comprometimento econômico devido ao custo da separação. Assim, separar a fase aquosa da emulsão do petróleo bruto antes dos processos de refino e transporte é uma área de interesse de pesquisa. Para desestabilizar uma emulsão, diversas técnicas são relevantes, como biológicas, químicas, mecânicas e térmicas. Esses métodos podem alterar as propriedades paramétricas da emulsão – viscosidade, pH, concentração, teor de água, concentração do emulsificante e tamanhos de gotículas – para efetuar a separação. Além disso, diversas técnicas instrumentais são utilizadas para monitorar o processo de separação no sistema de emulsão. A técnica de teste de garrafa é uma das técnicas mais utilizadas para estudar a separação de emulsões; outros são dispersão de luz, microscopia, métodos ultrassônicos, medição de condutividade e técnicas de RMN, que mostraram diferentes níveis de precisão de monitoramento de coalescência, formação de creme e sedimentação durante a separação de fases. Este estudo é uma revisão de trabalhos sobre emulsões, seus tipos, formação, mecanismos de estabilidade, modelos, aplicações industriais, caracterização e técnicas de desemulsificação. Apresenta ainda estudos comparativos de diferentes caracterizações e diferentes técnicas de desemulsificação. Técnicas de teste de garrafa e desemulsificação química são mais comumente relatadas na literatura do que outras. Por último, a atenção deve ser colocada na utilização de outras técnicas de desemulsificação que não exijam a utilização de produtos químicos devido a preocupações ambientais.

Palavras-chave: emulsão, emulsificação, refino, desemulsificação.

ABSTRACT

Water-in-oil emulsions are generated during activities in crude oil exploration and refining. They pose operational risks to facilities because of corrosion and require more economic commitment due to the cost of separation. Thus, separating the water phase from the crude oil emulsion before refining processes and transportation is an area of research interest. To destabilize an emulsion, various techniques are relevant, such as biological, chemical, mechanical, and thermal. These methods can alter emulsion parametric properties—viscosity, pH, concentration, water content, emulsifier concentration, and droplet sizes—to effect separation. Moreover, various instrumental techniques are used to monitor the separation process in emulsion system. The bottle test technique is one of the most widely used techniques to study emulsion separation; others are light scattering, microscopy, ultrasonic methods, conductivity measurement, and NMR techniques, which have shown different levels of accuracy of coalescence, creaming, and sedimentation monitoring during phase separation. This study is a review of work on emulsions, their types, formation, stability mechanisms, models, industrial applications, characterization, and demulsification techniques. It further presents comparative studies of different characterization and different demulsification techniques. Bottle test and chemical demulsification techniques are more reported in the literature than others. Lastly, focus should be placed on the use of other demulsification techniques that will not require the use of chemicals due to environmental concerns.

Keywords: emulsion, emulsification, refining, demulsification.

INTRODUCTION

Emulsions become unstable over time or when subjected to certain physical or chemical processes by going through mechanisms such as creaming and sedimentation, coalescence, flocculation, Ostwald ripening, and phase inversion (AKBARI, 2018). Emulsions are found in industrial applications such as foods and pharmaceuticals for topical drug delivery and food quality attainment. They are also found at different stages in refining processes, such as crude oil emulsions in petroleum industries (IRFAN ET AL., 2023). Emulsions of crude oil are created at all production stages, from the oil reservoirs to the shipping procedure. Although, they are undesirable because they complicate the process of refining crude oil, cause accident in the oil industry due to corrosion of pipelines, high production costs associated with separating water from oil, and downstream toxicity from industrial catalysts (ABED ET AL., 2019). Thus, from an operational and economic perspective, crude oil must be fully isolated from water before transportation and processing (ERFANI ET AL., 2024).

