Methyl Ester Sulfonate as an Alternative to Petrochemical Based Surfactants

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Abstract: Surfactants are amphiphilic surface-active compounds that reduce the interfacial tension between two liquids, between a gas and liquid, or between a liquid and a solid. This group of surface-active molecules involving both hydrophobic and hydrophilic moieties in their organized structure may perform their role as detergents, emulsifiers, foaming agents, dispersants, or wetting agents. According to the market research report of 2020, the global surfactants market size was USD 44,157.4 million in 2019. However, a substantial segment of the overall surfactants' production is based mainly on petrochemicals. The progressive improvement in the standard of living & society's lifestyle with the increasing awareness towards the environment engenders to seek eco-friendly, cost-effective, and high-performance alternatives. Methyl Ester Sulfonates (MES), a bio-based surfactant, offers a viable green substitute over petrochemical-based detergent alkylates. Efforts have been made to discuss the conventional detergents and possible harms associated with them, basic ingredients constituting the detergent and their functioning, MES as an eco-friendly alternative, its production, limitations involved, and future opportunities.

INTRODUCTION OF DETERGENTS

Generally, the term 'Detergents' is applied to materials and/or products that provide the following functions: 1. Promote removal of material from a surface; 2. Disperse and stabilize materials in a bulk matrix.

The ability of a detergent to perform either of these functions depends on the composition of the formulation, the conditions of use, the nature of the surfaces being treated, the nature of the substance to be removed and/or dispersed, and the nature of the bulk phase. Accordingly, detergent formulation is a complex process driven by the specific needs of the end user, economics, and environmental considerations. By far the most common and familiar detergents are those used in household cleaning and personal care. These products can be grouped into four general categories:

1. Laundry detergents and laundry aids: These comprise mainframe laundry detergents in powder, liquid, tablet, gel, and bar form, fabric conditioner products typically in liquid form, and an array of specialty products like pretreaters, presoaks, and bleaches. Typical laundry detergents are formulated to provide general cleaning, which includes removal of soils and stains as well as the ability to maintain whiteness and brightness. In addition, many premium laundry detergents offer additional benefits like fabric softening, dye lock, fiber protection, and disinfectancy.

2. Dishwashing products: These include detergents for hand and machine dishwashing and are typically provided in liquid, gel, powder, or tablet form. Hand dish wash products are formulated to remove and suspend food soils from a variety of surfaces. They also must deliver long-lasting suds, even at high soil loads, and they must be mild to skin. Products designed for automatic dishwashing must provide soil removal and suspension, control of water hardness and sheeting of water off dish surfaces in order to achieve a spot- and film-free finish, and produce little or no suds that would otherwise interfere with the operation of the machine.

3. Household cleaning products: These are 'all-purpose' cleaners designed to penetrate and loosen soil, control water hardness, and prevent soil from redepositing onto clean surfaces. Many of these products also contain low levels of antibacterial actives like Triclosan to sustain disinfectancy claims.

4. Personal cleansing products: These include products for hand and body washing as well as shampoos, conditioners, and toothpastes. They are marketed primarily in bar, gel, and liquid forms. A major consideration in formulation of such products is the desired consumer aesthetic such as lather, skin feel, rinsability, smell, and taste. Within each of these categories products are formulated with specific ingredients selected on the basis of their ability to perform the desired function and deliver 'consumer preferred' aesthetics while meeting specific cost constraints, environmental regulations, and human safety guidelines.

In addition to these familiar consumer products, detergent formulations are used in a number of other applications and industries. These include environmental remediation (surfactant systems have been developed to aid in the cleanup of contaminated groundwater supplies), enhanced oil recovery (micellar and surfactant 'floods' are among the most successful methods of enhancing recovery of oil from depleted reservoirs), nanoegineering (phase behavior of surfactants are used to generate self-assembling nanosystems), formulation of paints and printing inks (the dispersion in paints is typically achieved with surfactants), preparation of synthetic polymers (emulsion polymerization and the preparation of latexes represent one of the largest uses for surfactants outside the cleaning area), industrial/metal parts cleaning, medical applications, lubricants, textile processing, agricultural preparations.

