DEMULSIFICATION OF EMULSION EFFLUENT USING MODIFIED PALM OIL FUEL ASH (POFA)

by

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LIST OF ABBREVATIONS

BET	Brunauer-Emmett-Teller
DE	Demulsification efficiency
FTIR	Fourier transformed infrared
HLB	Hydrophilic/lipophilic balance
MDGs	Mono- and diglycerides
O&G	Oil and Grease
O/W	Oil in water
PGE	Polyglycerol esters
POFA	Palm oil fuel ash
STS	Sorbitan tristearate
W/O	Water in oil

PEMECAHAN EFLUEN EMULSI MENGUNAKAN ABU MINYAK KELAPA SAWIT (POFA) YANG DIUBAH SUAI

ABSTRAK

Minyak dan gris adalah masalah biasa yang timbul di loji rawatan air sisa industri makanan. Komplikasi daripadanya dapat dikurangkan dengan memisahkan minyak dalam emulsi air menjadi dua fasa yang berbeza. Oleh itu, pemisah emulsi yang berkesan dan murah diperlukan dan abu minyak kelapa sawit (POFA) yang merupakan produk sampingan industri minyak sawit yang terkenal di negara-negara seperti Indonesia dan Malaysia dianggap sesuai untuk memenuhi tujuan kajian ini. POFA menunjukkan potensi yang besar untuk digunakan sebagai pemecah emulsi kerana struktur, ketersediaan, dan sifatnya yang menjimatkan. Kajian ini menyelidiki pengubahsuaian optimum yang harus dilakukan pada POFA sebagai pemecah emulsi yang melindungi rawatan terma dan kimia untuk menghasilkan prestasi yang luar biasa semasa proses pemecahan emulsi. Untuk menganalisis sifat tertentu seperti morfologi dan keliangan POFA yang mentah dan POFA yang diubah suai sebelum dan selepas proses pemecahan, kajian pencirian dilakukan melalui Fourier transformed infrared (FTIR) spektroskopi dan analisis luas permukaan BET. Pengubahsuaian melalui rawatan kimia menunjukkan kecekapan pemecahan yang lebih baik berbanding dengan rawatan terma kerana struktur yang lebih berpori dan peningkatan luas permukaan POFA. Kesan parameter proses yang berbeza termasuk dos pemecah emulsi dan masa interaksi dikaji pada suhu dan kepekatan emulsi yang ditetapkan pada 30 °C dan 5000 ppm masing-masing. Keberkesanan pemecahan emulsi yang optimum diperoleh menggunakan 1.5g POFA

selama 120 minit. Kecekapan pemisahan yang luar biasa oleh POFA yang diubah suai diperhatikan pada emulsi yang distabilkan oleh pengemulsi sorbitan tristearate (STS) berbanding dengan pengemulsi polyglycerol esters (PGE). Maka, terbukti bahawa POFA akan menjadi agen pemecah yang cekap dan layak dari sudut ekonomi untuk digunakan dalam perawatan emulsi minyak dalam air dari industri makanan.

DEMULSIFICATION OF EMULSION EFFLUENT USING MODIFIED PALM OIL FUEL ASH (POFA)

ABSTRACT

Oil and Grease is a common issue arising in the food industry wastewater treatment plant. The complications from it can be greatly reduced by separating the oil in water emulsion into two distinct phases. Thus, in order to fulfill the purpose, an effective and cheap demulsifier is required and Palm oil fuel ash (POFA) which is a prominent palm oil industrial byproduct in nations such as Indonesia and Malaysia considered propitious. It exhibits significant potential to be employed as a demulsifier owing to its outstanding structure , availability, and cost-effective properties. This study investigates the optimum modification to be done on POFA as a demulsifier including thermal and chemical treatment to result in an outstanding performance during the demulsification process of oil in water emulsion. To analyze the properties such as morphology and porosity of the pristine POFA and modified POFA before and after demulsification, characterization studies were carried out via Fourier transformed infrared (FTIR) spectroscopy and BET surface area analysis. Modification via chemical treatment demonstrated better demulsification efficiency compared to thermal treatment due to the more porous structure and increased surface area of POFA. The effects of different process parameters including demulsifier dosage and contact time were analyzed via batch demulsification study at fixed temperature of 30 °C and emulsion concentration of 5000 ppm. An optimum demulsification efficiency was obtained using 1.5g of POFA for 120 minutes. An outstanding separation efficiency by modified POFA was observed on

emulsion stabilized by sorbitan tristearate (STS) emulsifier compared to polyglycerol esters (PGE) emulsifier. It is certainly proved that POFA will be a promising and economically feasible demulsifying agent to be utilized in treating oil in water emulsion from food industries.