Mechanical, biological, thermal, microwave, electrical, ultrasonic, and membrane demulsification techniques are the techniques utilized in industrial crude oil emulsion separation (ABED ET AL., 2019) while the techniques for observing and quantitatively studying emulsions during creaming, sedimentation, changes in droplet size distribution, and volume of dispersed phase separation include visual observation, light scattering, microscopy, ultrasonic methods, NMR, conductivity measurement, turbidimetry, chromatography, and Raman spectroscopy (HU ET AL., 2017). In this paper, emulsions, their types, formation, stability mechanisms, models, industrial applications, characterization, and demulsification techniques are discussed. Furthermore, comparative studies of different characterization and different demulsification techniques are also discussed; and lastly, the use of other demulsification techniques that will not require chemicals usage due to environmental concerns is recommended.

METHODOLOGY

Articles for this review were collected from reputable databases and publishers including Science Direct, Elsevier, and ResearchGate. The search was done using the following keywords: *emulsions and their types, emulsion stability, emulsion characterization, crude oil emulsion, crude oil emulsion treatment and separation, and models for mechanisms and processing in emulsion*.

Selection criteria:

Relevance to crude oil emulsion: Papers chosen from the list of results are those that have titles and abstracts that specifically addressed crude oil emulsions and processes related to them.

Citation count: Considering the credibilty and impact of the articles, those with high citation counts were considered.

Search Depth: Search no further than the first five tabs (pages) of search results to ensure that most relevant and accesible reseach were considered.

Recency: Studies on emulsion is evoloving, to capture relevant information over years within the scope of this paper, papers published within the last ten years were given preference while others outside this period were only cited when information from them are very important.

Abstract screening: The abstracts of the selected papers were read to check their relevance to crude oil emulsions, excluding studies focused solely on other emulsions such as foods and pharmaceuticals.

Specific keywords search: For the review on crude oil emulsion characterization and demulsification techniques, keywords for each characterization or demulsification techniques were searched over the period of last ten years to further narrow the search and the number of articles where they were used were recorded.

RESULTS AND DISCUSSION

A total number of seventy-four articles were selected for this review; for the search for emulsions and their types, ten articles, four of which were published in 2018 and two each from years 2019 and 2023 were finally selected. Most papers were collected for emulsion stability, out of which five and four were published in 2018 and 2021, respectively. In addition, nine articles each were finally reviewed for industrial applications of emulsion and techniques for crude oil treatment or separation. Furthermore, for crude oil emulsions, crude oil emulsion characterization techniques, and mathematical models describing mechanisms in emulsion, five, fourteen, and seven articles, respectively were finally selected.

EMULSION, FORMATION, TYPES, AND STABILITY

An emulsion contains two or more liquids that do not readily mix but have one dispersed in the other. The suspended phase is the continuous phase, while the phase present in the form of droplets is the dispersed phase (BLAU ET AL., 2023). Emulsions can typically be water-in-oil (W/O), oil-in-water (O/W), and multiple emulsions (oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W) emulsions based on what phase is present as the continuous and dispersed phase, as shown in figure 3 (WONG ET AL., 2015). Effective energetic mixing and the presence of surfactants are two crucial criteria that facilitate the formation and stability of an emulsion. Thus, surfactants are molecules with hydrophilic and lipophilic properties, figure 1, making them naturally migrate to the interface between oil and water, figure 2. They lower the interfacial tension between oil and water, which, in turn, reduces the energy needed for emulsion formation (KATEPALLI, 2014).

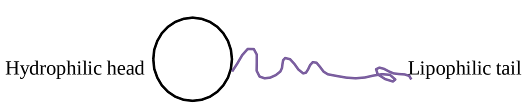


Figure 1: General Structure of emulsifier

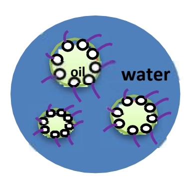


Figure 2: Emulsifier interaction in the oil-water interphase.