COMMON DETERGENT INGREDIENTS

Modern detergents can comprise 20 or more ingredients depending on what benefits the detergent is meant to deliver. Some of the common detergent ingredients and their functioning are described as follows:

A. Surfactants: Surfactants are the most common ingredient of the detergent and their primary function is to modify the interface between two or more phases in order to promote the dispersion of one phase into another. The ability of surfactants to concentrate at interfaces derives from their amphiphilic character—the combination of hydrophilic and hydrophobic moieties within the same molecule. Generally, surfactants are classified according to their hydrophilic component as nonionic, anionic, cationic, or amphoteric. Typical nonionic groups consist of polyoxyethylene, polyoxypropylene, alkanolamides, or sugar esters. As the name implies, the hydrophilic component of anionic surfactants comprises an anionic group, typically a sulfate, sulfonate, or carboxylate moiety. Likewise, the cationic surfactants comprise molecules containing a positively charged group such as a quaternary amine. The amphoteric surfactants are perhaps the most unique in that they comprise a hydrophilic group containing both anionic and cationic character such as the amino acids. Typical hydrophobes for surfactants are the alkyl chains between C_{10} and C_{20}, principally with the sodium or potassium salts of C_{12}–C_{18} chain length fatty acids.

B. Dispersing Polymers: The suspension of solids or liquids in a continuous phase is a critical aspect in the formulation of paints, inks, coatings, and agricultural products such as herbicides. Generally speaking, the particles to be suspended are sufficiently large that definite surfaces of separation exist between the dispersed phase and the dispersion medium. In order to keep the dispersed phase stable it is important to adsorb functional actives at these surfaces to prevent aggregation. This is one of the critical functions of surfactants.

C. Builders and Chelants: Builders, a generic term used to refer to any number of materials whose primary function is the removal of Ca2+ and Mg2+ ions from aqueous solutions, and Chelants are widely used in the formulation of various detergents. Sodium tripolyphosphate (STPP) is among the best known and widely used detergent builder. In laundry detergent formulations it serves not only as an extremely effective calcium control agent but also provides dispersion, suspension, and anti-encrustation benefits. However, environmental concerns associated with large-scale release of phosphates into the environment lead to the development of a number of substitutes. Citric acid and sodium nitrilotriacetate are representatives of soluble detergent builders

D. Bleaching Systems: Bleaches are common components of laundry, automatic dish wash, and hard surface cleaning detergent formulations where they act to destroy chromophoric groups responsible for color in soils via oxidative attack. Chlorine-based systems are common in some powdered abrasive hard surface cleaners and automatic dishwashing products.

E. Solvents: The selection of solvents for use in detergent formulation depends on the nature of the actives being formulated, the intended application of the detergent, and economics. Water is the dominant solvent in most household and industrial cleaning formulations. Generally speaking, water-based detergents are less toxic, more environmentally friendly, cheaper, more surface compatible, and easier to handle than petroleum-based solvents. However, many common detergent actives have limited solubility in water requiring formulation of a co-solvent and/or hydrotrope. Typical co-solvents used in household cleaning formulations include ethanol, glycerol, and 1, 2-propanediol.

F. Performance Enhancing Minor Ingredients: Depending upon the end use of the detergent formulation and the benefits to be delivered a number of performance enhancing minor ingredients may be used. These include:

1. Enzymes: Enzymes promote soil removal by the catalytic breakdown of specific soil components. Proteases (enzymes that degrade protein) are the most common of all the detergent enzymes but amylases (starch degrading), lipases (lipid degrading), and cellulases (cellulose degrading) are also used.

2. Brighteners/fabric whitening actives: These materials enhance the visual appearance of white surfaces, typically cotton fabrics, by absorbing ultraviolet (UV) radiation and emitting via fluorescence in the visible portion of the spectrum. Among the most commonly used whiteners in laundry detergents are the derivatives of 4, 4-diaminostilbene-2, 2-disulfonic acid.

3. Foam boosters: In some applications, most notably hand dishwashing and shampoos; it is desirable for the detergent formulation to generate a large-volume, stable foam. While most surfactants are capable of generating and sustaining foam in the absence of soil, these foams rapidly collapse in the presence of soil, especially particulate and fatty soils. In applications where foam must be maintained throughout the course of detergent use, specific boosters may be added e.g. Alkanolamides

4. Antifoam agents: Antifoam agents act to reduce or eliminate foams. They either prevent formation of the foam or accelerate its collapse. Alkyl ethoxylate, nonionic surfactants are commonly used as foam control agents. The hydrophobic oil promotes spreading of the particles at the air-water interface thereby ensuring entrapment in the foam film and subsequent foam disruption.

