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Sustainable Production of Surfactants from Renewable Resources

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Abstract: Surfactants are important chemical products, serving as emulsifiers and interfacial modifiers in the household detergents, personal care products, paints and coatings, foods, cosmetics, and pharmaceuticals industries. This review focuses upon recent advances in research and development to improve the ecological sustainability of surfactants throughout their life cycle, including derivation from renewable resources, production using green manufacturing principles, and improved biocompatibility and biodegradability during their consumer use and disposal stages. Biobased surfactants, derived from vegetable oils, polysaccharides, proteins, phospholipids, and other renewable resources, currently comprise approximately 24% of the surfactant market, and this percentage is expected to increase, especially in Asia. The use of renewables is attractive to consumers because of reduced production of CO_2, a greenhouse gas associated with climate change. Enzymes can greatly increase process sustainability, through reduced use of organic solvent, water, and energy, and reduced formation of by-products and waste products. Among the enzymes being investigated for surfactant synthesis, lipases are the most robust, due to their relatively high biocatalytic activity, operational stability and their ability to form or cleave ester, amide, and thioester bonds. For enzymes to be robust catalysts of surfactants, further research and development is needed to improve catalytic productivity, stability and reduce their purchase cost.

Key words: biobased; enzymes; green manufacturing; surfactants; sustainability; renewable

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1. INTRODUCTION TO SURFACTANTS

Surfactants play a critical role in our everyday life. Surfactants are chemical substances that lower the energy between phases at liquid-liquid, liquid-solid, and liquid-gas interfaces. On a molecular level, surfactants possess separate regions of hydrophilicity and hydrophobicity (i.e., “lipophilicity”) that lead to their self-assembly at interfaces. Surfactants enable emulsification of water into oil (and vice versa), the deposition of coatings onto solid surfaces, and the removal of oily stains or dirt from clothing or human skin.

Surfactants undergo self-assembly at interfaces (depicted in Figure 1 for the water-air interface). When the surfactant concentration in liquids is small (millimolar or smaller), surfactants partition directly to the liquid’s interface with gas or an immiscible liquid (pathway A→B, Figure 1). As a result, the interfacial energy (i.e., interfacial tension) decreases. (For water-gas systems, per Figure 1, the term “surface tension” is more commonly used than “interfacial tension”.) The further addition of

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surfactant leads to a further decrease of interfacial tension until a critical surfactant concentration is reached, at which the interface becomes saturated with surfactant (pathway B→C, Figure 1). Further addition of surfactant leads to formation of self-assembly structures in liquid, but does not further decrease the interfacial tension (pathway C→D, Figure 1). For water, the self-assembly structures are micelles, nanometer-sized droplets (typically spheres) where surfactant molecules align so that their hydrophilic groups are facing outward and their lipophilic groups face inward. Oil present in the system would solubilize in the nanodroplets' interiors. The surfactant molecular architecture can be modified by the chemist to control surfactant self-assembly, including the size and shape, of micelles, emulsions, or other structures, to fulfill the requirements of the specific application.

The molecular structures of several prominent biobased surfactants are given in Figure 2, as examples of anionic, cationic, nonionic and amphoteric surfactants. The surfactant types correspond to the chemistry of the surfactants' polar or "head" group. Both polyethylene oxide (i.e., -$(OCH_2CH_2)_n$, referred to as "ethoxylate") and sugars are common nonionic surfactant head groups. Amphoteric surfactants possess