CHAPTER 1

INTRODUCTION

Within an emulsion, there are numerous oils and surfactants present which hold it strongly and make it significantly stable. They spread as tiny liquid drops in water. Oily water emulsions are amongst the most common contaminants released into the environment by numerous industries. The presence of emulsions in the wastewater stream leads to many consequences within the system. If the emulsions are decided to leave unregulated, they frequently result in significant wastewater treatment loads. The oil particles from unseparated emulsions tend to coagulate and deposit on the edges of settling tanks, digesters, pipes, pumps, and sensors presents future issues. This contributes to pipeline blockage, which necessitates cleaning and repair operations (Saifuddin and Chua,2006)

As a result, emulsion breaking is essential to the treatment of emulsion wastewater produced by the food industry. In order to reduce the environmental risk that these waste emulsions pose, this paper to a great extent focuses on the discovery of the suitable type of demulsifier to demulsify the O/W emulsion. Through demulsification, the emulsion is decomposed into its basic liquids. Demulsification is proposed as a method to treat the emulsions produced in food industry owing to its effectivity and cost effectiveness. The selected demulsifier necessarily must be economically friendly and cause minimal pollution to the environment throughout its utilization, results in nominal generation of secondary pollutants and most certainly exhibit enhanced efficiency in oil removal efficiency. The performance of the demulsifier is further observed based on several factors and constantly improved to provide a better activity.

1.1 Background of Study

According to Becher,(1957), an emulsion is defined as a heterogeneous combination made up of at minimum one immiscible liquid extensively distributed in another in the appearance of droplets with a diameter greater than 0.1mm in most cases (Groves and Freshwater,1968). Of that kind systems have a low level of stability, which can be further increased by adding additives such surface-active compounds, finely divided particulates, and so on.

The distribution of the oil and water phases in the scattered environment dictates the form of emulsion. The terms oil and water correspond to the less polar and more polar of the two main immiscible phases, accordingly. Traditionally, the merging of water and oil portions should potentially result in two basic forms of emulsions named as simple emulsions. The first is a water-in-oil (W/O) emulsion, for which the oil is the uninterrupted layer, and the water is scattered throughout the oil in spherical droplets configuration with the diameter that commonly ranges between 100 nm and 100 µm. The oil-in-water (O/W) emulsion, on the other hand, distributes the oil molecules in the water. Followed by this the formation of biemulsions takes place under certain operating conditions where the emulsions with two intermediate phase droplets that possess similar nature with varying size of droplets or unique characteristics regardless of their droplet dimensions. Multiple emulsions on the other hand are denoted as w1/o/w2 or o1/w/o2 based on the nature if an oil phase (hydrophobic) divides the internal and external aqueous phases, or an aqueous phase (hydrophilic) splits the internal and external oil phases. In this formation, the internal and external parts might not always be equivalent (Yaqoob et al.,2006).

Emulsion research and engineering fundamentals are widely used in the food sector to generate a diverse range of emulsified foods, including drinks, milks, creams, dips, sauces, desserts, dressings, mayonnaise, margarine, and butter. Such items have particular functional properties due to the characteristics of emulsions, such as appealing looks, textures, mouthfeels, and fragrance profiles (Tan and McClements,2021). After leaving the production, the form of the goods may proceed to alter as a response of heat or mechanical stresses, or biological activity. As a result, it is core of the food processor's expertise to offer structures that are not only generally acceptable, but also strong enough to endure changes during the product's shelf life (Guzey and McClements,2006).

Food emulsions are commonly classified into two major types such as water-in-oil (W/O) emulsions and oil-in-water (O/W) emulsions. Examples of food products that are synthesized from W/O emulsion are butter, margarine, or low-calorie spreads while milk and cream are based off O/W emulsions (Krog,2011).The initial stage in the development of a persistent emulsion involves the scattering about one liquid phase in some other liquid phase through a powerful mechanical agitation (Adheeb Usaid et al.,2014). The mechanical integrators or homogenizers employed in this operation depend on the sort of emulsions being developed. W/O emulsions are created by uniting the water and oil phases while stirring with a minimal energy requiring propeller-type stirrer according to Figure 1.1 below, producing a relatively fine dispersion of water droplets varying in size from 5 to 50 mm or above. The majority of O/W emulsions, including dairy-based emulsions, are created through energy intensive homogenization operation, in which oil or fat molecules form in turbulent flowing circumstances. Throughout homogenization, emulsifiers bind to the sides of newly synthesized particles, lowering interfacial tension and allowing for additional droplet rupture (Adheeb Usaid et al.,2014).