Figure 3: Types of emulsion

The emulsion's stability is enhanced through the creation of films, which raises interfacial viscosity while reducing interfacial tension. Therefore, the overall stability of the emulsion depends on the quality of the interface layer and how surfactants adhere to it (RAVERA ET AL., 2021). Droplets size, water concentration, mixing speed, and temperature are also some other factors that can affect the emulsion's stability (ONYEJEKWE & CHIGOZIRIM, 2021). However, emulsions can be stabilized through four different mechanisms:

Electrostatic repulsion - This process takes place through the adsorption of an ionic surfactant. The electrostatic force arises from the interplay of electrical double layers surrounding charged droplets, as shown in figure 4, which works to hinder the contact between these droplets (VARANASI ET AL., 2018).

Steric repulsion - In this process, surfactant molecules coat the dispersed water droplets, and the hydrophobic tails of the surfactant molecules attach to the particle surfaces, figure 5, preventing the droplets from coming into proximity.

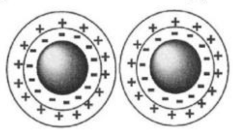


Figure 4: Diagrammatic illustration of electrostatic stabilization in emulsion (Y. LIU ET AL., 2006).

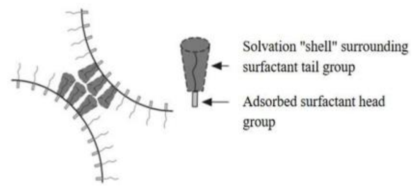


Figure 5: Diagrammatic illustration of steric repulsion stabilization in emulsion (SPIECKER, 2001).

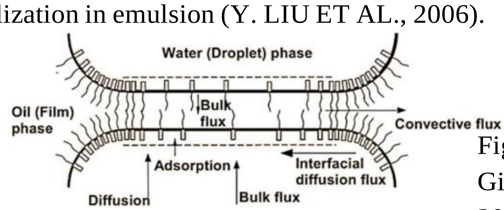


Figure 6: Diagrammatic illustration of Marangoni-Gibbs effect stabilization in emulsion (SPIECKER, 2001).

Steric stabilization is typically observed in systems that are stabilized by non-ionic surfactants and polymers. This type of stabilization is accountable for maintaining the stability of water-in-oil (W/O) emulsions.

The Marangoni-Gibbs effect - The Marangoni-Gibbs effect helps to maintain the stability of emulsions by stopping the flow of the surrounding liquid phase from moving away between two adjacent droplets. Over time, the continuous phase of an emulsion tends to drain in between the droplets of the dispersed phase due to differences in surface tension. This causes the emulsion to break. To curb this and maintain the stability of the emulsion, the Marangoni-Gibbs effect comes into play. This effect prevents drainage of the continuous phase from between the droplets of the dispersed phase by redistribution of the liquid in such a way that the stability of the emulsion is maintained, as illustrated in figure 5 (RAVERA ET AL., 2021).

Thin film stabilisation - This mechanism involves the formation of a rigid and viscoelastic film around water droplets while preventing the droplets from coalescence. The process depends on asphaltene chemistry, solvency, and the kinetics of diffusion and adsorption (CAMPEN ET AL., 2017).

When two emulsion droplets come into contact, they create a thin liquid layer, known as a lamella, between them, coalescence occurs when this film gets broken and the droplets merge (LANGEVIN, 2019). On another hand, flocculation occurs when a pair of droplets interact such that the free energy of their interaction becomes noticeably negative at a given separation while the emulsion droplets agglomerate without rupturing the stabilizing layer at the interface. In an emulsion, the formation of flocs from droplets determines how quickly cream rises and increase in viscosity in emulsions (MAPHOSA ET AL., 2018). Creaming occurs in an emulsion because of gravity influence, mainly when the density of the droplets is smaller than that of the continuous phase. When droplets with a radius greater than 1 μm are present in the emulsion, the system goes through a separation process, which causes the creation of two distinct layers. In other words, creaming takes place when dispersed droplets travel upward because they are less dense than the surrounding continuous phase. The direct opposite of creaming is sedimentation. It occurs when the droplet density is higher than that of the continuous phase density and this results in the droplet settling at the bottom of the emulsion. Ostwald ripening is the gradual growth of larger droplets at the expense of smaller ones in an emulsion, caused by the movement of the soluble dispersed phase through the continuous phase while phase inversion occurs when an oil-in-water emulsion may change into a water-in-oil emulsion or vice-versa over time or as a result of changing environmental factors (T. F. TADROS, 2013).