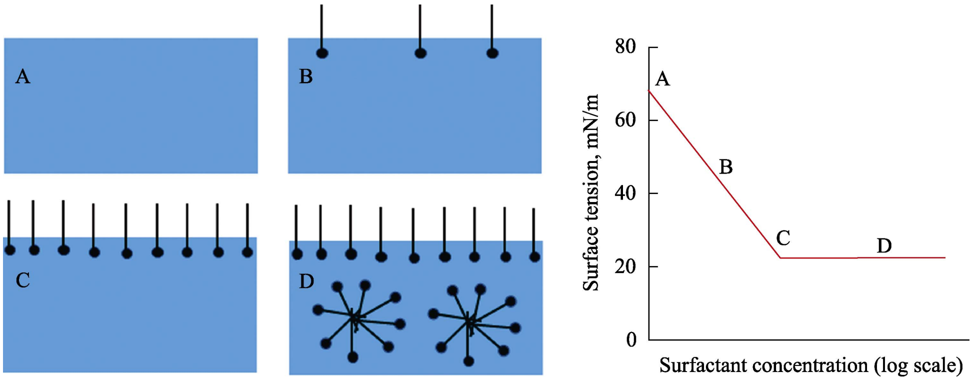

Fig.1 Surfactant self-assembly in water. As the surfactant concentration increases from 0 (A), surfactants partition to the liquid-liquid interface (B) and ultimately the interface becomes saturated with surfactant (C), at a surfactant concentration known as the critical micellar concentration (CMC). As the surfactant concentration is further increased, micelles form (D); but, the surface tension does not undergo a further decrease.

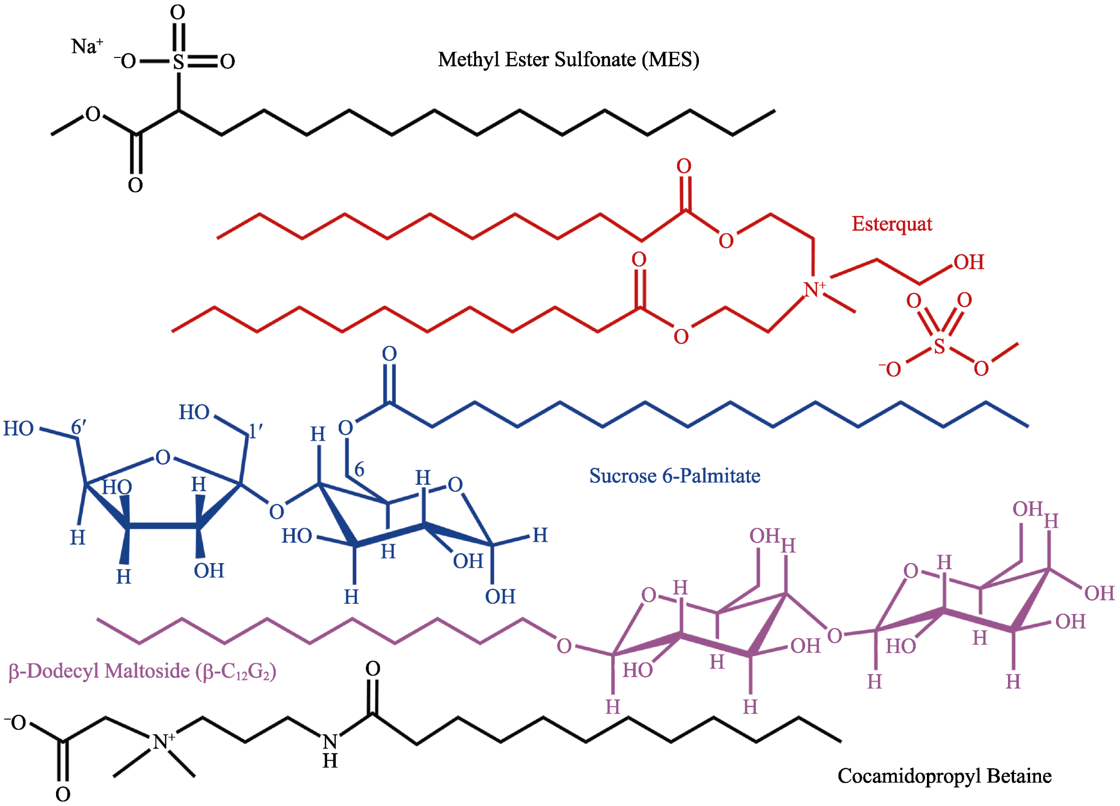

Fig.2 Molecular structure of commonly used biobased surfactants

head groups with positive and negative charges.

Therefore, surfactants are widely employed across several industries, listed in their approximate order of prominence: detergents (e.g., for laundry and dishes: ~42% of the market), industrial surfactants (e.g., paints and coatings, lubricants, and for enhanced oil recovery; 29%), personal care products (e.g., hand and body cleansers, shampoo, and toothpaste; 16%), and pharmaceuticals (7%). Surfactants are also employed in cosmetics, foods, agrochemicals, environmental remediation, and numerous other applications[1]. The market size of the surfactant industry was estimated to be $ 36.5 Billion (20.9 million metric tons) in 2017 [1].