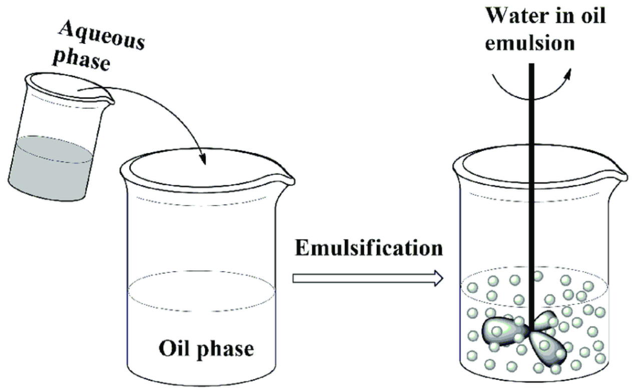


Figure 1.1 Schematic Representation of Emulsification Process (Ganesan et al.,2018)

Furthermore, they establish a shielding barrier surrounding the droplets, which may aid prevent accumulation by establishing repulsive interactions. This yields a scattered phase with droplets sizes extending from 0.3 to 3 mm, having a mean particle dimension of 0.5 mm (Krog,2011). The emulsifier's development of a monomolecular membrane at the lipid/water interphase is a crucial step in the emulsification mechanism (Adheeb Usaid et al.,2014).

Emulsifiers are chemicals that aid in the creation of emulsions or improve their stability (Hasenhuettl and Hartel,2008). Emulsifiers' activity differs substantially in their ability to produce microscopic oil particles throughout homogenization and in their capability to resist droplet aggregation under various external conditions such as pH, ionic force, heating, and freezing(McClements,2004). Other factors that come in line in utilizing the suitable emulsifier are price, accessibility, flexibility of usage, compatibility with other substances, and eco- friendliness. As a result, no one particular emulsifier is suited for usage across each sort of food item. The ideal emulsifier or mixture of emulsifiers for a certain food product is determined by the sort and concentration of other substances involved, the method of production, and the environmental parameters that it encounters during manufacturing, storage, and consumption (Guzey and McClements,2006). Mustard, soy, and egg lecithin, mono- and diglycerides, polysorbates, carrageenan, guar gum, and canola oil are among prominent emulsifiers employed in conventional food preparation (Zelman,2017).

In this study, the type of emulsion being focused is oil-in-water (O/W) emulsions and the main food product that falls under that category such as ice creams. Additives such as emulsifiers and stabilizers are utilized in the conventional ice cream production. Emulsifiers regulate lipids in the compound to enhance chewability, texture in terms of smoothness and creaminess, and heat impact tolerance throughout the ice cream's targeted shelf life. The addition of stabilizers on the other hand is completely noncompulsory in this process taking into account water/ice and fat are appropriately regulated. However, as time progresses and conditions of the supply chain varies, the risk to specified textural attributes during the consumption rises. As a result, there is a continual requirement for stabilization (Potter and Williams,1950). The primary objective of an ice cream stabilizer is to minimize the proportion of free water within ice cream formulation by attaching it as "water of hydration" which in return increases the viscosity of the product thus making it stable under fluctuating environmental conditions (Hooinee,2020).

The employment of emulsions and stabilizers in this manufacturing of food products mainly leads to the elevation of the oil and grease (O&G) content in the wastewater stream of the industries. The presence of this O&G ultimately brings future complications in the wastewater treatment procedures as it is challenging to breakdown the emulsions naturally as surfactant compounds, which perform as 'binding agents' and locates themselves among the non-miscible components, additionally strengthens their stability. It is among the very challenging and complex discharges to treat since food processing effluent seems to have a significant concentration of nutrients, organic carbon, inorganics, suspended and dissolved particles, and elevated biochemical as well as chemical oxygen demands. Treating the effluent in several stages is necessary so that it will not impact incoming streams result of extreme nutrients or oxygen demand if released directly, plus that would neither interrupt publicly owned treatment works (POTWs) if emitted to drains (Lindsey,1998).

1.2 Problem Statement

Contribution of emulsions to various industries such as oil and gas industry, pharmaceutical industry, manufacturing industry and primarily in food industry is immense. Every process of the food production mainly consists of the utilization of emulsion for numerous purposes. From the industry's point of view, emulsions are a stable compound that needs an additional chemical agent to be broken down into water and oil particles to make treatment method easier. This is due to the formation of this O/W emulsion which does not occur under natural influences but with an aid of chemical agents.

However, this emulsion somehow needs to be segregated in the pre-treatment stage to withdraw the accumulated oil particles at that stage itself. Flow emulsion effluent from the raw tank to the subsequent treatment stages causes future complications as they have the ability to coagulate and settle on the edges of settling tanks, digesters, pipes, pumps, and sensors (Husain et al.,2014). This contributes to blockage of pipelines in treatment facilities that require cleaning and, in some cases, pipe reconstruction which eventually requires additional service and inspection expenses.

Unseparated oil particles from the effluent at the beginning stage of wastewater treatment also gives rise to downstream complications by leading to blockages developed when coarser particles, such as personal care wipes, obstruct sewage pipelines. Accumulated oil particles will cover these chunks and permit debris to bind to them, resulting in larger jams that can load over than 150 tons under certain circumstances. They are harder to eliminate, and when they have completely plugged a sewage stream, spills can occur, disrupting everything in a city from traffic to drinking water source (Hubbard-Hall,2020).