EMULSION IN INDUSTRIAL PROCESSES

In the pharmaceutical industry, "emulsion" is usually only used to describe drugs intended for internal consumption. Emulsions meant for external use are usually labelled differently, with terms like "lotion" or "cream" commonly reflecting their intended use (LANGLEY & BELCHER, 2008). Emulsions' ability to transport active ingredients makes them useful in the pharmaceutical industry. In food, emulsion stability over a long period of time at different temperatures is very important. In our daily food intake, we often come across a multitude of emulsified products, such as salad dressings, sauces, pre-packaged foods, mayonnaise, desserts, beverages, milk, peanut butter, ice cream, and sausages. Compared to nano and microemulsions, macro emulsions are used in the food sector more often. In addition, emulsions in food often have emulsifiers such as fatty acid esters, fat globules, or their by-products such as lactic, acetic, or citric acid esters, or vegetable fat. Emulsified dressings and sauces, such as mayonnaise and related items, are mainly made of emulsions of oil in water with a percentage of water ranging from 20 to 80 (KUMAR, 2014).
Emulsions have desirable properties that make them useful for many industrial processes, but they can pose some problems. This is the case in the oil industry when crude oil is produced. Crude oil emulsions are not desired as they make refining crude oil very difficult, and the water content in them poses operational malfunctions for refining facilities (ABED ET AL., 2019). Other problems posed by emulsions in oil industries are high production costs and corrosion of pipes. Before transportation for refining, crude oil emulsion must be completely separated from water from operational and economic standpoint (ALJABRINE & FAIRWEATHER, 2023). Emulsions are also applicable in paints, coatings, agriculture, and cosmetics (TITUS ET AL., 2024), (HUSEN ET AL., 2023) & (KANDWAL ET AL.,2023).

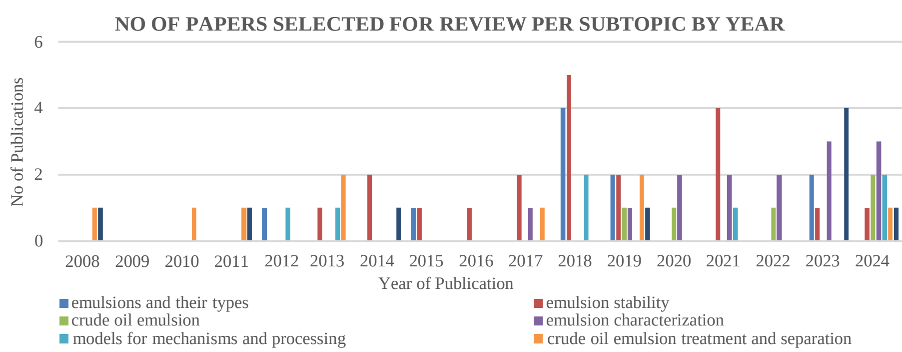


Figure 7: Number of selected papers for review for each subtopic per year

CRUDE OIL EMULSION

Crude oil is produced together with water to have a mixture known as crude oil emulsion or oil field emulsion. Crude oil emulsions are common throughout several phases of petroleum recovery and production, drilling, transportation, and treatment (HASAN ET AL., 2024). Owing to their unfavourable characteristics in the petroleum sector, emulsions are often associated with elevated pumping costs, decreased throughput, and facility damage due to corrosion (RYSKOL ET AL., 2020). As constituents, crude oil contains asphaltenes, resins, and acidic chemicals (fatty acids, aromatic acids, and naphthenic acids) that act as natural emulsifiers (CHU ET AL., 2024).