2. THE IMPORTANCE OF SUSTAINABILITY IN THE SURFACTANTS' PREPARATION, USE, AND DISPOSAL

Improvements are needed so that the life cycle of surfactants, from cradle-to-grave-to-cradle, is sustainable. A conceptual diagram of a sustainable life cycle for surfactants is given in Figure 3. A major worldwide effort has occurred over the last 50 years to improve surfactants' end-of-life, to lower the ecotoxicity and increase the biodegradability of surfactants, particularly in rivers, lakes and groundwater, where surfactants and their breakdown products often reside[2]. This effort has led to many accomplishments. On example is the decreased use of nonylphenyl ethoxylate surfactants, which are endocrine disruptors[3]. A second example is reduced employment of sodium tripolyphosphate (STPP) as a detergent "builder", a component required to remove multivalent cations such as calcium that diminish cleaning performance. STPP promotes eutrophication in lakes and rivers, leading to an excessive growth of algae[4-5]. A third example is the reduced formation of 1,4-dioxane, a co-product produced during the production of sodium lauryl ether sulfate (SLES), a commonly used surfactant in laundry detergents and personal care products. 1,4-Dioxane is ecotoxic and difficult and expensive to remove from water[6]. Detergent producers have addressed this problem through improved efficiency in the catalytic production of SLES or by replacing SLES with other surfactants in the formulations. Research and development continue today to improve the rate and extent of microbial assimilation of surfactants and reduce surfactants' toxicity to microorganisms, fish and other marine life.