The emulsified oil droplets(O/W) present in the wastewater stream are made up of relatively narrow size distribution and a high viscosity, and the oil particles carries negative charges. Ineffective handling of these particles in the raw tank itself allows permits them to be released into natural water lines, obstructing gas interchange, affecting photosynthesis process, contaminating the soil, and endangering human health conditions in the end (You et al.,2018).

Dairy wastewaters are distinguished by a broad pH spectrum value ranging from 3.5 to 11, as an outcome of the utilization of alkaline and acid surfactants and sterilizers (Noukeu et al.,2016).The dairy sector produces powerful wastewaters typically exhibit elevated levels of organics (BOD5, COD), primarily carbohydrates, proteins, and lipids derived from milk which can be 10–100 times significantly higher than levels observed in household effluent. Because the dairy sector generates a variety of goods (milk, butter, yoghurt, ice cream, and cheese), the breakdown of the wastewater fluctuates depending on the nature of product and technique employed (Noukeu et al.,2016).

Any unremoved oil particles that flow through the effluent to the second level of wastewater treatment (physical-chemical treatment) section requires additional chemical substances to treat them. This secondarily increases the investment cost involved in purchasing the amount of chemicals needed to treat the effluent.

Moreover, the breaking of emulsion which subsequently results in coalescence of the oil droplets is crucial because failure to do so will develop consequences to the microbes in the biological treatment stage. The oil and grease coating decreases the biological action of the treatment operation by forming an oil coating surrounding bacteria in suspended debris and water causing microorganisms to flow away from the system (El-Gawad ,2014).This results in lower dissolved oxygen concentrations in the stream due to the interference occurred with oxygen-transfer efficiency (Schultz,2005).The oxygen molecules are then unable to be oxidative for microbes on hydrocarbon molecules, contributing in ecological damage to water bodies. Furthermore, in an aerobic operation, the biodegradation of emulsion compounds requires a large amount of oxygen, which demands a lot of energy and has considerable operating expenses (Condorchem Envitech,2016).

1.3 Objectives

1. To synthesize and modify POFA for optimum oil in water emulsion effluent demulsification treatment.

2. To evaluate the performance of POFA resulting from different modifications via thermal ,chemical and combination of both treatments.

3. To identify the effect of demulsifier dosage, contact time and type of emulsifier used on the demulsification efficiency.

1.4 Scope of Study

The initial level of this study includes the screening of demulsifier synthesized via thermal and chemical treatment. This study intends to select the most effective modified POFA that would result in the optimum demulsification efficiency. During thermal modification, the POFA was treated at various calcination temperature ranging from 250,550,750 and 1000. On the other hand, chemical activation was done using two chemical groups namely acid groups including sulphuric acid and hydrochloric acid and alkali groups including sodium hydroxide and potassium hydroxide. After the selection of outstanding chemical to result in remarkable performance, the concentration of that chemical was varied to study the difference in the demulsification efficiency. To further enhance the performance, the research extended to combine both thermal and chemical treatment to observe its effect on the performance.

The second stage of the study includes the analysis the effect of contact time and demulsifier dosage on the demulsification efficiency of the emulsion. The potential of the demulsifier was additionally investigated by using two different emulsifiers namely polyglycerol esters and sorbitan tristearate. Followed by this, the reusability of the demulsifier was examined as an initiative to minimize the waste produced and the cost involved to synthesize the demulsifier.

The subsequent stage involves the characterization study of the demulsifier using Fourier Transform Infrared Spectroscopy (FTIR) and BET surface area analysis. This aided in understanding further the role of the demulsifier in this demulsification process. In addition, another test was carried out to identify the oil and grease content in the emulsion before and after the process utilizing the modified POFA.

CHAPTER 2

LITERATURE REVIEW

2.1 Emulsion Generation in Industries

Emulsion is predominantly being utilized or produced in various industries such as in oil and gas industries, food industries, metal manufacturing industries, medical industries and so on. In the crude oil manufacturing industry, the formation of emulsion occurs naturally without any chemical activities when the oil or water particles propagates into one another as it is circulated through the manufacturing processes. The further shearing generated throughout circulation, as well as the presence of natural surfactant compounds in crude oil, makes the emulsion become more resistant to breaking. The typical type of emulsion formed in this oil refinery industry is W/O emulsion due to the common presence of the indigenous surfactants that exhibit lipophilic properties (Yan et al.,2014).

In the other case, emulsions are formed as a byproduct of an operation carried out in a particular industry. Commonly, in metal assembling industries, surface treatment is an essential phase before assembling all the finished products. This surface treatment process consists of several activities such as drawing, spraying, and electroplating of iron and steel and requires the metal surface to be free from dirt and dust particles which might result in unprofessional finishing. To do so, hydrochloric acid pickling is employed due to its superior picking capacity and speed. Throughout this pickling process, a huge volume of emulsified oils reaches the scrubbing solution, and this uncontrolled number of emulsified oils in the cleaning solution are a major factor in the pickling solution being discarded (Zuo et al.,2017).