5. Thickeners: It is often desirable to modify the rheology of a detergent formulation to fit a particular application. For example, gel-type automatic dishwashing detergents are thickened to help suspend phosphate and other solids that would otherwise separate out from the liquid phase. Thickening can be achieved through the use of inorganic electrolytes, e.g. NaCl, carboxymethylcellulose (CMC).

6. Soil release polymers: Soil release refers to the enhanced removal of soil from a surface as a result of modification of that surface with a specific agent, typically a polymer that alters surface polarity thereby decreasing adherence of soil. CMC is the archetypical soil release polymer.

CONVENTIONAL DETERGENTS USED IN INDUSTRIES

Sodium Lauryl Sulfate: Sodium Lauryl Sulfate (commonly known as SLS) is an inexpensive detergent added to a huge number of personal care products such as shampoos, toothpastes, and soaps. Its purpose is to increase the lather that these products produce which assists with cleaning. SLS is produced by adding Sulfonic Acid and Dodecanol. This process is better known as Esterification. Once this has taken place it is then neutralized with Sodium Carbonate which then results in Sodium Lauryl Sulfate. Technically, SLS is a surfactant (surface active agent). This essentially means that it breaks the surface tension between two liquids, or a liquid and a solid.

While it does help cleaning products perform better, many are skeptical of using products that contain SLS/SLES because it is known to irritate the skin, gums, and scalp. There are many who are concerned about the long term health risks that SLS/SLES containing products can pose. In studies, there are significant correlations between SLS/SLES and contact dermatitis. The Journal of the American College of Toxicology says that it has “a degenerative effect on the cell membranes because of its protein denaturing properties”. It mentions that the high levels of skin penetration may occur at even low use concentration.

POTENTIAL RISKS INVOLVED

Some of the detrimental effects that can be associated with SLS/SLES are listed as follows:

a) Skin, Eye Irritation: It was shown to cause cataracts in adults, and is proven to inhibit the proper formation of eyes in small children.

b) Environmental Damage & Groundwater pollution.

c) Bioaccumulation

d) Toxic fumes release: Toxic Sodium Oxides and Sulfur Oxides are released when SLS is heated.

e) Corrosion: According to the American College of Toxicity, this includes corrosion of the fats and proteins that make up skin and muscle.

f) Long-term permeation of the body’s tissues.

g) Nitrate and other solvent contamination: Toxic solvents, including carcinogenic nitrates are used in the manufacturing of SLS, traces of which can remain in the product.

h) Highly polluting manufacturing process: cancer-causing volatile organic compounds, sulfur compounds, and air particulates are usually released during its manufacturing.

i) Penetration enhancer: Its molecules are so small they’re able to cross the membranes of body’s cells. Once cells are compromised, they become more vulnerable to other toxic chemicals that may be with the SLS.

SLS is not a recognized carcinogen itself; however when it is mixed with triethanolamine (or T.E.A) carcinogenic substances called nitrosames can form and be released. According to U.S. environmental protection agency study, SLES applied above 5% concentration produced severe irritation, hair loss and may lead to cancer. However in countries like India, Indonesia, Canada, Russia, Italy, Ireland and many more, the content of SLES is not maintained within the specified limit, and it is usually greater than 5%. Thus, it may affect human health in an adverse way and sometimes also leads to fatal conditions. Thus it is ours need to find an alternative surfactant which would be more eco-friendly, compatible, economical and more efficient over SLS/SLES.

METHYL ESTER SULFONATES (MES) AS AN ALTERNATIVE SOLUTION & ADVANTAGES OVER PETROCHEMICAL-BASED SURFACTANTS

Methyl Ester Sulfonates (MES) from palm and coconut derivatives have been getting the attention today with the increase in the crude oil prices and the resultant increase in the prices of the petrochemicals. MES offers an environmentally friendly and viable alternative to the currently used workhorse surfactant alkyl benzene derived from linear alkyl benzene (LAB). The appeal of MES is based on its origin from a renewable oleo-based raw material, its excellent biodegradability, improved calcium hardness tolerance and a good detergency. MES also offers a viable cost alternative to the LABS currently used by detergent producers. As compared to LABS which is the workhorse of the detergent industry today, the cost of producing a ME and a MES is also significantly lower. In addition, MES is environmentally friendly and reduces the CO_2 emissions when compared with using fossil fuels as the raw material sources.