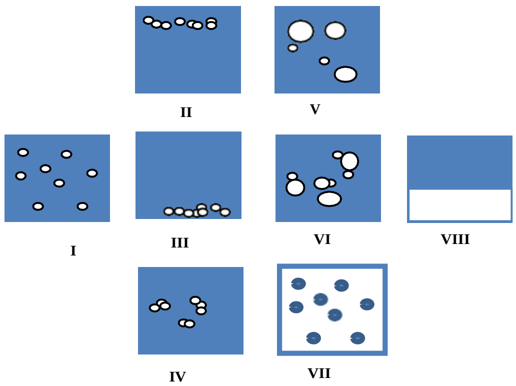
MODELS FOR PROCESSES AND MECHANISMS IN EMULSION SYSTEMS

Mechanisms in emulsions are described using mathematical models from which the most widely applied is the Stoke's model. Stoke's model can be used to calculate the rate of creaming or sedimentation in an emulsion (BACKI ET AL., 2018). The model balances the hydrodynamic force with the force of gravity and given as in equation 1:

$$v_0 = \frac{2}{9}\frac{\Delta\rho g R^2}{\eta_0} \quad (1)$$

where; v_0 is Stoke's velocity, η_0 is the viscosity of the medium, R is the radius of the particle, g is the acceleration due to gravity, and $\Delta\rho$ is the change in density of the two phases

This model is useful for very dilute emulsions ($\varphi<0.01$) where droplet-droplet interactions are negligible. Using the population balance modelling (PBM) paradigm is advantageous when the creaming or sedimentation process is heterogenous. PBM method is useful for describing these related phenomena while considering the wide range of droplet sizes (ALEEM & MELLON, 2018). Other models such as the Smoluchowski coalescence equation, Kelvin equation and Gibbs-Thomson equation for Ostwald ripening (WU ET AL., 2021), Derjaguin-Landau-Verwey- Overbeek theory for flocculation (PENG ET AL., 2024), and Hydrophilic-Lipophilic Balance concept for phase inversion among others (SARAIVA ET AL., 2024) have also been developed.



I. Normal Emulsion
II. Creaming
III. Sedimentation
IV. Flocculation
V. Ostwald Ripening
VI. Coalescence
VII. Phase Inversion
VIII. Phase separation

Figure 8: Instability mechanisms in emulsions

EMULSION CHARACTERIZATION

Emulsion properties play important roles in the nature and behaviour of emulsion. There determination at an instant or over a period is important to understand the emulsion system. The following are some of the essential emulsion properties and techniques used in characterizing them:

Water Separation Efficiency – This property is usually monitored using bottle test experiments, whereby the quantity of water separated of the emulsion is measured over time (AHMADI ET AL., 2022).

Droplet size distribution – DSD are determined by using techniques such as dynamic light scattering (BABICK, 2020), laser diffraction, and high speed imagery with image analysis (SALUM et al., 2022). Also, Scanning Electron Microscopy (JIA ET AL., 2023) and Transmission Electron Microscopy (MUSTAFA ET AL., 2024) are electron microscopy techniques for studying the microstructuralproperties of emulsions.

Droplet Concentration using turbidity measurement technique (ALADE ET AL., 2021).

Electrical property of emulsion measurement using zeta potential**,** a measure of the electrostatic charge of an emulsion determined using techniques such as electrophoresis (AL-SAKKAF & ONAIZI, 2024).

Rheological Properties such as flow behaviour, emulsion viscosity, and shear-thinning properties can be measured using the techniques of rheometers and viscometers. Other techniques such as Raman (DE SOUZA SOARES ET AL., 2017), Infrared Spectroscopy (SHEN ET AL., 2021), Nuclear Magnetic Resonance (SHILLIDAY, 2023), and X-ray Scattering (MACHALE ET AL., 2023) are also employed in other literature to measure emulsion properties like the chemical composition of substances, insight into emulsifying agents, inestigating chemical reactions in emulsions, and also to investigate deeper about the motion and interactions of molecules in emulsions, such as water and oil and analyse emulsions' internal structure on a very tiny scale.