Major industries such as petroleum industries undertake many techniques as an effort of extraction process. Among them, water blending has been widely employed in numerous mining activities namely tertiary oil extraction and heavy oil viscosity reduction innovation. Owing to the existence of both water and oil particles in this process, in the refinery activities generation of significant amounts of oil-in-water (O/W) and water-in-oil (W/O) emulsions or greasy wastewater is highly expected and consistent (Liu et al.,2017). In the same oil extraction operation conducted in massive oilfields, common waste that is being generated is Super heavy oil wastewater (SHOW) which comprises numerous pollutants including high amounts of oil, SS (total suspended solid), reductive substances (such as sulfide, Fe and Mn) and saline materials and dissolved recalcitrant organic compounds such as polymers and surfactants. Together with this the presence of natural occurring emulsifiers such as asphaltenes, resins, and naphthenates become a reason for the synthesis of O/W emulsion in the SHOW due to their immense hydrophilic properties. Moreover, nonionic surfactants like nonyl phenol ethoxylate are also introduced to promote the mobility of heavy-viscous crude oils via the pipelines. Such organic agents diminish the interfacial resistance between crude oil and water and enhance emulsion resilience towards breaking (Tong et al.,2013).

In some rare scenarios, the emulsions that exist in the environment may also be a result of tragedies involving spillage for example Gulf of Mexico oil spill, which have led to a wide range of enormous quantities of crude oil discharge into seas and rivers.

2.2 Emulsifiers in Food Industry

Food colloids, emulsions, and foaming agents are naturally found in the environment and have undergone subsequent changes driven by the evolving food processing technology. As an instance, milk contains a naturally present membrane that permits solid fat to distribute into an aqueous layer. The naturally available emulsifying agent was utilized vastly in the ancient time to produce butter, cheese, whipped cream, and ice cream. Artificial emulsifiers were not widely used commercially until the second half of the last century. The industrialized food business, which demanded shelf-stable items for delivery via widespread networks, is one of the major driving forces which propelled their advancement further. Thick salad dressings, for example, can be maintained for nearly to a year without observable breakdown. Other characteristics, including rancidity, are becoming increasingly significant in determining item longevity (Hasenhuettl,2008). Surfactants exhibiting enhanced and greater cost-effective properties were synthesized as a result of the development in chemistry and engineering. The availability of a diverse range of food emulsifiers has resulted in a variety of regional dispersion of processed food. This feature enhances economic benefits, allowing for further affordable costing for buyers (Hasenhuettl and Hartel,2008).Food emulsifiers are classified according to their origin, whether synthetic or organic; their ability to ionize, nonionic or ionic; their hydrophilic/lipophilic balance (HLB); and the availability of functional groups.

Firstly, food emulsifiers can be divided into four groups depending on their charge when they are solubilized in the water. The dissociation of the emulsifier in the water can produce emulsifiers that are either anionic, cationic, or amphoteric in nature. Anionic emulsifiers produce negatively charged ions after the dissociation. This type of emulsifier functions well in environment that possesses neutral to alkaline pH. Moreover, anionic emulsifier is responsive towards ionic strength, thus it mostly shows weak performance in concentrated salt conditions. This is because, the salt conceals the negative charges, rendering the anionic emulsifiers useless and the emulsion gradually degraded. Examples of anionic emulsifier include Sodium stearoyl-2-

lactylate (SSL) and alkyl carboxylates, phosphates .Meanwhile, Polysorbate 60, Steareth 20 and Cetearyl Glucoside are examples of cationic emulsifiers which release positively charged ions in water and behave optimally at acidic pH levels.

In most cases, cationic emulsifiers are not employed in food emulsions to produce emulsion-based items as they are fairly poisonous which might raise health hazards. Nonionic emulsifiers exhibit neutral charge once it is mixed in water. This emulsifier is versatile and displays excellent performance alongside all existing forms of emulsifiers. They are not particularly sensitive to pH or saline levels. Mono- and diglycerides (MDGs) are some of the common examples. Lastly, amphoteric emulsifiers produce equally positive and negative charged ions when exposed to water. Apart from some that are ineffective at the isoelectric threshold, they are uninfluenced by pH settings. As an instance, lecithin is mostly used amphoteric emulsifier in food technology (Miller,2016).