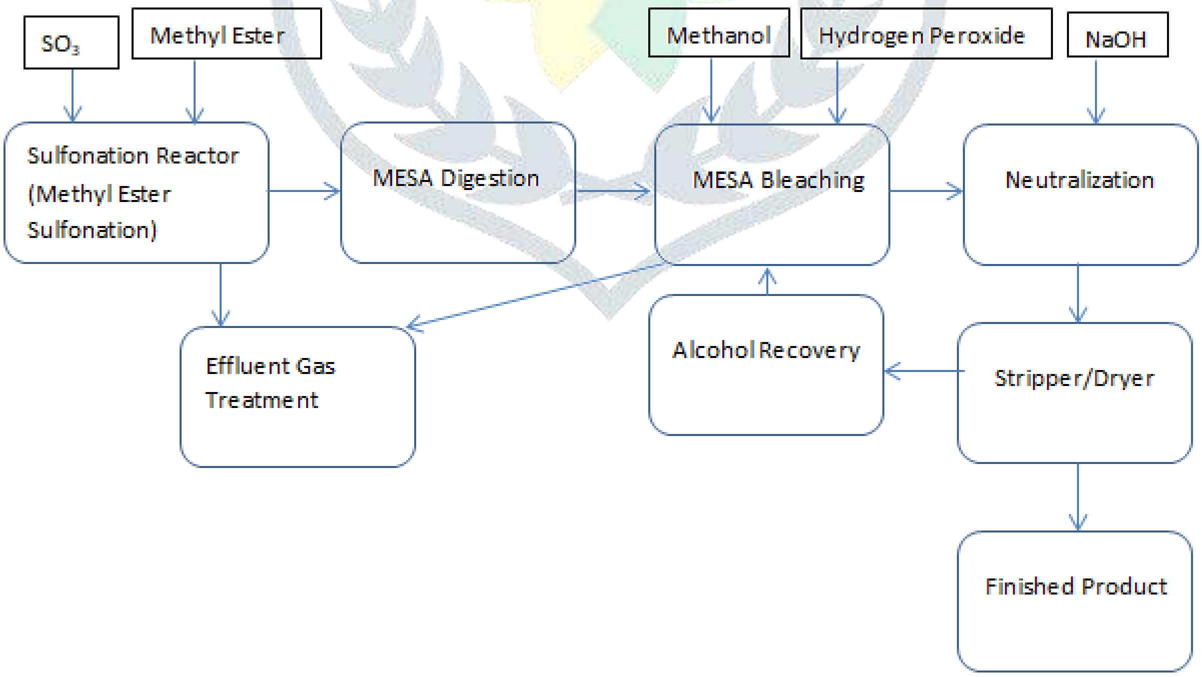
Methyl Ester Sulfonates (MES) can be produced from a large number of different renewable natural oils; however one that is specifically used often is palm oil (palm stearin). Palm oil trade is continuously increasing across the globe thereby significantly decreasing the cost per ton of ME as compared to their LAB counterparts. Furthermore, less quantity of MES is needed for equivalent washing power as compared to LAB. In addition, MES provides high calcium ion stability and detergency that ultimately improves its performance substantially. Besides, the main advantage of using MES is that it provides high biodegradability, environmental soundness, and low toxicity.

ME FEEDSTOCK PRODUCTION

Detergent grade methyl ester (ME) can be made by trans-esterification the oil or fat (palm, palm olein or palm stearin) with methanol and use a fractionated C_{16} or C_{1618} after removal of the unsaturated components. ME can also be made by trans-esterifying a palm oil stream after the extracting the minor components (Vitamin E, beta carotene, etc.), separating the glycerine and fractionating the stream to isolate the C_{16} ME. The trans-esterification step is a low pressure, low temperature process which has been used by the oleo chemical industry. ME can also be produced from esterification of fatty acids, palm fatty acid distillate (PFAD) and acid oils obtained during the processing of palm oil. But, this esterification process needs catalyst as well as high pressure & temperature that results in costly processing step. As compared to LAB, which is the workhorse of the detergent industry today, the cost of producing ME and MES is significantly lower. On an equal capacity basis, the cost of an ME plant would be around a fifth of that required for producing LAB. MES is also environmentally friendly and reduces the CO_2 emissions when compared with using fossil fuels as the raw material sources.