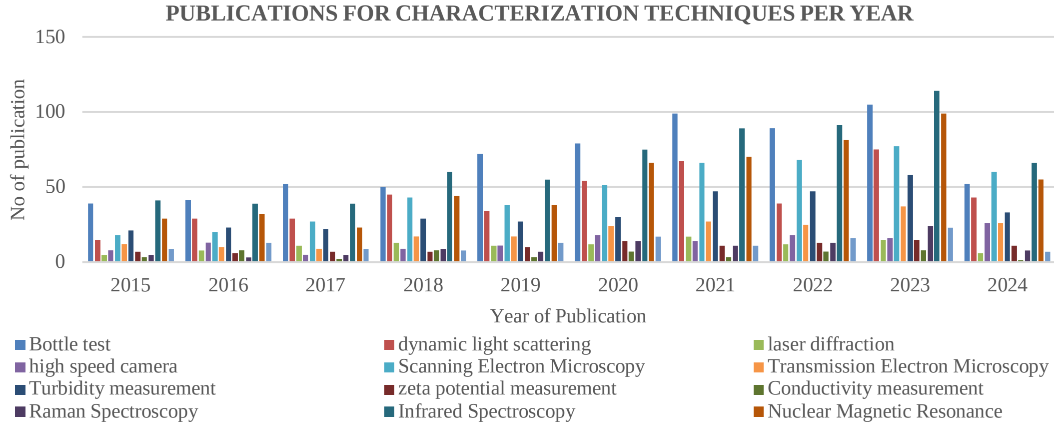


Figure 9: Characterization techniques for emulsions per year

As shown in figure 9, the bottle test technique is the most used technique over years more than others. About one hundred research used the technique in 2023 as the second most used technique to IR spectroscopy with one hundred and fourteen research where they were used to characterize emulsions. Furthermore, The IR spectroscopy technique was the second most reported after the bottle test technique in research in the remaining years. Other techniques that were also used are the Scanning Electron Microscopy and Nuclear Magnetic Resonance techniques recording on average of thirty-five reports over the last ten years. Considerably, many studies also used turbidity measurement and dynamic light scattering techniques while conductivity measurement and high-speed imaging techniques are the least used techniques in recent years.

CRUDE OIL EMULSION DEMULSIFICATION AND SEPARATION TECHNIQUES

Crude oil emulsion separation, also known as demulsification, describes the process of separating an emulsion into oil and water phases. Demulsification can be carried out using different techniques, such as chemical, biological, mechanical, thermal, microwave, electrical, ultrasonic, and membrane demulsification. Demulsifiers are used in the chemical demulsification process to influence the coalescence of droplets in emulsions. They can alter the interphasial characteristics of emulsions to cause coalescence and subsequent separation of the oil and water components of the emulsion (ABED ET AL., 2019). In addition, the biological demulsification technique started getting attention and consideration aside from chemical demulsification in the petroleum industry in the early 1980s (STEWART ET AL., 1983). Studies reported the use of S-XJ-1 (WEN ET AL., 2010) and rhamnolipid (LONG ET AL., 2013) as biological demulsifiers, where 81.3% and 90% demulsification efficiencies were recorded, respectively. As for the mechanical demulsification technique, there can be the use of cyclones to centrifugal separators and gravity separation tanks to carry them out. Out of these techniques, the most widely used is the use of gravity separation tanks due to their easier usage and low capital cost (ABED ET AL., 2019).