The nature of emulsion developed is determined by an emulsifier's solubility parameter. The layer containing the least soluble emulsifier forms the continuous phase. Emulsifiers are amphiphilic, which is a critical property. This forms the structure of the emulsifier which constitutes of lipophilic and hydrophilic ends. The figure below reveals the structure of an emulsifier structure which is made up of a tail and a head. The tail part is the lipophilic end which is often a long-chain fatty acid derived from food class fat or oil. This end solubilizes very well in oil phase hence it is commonly also known as oil loving. The head section is the hydrophilic end and typically termed as water-loving due to its polar characteristics that make it highly soluble in water. O/w emulsions are prepared by emulsifiers that seem to be highly soluble in water phase. The added emulsifier reacts significantly only with water, lowering the surface tension of the water to practically 0. The mixed water now turns out to be the outermost layer of the emulsion due to the grouping of the water droplets. This retains the included oil to be scattered as individual particles to form an o/w emulsion. On the other hand, emulsifier that is highly soluble in oil phase tends to react weakly in water phase which prevents the water's surface tension to remain the same. Due to this, the water droplets are not able to combine together ,thus persists as distinct droplets in the oil, yielding a w/o emulsion (Miller,2016).

In most industries, HLB is the commonly utilized parameter in identifying the ideal class of emulsifier to be used. HLB is a measure of emulsifier solubilizing characteristics that identifies the form of emulsion for which the emulsifier is ideally adapted . HLB levels can indeed be estimated using the emulsifier's molecular nature or discovered experimentally. Emulsifiers that exhibit low HLB values dissolves rapidly in oil phase whilst high HLB values indicate that the emulsifier is inclined towards water-soluble properties. Emulsifier performance is influenced by operating environments and substances like sugar, salt, as well as protein. The degree of the contact has been shown to be significantly essential than the presence of reactive compounds in influencing the hydrophilic qualities of emulsifiers employed in food industries. Identifying the best emulsifier or pairing of several emulsifiers frequently necessitates research and testing (Miller,2016).

Reactions such as alcoholysis or rapid esterification of consumable fatty acids derived from animal or vegetable feedstock combined polyols produces food emulsifiers (i.e., glycerol, propylene glycol, and sorbitol). Subsequent treatment employing ethylene oxide or esterification with organic acids results in something like a diverse variety of emulsifiers having varying characteristics. MDGs, stearoyl lactylates, sorbitan esters, polyglycerol esters, sucrose esters, and lecithin are regularly exploited food emulsifiers. The range of food items that can be manufactured utilizing those emulsifiers are summarized in Table 2.1 below (Miller,2016).

Table 2. 1 Typical Emulsifiers and their Functions (Miller,2016).

Emulsifier	**Food Items**
Mono- and diglycerides	Bread, cake, pasta, frozen dessert, icing, topping, peanut butter, margarine, coffee whitener, and pasta
Glycerol monolaurate	Bread, whipped topping, frosting, glaze, and cheese products
Ethoxylated monoglyceride	Bread, whipped topping, icing, frozen dessert, and coffee whitener
Diacetyl tartaric acid esters of monoglyceride	Bread, extruded products, icing, margarine, and salad dressing
Succinylated monoglyceride	Bread
Calcium stearoyl-2-Lactylate	Bread and egg whites
Propylene glycol esters	Cake, whipped topping, dehydrated potatoes, and shortening
Sorbitan esters	Whipped topping, cake, cake mix, cocoa, icing, filling, and coffee whitener

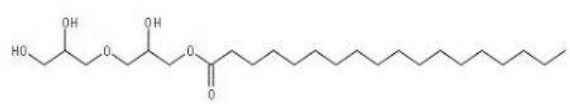
Polysorbate 60	Whipped topping, cake, cake mix, cocoa, icing, filling, coffee whitener, shortening, salad dressing, and edible oil
Sucrose esters	Bread, bakery mixes, frozen dessert, whipped milk products, and ice cream
Lecithin	Baked goods, chocolate, cooking spray, instant foods, and margarine

2.2.1 Polyglycerol Esters

Polyglycerol esters (PGE) are a form of emulsifier that is widely employed throughout the food business due to its amphiphilic behavior in a variety of foods. Due to the obvious combination of hydrophilic and lipophilic components in the same molecule, the esters (fatty acid esters of polyglycerol) have distinct interfacial abilities. The polyglycerol in the emulsifier, which forms the hydrophilic portion, is made up of a succession of oligomeric hydroxyethers of glycerol. Intermolecular condensation of glycerol is a reaction that is performed in elevated temperature settings that leads to the production of alkoxy intermolecular bonds connecting the glycerol subunits. The equivalent polyglycerol esters are synthesized by polyglycerol and fatty acids via explicit esterification of (or inter-esterification of) triglycerides and polyglycerol (Norn,2014).

In comparison to several conventional food emulsifiers, these emulsifiers are non-ionic and possess a vast span of polarity or hydrophilic-lipophilic balance (HLB) levels extending from 6 to 11. The variation in the polarity values is influenced by numerous elements arising from fluctuations in the degree of glycerol polymerization, the forms of esterified fatty acids involved, or the degree of esterification. This wide choice of this emulsifier that exhibits different characteristics, allows it to be widely utilized in food industries to manufacture numerous forms of food items (Norn,2014). The physicochemical properties of this emulsifier are as summarized in Table 2.2 below.