GENERAL DESCRIPTION OF MES PRODUCTION

The brief description of MES production is provided as follows. Sulfur trioxide (SO_3) diluted with air is circulated from a burning sulfur unit attached to a sulfur dioxide to SO_3 converter. Process of sulphonation is performed in a reactor with a sulfonic acid recycle system that minimizes the effluent gas particulate load by using a high-performance cyclone. The reactor is continuously cooled with a large flow of tempered water through external jacketing. The sulfonation is carried out at process temperatures higher than are typical when making other anionic surfactants. The methyl ester sulfonic acid (MESA) is discharged and passes through a plug-flow digester for the aging process which results in the dark coloration of MESA. The digested MESA, methanol and dilute hydrogen peroxide are combined and the reaction mixture is passed through a refluxing vessel where the bleaching of the MESA is completed. The process temperature in the bleaching vessel is controlled by heat transfer surfaces submerged in the reactants. The process pressure is independently controlled. The non-condensable vapors discharged from the bleaching vessel are processed in an effluent gas treatment system. The bleached MESA is continuously neutralized with sodium hydroxide. The neutral paste is transferred to a concentrating and / or methanol removal system. MES based on a methyl ester below a molecular weight of 245 is stripped rather than dried to remove the methanol making the concentrated product. Higher molecular weight MES is dried, removing both methanol and water, making the ultra-concentrated solid product forms. The recovered methanol is distilled and recycled back to the bleaching process.



Flowchart of MES Production Process

MES PRODUCTION BARRIERS IN BRIEF & WAY-OUTS EMPLOYED

Specific problem that must be addressed to produce high quality MES are colour and di-salt formation. This dark colouration results due to the high molar ratio of SO_3 to organics, and high temperature digestion process. To improve the colour, usage of Refined & Bleached Oil with a low iodine value is often recommended mainly because of its economized way. Low iodine value corresponds to low level of unsaturation in oils, which can be achieved either by fractionating the oil or low pressure hydrogenation. For further colour reduction, acid bleaching process is widely employed. Di-salt is a sulfonated soap which is generated during MES production. This di-salt is undesirable as it reflects poor surfactant properties in terms of detergency and surface tension, as well as having poor cold and hard water properties. Good quality MES will have less than 5% di-salt. Considering the methanol content of MES, it is usually dried with the help of a vacuum dryer, after which the resultant actives can be agglomerated to form a final product.

CONCLUSIONS

Petrochemical-based surfactants engendering contamination of the environmental system pose a grave threat to human health and the ecosphere. Given the human health effects of synthetic surfactants, effective and cost-competitive remediation technologies are encouraged. MES has shown promise as a potentially effective and comparatively low-cost treatment option. It abounds robust prospects as its feedstock is relatively inexpensive, green, renewable, and has considerable potential to substitute petrochemical-based detergent alkylate. MES provides remarkable surfactant properties with high biodegradability at low cost with low toxicity, and thus presents a strong economic incentive to supplant MES for traditional surfactants like SLS, SLES in many applications.

Conversion of ME into MES requires a finished product with acceptable colors and with minimal disalt content. Thus, more formulation work based on the concentrated forms of MES can be expected utilizing different types of ME feedstock. Although the process challenges for making good-quality MES have been addressed, there is still scope for technology enhancement to minimize the consumption of bleach and solvents used in the process. There is also a need to produce the MES as granules to facilitate its use in a post-addition process. This will provide the detergent formulators with the flexibility to produce mixed active detergent surfactants and optimizing their formulations based on the market dynamics of the raw materials.

The success of MES is contingent upon an organized and dedicated outlook by its producers as well as its consumers. The crude oil prices have been increasing continuously and are expected to remain at their peak due to market volatility. Adequate availability of ME will prompt drivers to produce MES, which can be used as a stand-alone or co-active surfactant in numerous detergent formulations.

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