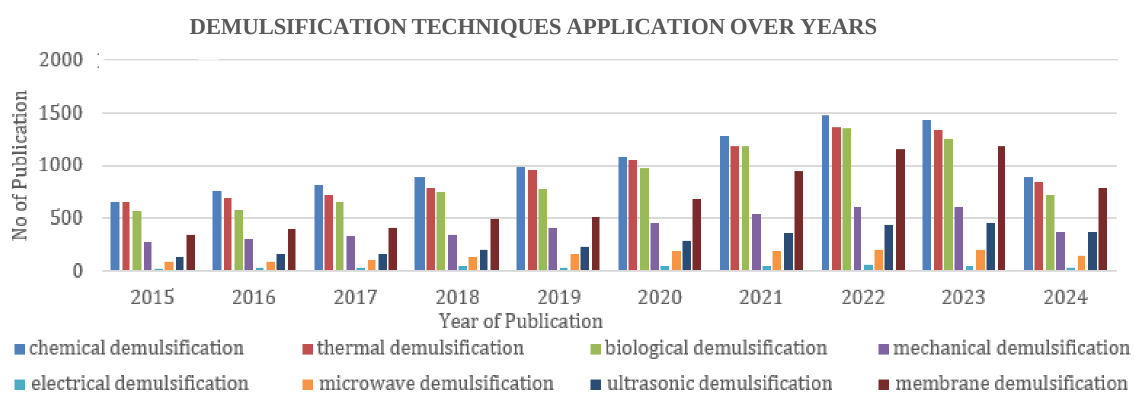


Figure 10: Demulsification techniques for crude oil emulsion

In oil fields, thermal demulsification uses heat to help break apart emulsions. High temperatures might affect the interphase's stability, which would encourage droplet coalescence when they collide. Higher temperatures can also hasten droplet collisions, which can reduce the stability of the emulsion (KOKAL & AL-JURAID, 1998). It is also a common practice to use more than one technique to separate an emulsion; for example, thermal and chemical techniques are often used together at the same time to promote demulsification efficiency (DALING ET AL., 2003). Moreover, by applying electric filed in emulsion solution, electrical demulsification process can also be used. This process changes the morphologies of the droplets by creating an attractive force that causes the droplets to coalesce. Electrical demulsification is considered a better choice than thermal or chemical demulsification but it is still unclear how best to modify this technique to accommodate different emulsion characteristics (LUNDGAARD ET AL., 2006). Other demulsification techniques, such as ultrasonic demulsification and membrane demulsification are also used in some studies for wastewater treatment and emulsion separation (ABED ET AL., 2019). Ultrasonic demulsification is especially reported to be more effective than other techniques due to its simplicity and efficiency (LEONG ET AL., 2013).
As shown in figure 10, the chemical demulsification technique was used in about 1,500 research in 2022 and was the most used than other techniques over the last ten years while the thermal and biological techniques are also commonly used more than the other techniques especially the electrical that have just 22 and 32 reports in years 2015 and 2024, respectively. Each of the techniques discussed has unique advantages and limitations. Chemical demulsification, despite being the most widely used due to its usage efficiency raises concerns on environmental impacts because chemicals are used. On the other hand, biological demulsification technique is a good alternative because it raises no or very limited environmental concerns, but it has a limitation of practical and extensive industrial application. Gravity separation, a mechanical demulsification technique type, like others are economical but usually slower and ineffient unlike others. Moreover, thermal and electrical techniques are very effective but energy intensive thereby making them economically unfriendly. Despite their prospects in effectiveness, ultrasonic and membrane methods remain the least commonly applied techniques which may be due to inefficiency in applying them for large-scale demulsification processes.

Conclusion

This review is a highlight of emulsions, types, stability and instability. Studies into the mechanisms that enhance their stability, models that describes the mechanisms, and their applications in industries were also discussed. In petroleum industries, emulsion pose operational risks and economic burden to processes which necessitates separating water from crude oil emulsion before transportation and refining. We discussed the characterization and demulsification techniques used for investigating their properties and separating or treating them, respectively. Chemical demulsification method is the most used demulsification technique while the bottle test technique is the method most used in investigating emulsion properties, such as stability and water separation efficiency. However, despite its wide usage, chemical demulsification has limitations, such as environmental risks and cost of chemical additives, making the method less sustainable in the long term. In addition, bottle tests may not always accurately replicate field conditions,which can limit theit predictive power in large scale operations. Future reseach focus is recommended on improving other demulsification techniques such as gravity and biological techniques, which have the potentials to offer more sustainable solutions with less environmental issues. More robust and comprehensive studies on scalability that can capture field situations should also be considered. Lastly, explotation of hybrid techniques that combine two or more techniques of demulsification with greener alternatives could pave the way for more environmentally friendly processes in the oil industry.

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