Table 2. 2 Specifications of PGE Emulsifier (“Polyglycerol esters of fatty acids,” 2007)

Properties of PGE		**Chemical Structure**
Molecular Formula	$C_{24}H_{48}O_6$	
Molecular Weight	432.63432	
CAS Number	67784-82-1	
HLB (+-1)	6-11	
Physical Form	Solid	
Texture	off-white to brownish sticky liquids or solid powders with a waxy appearance in room conditions.	

Polyglycerol esters exhibits sticky liquids or solid powders with a waxy appearance in room conditions. It appears in multiple color form ranging from off-white to brownish depending on the surroundings. Although the surrounding environment influences the color, the main parameter that determines the color of the emulsifier is the origin of fatty acids. In the meantime, the polyglycerol component also plays as a minor contributor to the color of the ester. Given mild settings, the thermal stability of polyglycerol esters seems to be decent since esters are typically stable in nature. The solubility of polyglycerol ester in organic solvents is determined by the properties of the solvent as well as the polarity of the ester, although esters are most soluble in protic and dipolar aprotic solvents, including lower alcohols and dimethyl-sulphoxide (Norn,2014).

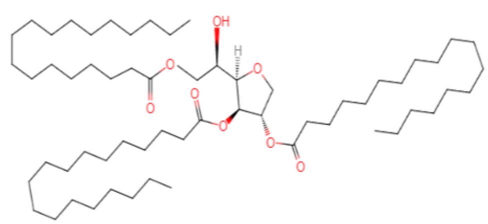
The common ingredient in most of food preparation like baking, frying and more which is margarine extensively utilizes PGE in the manufacturing process. The employment of this emulsifier not only helps in the emulsification activity but also enhance the margarine's functioning characteristics. It optimizes the organoleptic qualities of a margarine or low-fat distribution by minimizing the compression artifacts of the lipid phase, producing in margarine with the fluidity and flexibility of fresh butter. The margarine produced by using PGE emulsifier contributes greatly to the performance of the baking activities by producing baked foods with even more consistent layering, distinctly separate layers, and even growth of batter (Norn,2014).

Apart from margarine production, incorporating PGE emulsifier in cake batters directly, balances the batter, allowing the foam to remain together for a prolonged length of time without releasing air. Moreover ,it is able to promote the foam development, resulting in an improved final cake size, enhanced, and thin-walled crumb texture, excellent consistency and slicing features, and upgraded consumable flavor (Norn,2014).

2.2.2 Sorbitan Tristearate

Sorbitan tristearate (STS), commonly known as Span 65 are classified as non-ionic lipophilic emulsifiers possessing minimal HLB.The sorbitan ester's hydrophilic/lipophilic characteristics are determined by the extent and form of fatty acid that undergoes the esterification. Typically, the lower HLB value is produced by the shorter chain length of the fatty acid which means they are directly proportional to each other (Cottrell and Peij,2014). The physicochemical properties of this emulsifier are as shown in Table 2.3 below.

Table 2. 3 Specifications of STS Emulsifier (Bährle-Rapp, 2007).

Properties of STS		Chemical Structure
Molecular Formula	$C_{60}H_{112}O_8$	
Molecular Weight	963.51	
CAS Number	26658-19-5	
HLB (+-1)	2.1	
Physical Form	Solid	
Texture	pale cream to brown bead, flakes, or firm, waxy bulk with a mild smell.	

Sorbitan esters of fatty acids are synthesized by simply reacting sorbitol with a market quality fatty acid. STS emulsifier to be exact is synthesized by uniting three moles of stearic acid with one mole of sorbitol. .Sorbitol, and including mannitol, seems to be the primary raw source for sorbitan esters and has been formerly manufactured via hydrogenation reaction of sucrose. Conversely, a relatively cost-effective and purified and high-quality version of sorbitol is now extensively synthesized from d-glucose, a raw material obtained from sources like corn syrups or tapioca. Under pressure, d-glucose reacts along with hydrogen gas aided by a catalyst including nickel phosphate or ruthenium dichlorotriphenyl phosphine. Sorbitol falls under a class of chemical compounds known as sugar alcohols or polyols, all of which exhibit indistinguishable characteristics of glycerol (Cottrell and Peij,2014).

Sorbitan tristearate (STS) is an extremely lipophilic compound that is mostly used primarily as a crystal enhancer in food items that composed of fat as a major ingredient such as margarine ,chocolate. STSs mainly functions to limit fat crystallization by stabilizing the β’ crystal form and inhibiting the generation of the higher melting β crystalline structure. The β crystals develop very massive, resulting in a granular consistency in margarine or spreads which reduces the food quality. Identical fat crystal changes contribute to the formation of an issue known as "bloom," which looks like grayish patches on the exterior of chocolate items (Krog and Sparso,2004). Unless the beta crystal dimension is maintained within the perception cutoff value , the beta prime solidified margarine quality is retained. The STS emulsifier has also reported to be notably excellent in maintaining the polymorph β’ of margarine products and altering the solid fat content (SFC) level, hence creating fusion patterns optimal for varying body temperature (O Brien and Timms,2004). STS immaculate potential to co-crystallize with triacylglycerides in the β '-crystal form is very essential in manufacturing products such as cocoa butter substitutes (CBS) or cocoa butter replacers (CBR) and apparently it serves better performance in exhibiting the crystal altering operation compared to other commercial emulsifiers like LACTEM or CITREM (Faergemand and Krog,2003).

2.3 The Importance of Emulsion Breakdown

Every emulsion that presents in the processes that take place in any industries requires to be demulsified for various reasons. The reason behind the demulsification of the emulsions exist mainly depends on each industry and their wastewater treatment strategies. However, the main purpose of this demulsification process is mandated by past environmental legislation(Fang et al.,1988). The accumulation of oil, grease, soluble organic material, or gas condensate in waste effluent has a negative influence on human and animal wellbeing as well. The oil spills that occur in the seas and river areas have seriously contributed to the squandering of valuable marine resources which in a way has caused severe harm to families that depend on those resources for their living.

Apart from the environmental impact, the consequences brought by emulsions from an industry's point of view is extremely essential to be given adequate observation. Emulsion produced in the petrochemical sectors leads to huge issues to the equipment involved in the operation system when left unregulated as it potentially brings about significant rise in the wastewater management demands. The oil particles that exist in the effluent can drastically impair skimmer retrieval power, limit pumping volumes, and exacerbate handling, oily debris discharge, separation, and storage issues. Furthermore, the development of high viscosity emulsions reduces or eliminates the effectiveness of non-mechanical response indicators such as the application of dispersants and in situ incineration. They are also capable of inducing fouling and unit disturbances if they contact onsite operational systems (Saifuddin and Chua,2006).

In addition, the synthesized O/W emulsions considered troublesome in petroleum industry due to significant degradation rate to pipeline walls and distillation machinery, considerable poisoning effect to catalysts in refining steps, and other factors (Liu et al.,2017). Taking into account the cost that has been put into constructing this systems and pipelines for this process, thus, the elimination of the emulsions by breaking it is very important to minimize the maintenance and repairing expenses. Similarly, in the oil industry, the W/O emulsions that carry water and salt particles in it acts as a prime culprit that leads to corrosion of the apparatus and catalyst disablement (Yan et al.,2014). Besides, demulsification of emulsion is necessary to preserve the shelf life of certain chemical, for example in the metal industry, extracting emulsified oils from emulsified pickling solution can extend the serviceability of the pickling solution, resulting in less pickling effluent liquid output (Zuo et al.,2017).

2.4 Demulsification Process

The methods utilized to demulsify and separate the emulsions differ according to every industry and the preferred percentage of demulsification efficiency. Conventional procedures for oil/water demulsification encompass physical operations such as centrifugation splitting, floatation segregation, gravity separation, so on and so forth, chemical techniques such as neutralization, flocculation separation, and many more, electro-chemical methods such as electrolysis separation, electromagnetic separation, and as such on, and biological treatment processes such as biological rotating disc process, activated sludge, and quite forth. Although the majority of the procedures have been successfully implemented in real-world oil/water extraction circumstances, typical approaches have drawbacks such as low removal efficiency, additional contamination, sluggish demulsification speed, increased price, and etc. These disadvantages limit the growth of these old techniques and encourage the evolution of more effective technologies for oil/water split (Zhang et al.,2017).

Observation has been made that the demulsification of W/O emulsion is more well know and widely studied by other investigations which have produced satisfactory results. However, the demulsification of O/W emulsion in the petroleum industry has been a challenging issue till date because of various reason. Firstly, the amount of such emulsions being produced in the industry is considerably high which demands for either immense quantity of demulsifier or strong demulsifying agent. Secondly, the size of the oil droplets in the emulsion plays a significant role in the demulsification efficiency. The small size oil droplets(d < 20 µm) dispersed in the water phase reduces the effectiveness of the physical demulsification methods due to its dimensions and very persistent oil-water interface protective coating.

Study conducted by Liu et al.,(2017), proposed an excellent and practical demulsification procedure which is simplistic as well which involves the utilization of graphene oxide (GO) nanosheets. Demulsification conducted employing this agent noted to result in separation performance that is both quick and high. The main drawback faced by utilizing this demulsifier was the presence of GO nanosheets in the aqueous or oil phase of the separated emulsion. This brings to the contamination of the water or oil in the next level operation. Thus, magnetic nanoparticles (MNPs) such as (c-Fe3O4 and c-Fe2O3) come in play to separate the used nanosheets after the demulsification process. The wide application of these MNPs in environmental remediation, magnetic separation and in many other sectors makes it to be suitable for this recycling purpose. Binding of this MNPs to the nanosheets provide them outstanding magnetic field which aids in separating it after the demulsification activity through magnetic