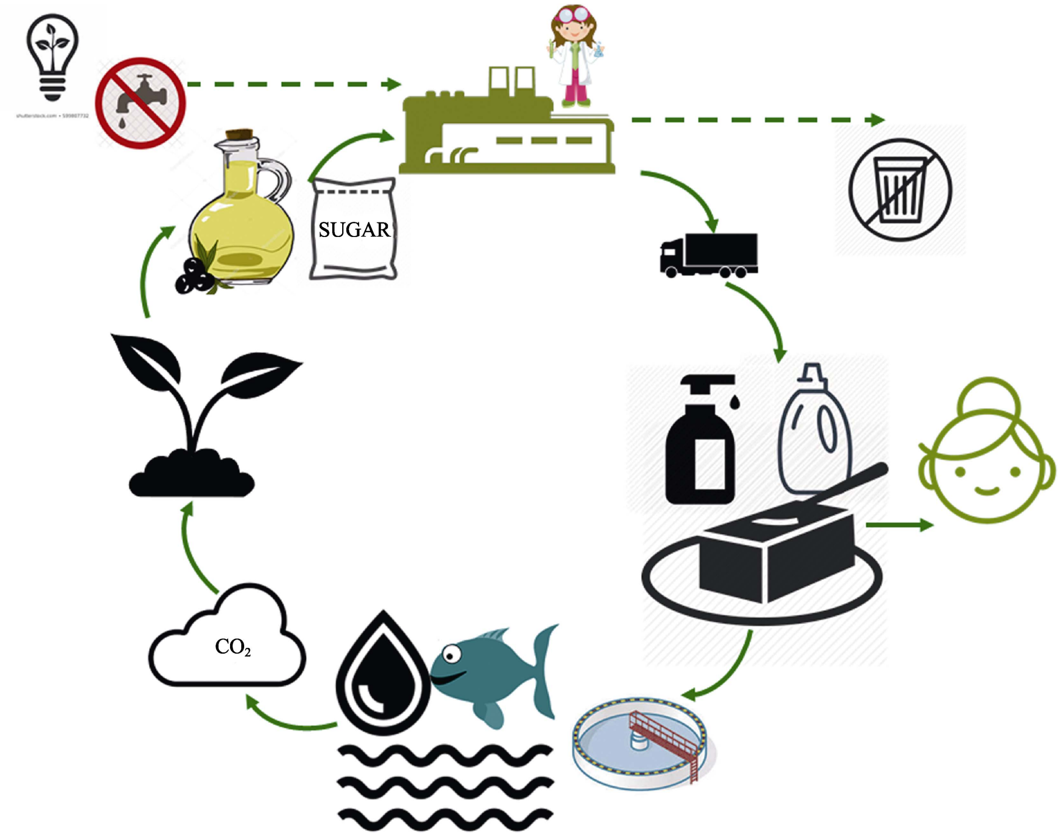

Fig.3 Life cycle for a sustainable surfactant. *left:* derivation of feedstocks from plants; *top:* green manufacturing (minimal input of water, energy and solvents; excellent safety for workers; minimal production of waste products); *right:* consumption and use (low toxicity); *bottom:* eco-friendly disposal (mainly in water treatment facilities, lakes, rivers, and oceans), producing CO_2 gas that is taken up by plants during respiration.

3. BIOBASED SURFACTANTS

Another recent focus on improved sustainability of surfactants is their beginning-of-life, i.e., the feedstocks used for preparation of surfactants. For the last 100 years, the principle source of surfactant raw materials has been petroleum and other fossil fuels. Although fossil fuels are generally inexpensive and readily available today, their availability in future years is uncertain. In addition, the use of fossil fuels is a major concern for the increased levels of greenhouse gases, particularly carbon dioxide (CO_2), in the atmosphere. Moreover, fossil fuels' carbon atoms, initially in an inert, stored state (underground), will ultimately transform into CO_2 as their final state. Greenhouse gases are associated with climate change, perhaps evidenced by extreme climactic events in recent years (e.g., frequent powerful cyclones, droughts, record high temperatures globally, and the rise of water levels in oceans due to the melting of glaciers in the Arctic and Antarctic regions)[7-8]. The other life stages of fossil fuels are also of concern for the potential occurrence of environmental hazards, including their recovery from the ground and shipment to refineries (for example, the Deepwater Horizon petroleum spill from an oil well in the Gulf of Mexico in 2008 and the 1999 oil spill from an oil tanker named *Exxon Valdez* in Alaska, USA), and fires that ignite in petroleum refineries.

These concerns have led to increased interest by consumers in biobased surfactants, i.e., surfactants derived from renewable resources in whole or significant part. In 2017, biobased surfactants account for approximately 24% of the surfactants market, and the percentage is projected to increase, particularly in Asia[1]. The most commonly encountered biobased building blocks for preparing surfactants are fatty acyl groups derived from vegetable oils, other seed oils (e.g., from bioenergy crops such as jatropha or castor, or used cooking oils and restaurant greases), animal fats or microbial "single cell" oils (e.g., from algae or bacteria) and phospholipids (co-products produced from the refining of vegetable oils). Fatty acyl groups can be reduced chemically to produce fatty alcohols or fatty amines. Biobased resources of surfactants' hydrophilic groups include sugars, amino acids (derived from proteins), glycerol (an inexpensive and underutilized co-product from the production of biodiesel), and citric acid.

Alternatively, surfactants can be directly recovered from microorganisms, and are referred to as "biosurfactants". Biobased resources (e.g., vegetable oils and sugars) are commonly used as carbon-energy sources in the fermentation of biosurfactants. Feedstocks for biobased surfactants have been recently reviewed [9].

The molecular structure of several prominent biobased surfactants are depicted in Figure 2. Methyl ethyl sulfonates (MES) are perhaps the most frequently used anionic biobased surfactant, commonly employed in detergents, particularly in Asia. Esterquats are common cationic biobased surfactants used as antistatic agents for clothes and possess antimicrobial activity, leading to their use as biocide in swimming pools. Sugar esters are common emulsifiers in foods, cosmetics, and pharmaceuticals, while alkyl polyglycosides (APGs) are effective wetting agents and foaming agents that are frequently used in detergents, personal care products, and cosmetics. Betaines, such as the alkyl amidopropyl derivative depicted in Figure 2, are common amphoteric surfactants used for personal care products (e.g., shampoos, liquid soaps, and hand dishwashing liquids). They possess excellent detergency, foam formation, hard water compatibility, and mildness to skin and hair. I have co-edited a book on Biobased Surfactants, with the book's 2nd Edition recently published[10]. Further information on general aspects of biobased surfactants and specific types is provided therein.

Several biosurfactants are prepared industrially, particularly glycolipids (e.g., sophorolipids and rhamnolipids) and lipopeptides (e.g., surfactin). Their molecular structure is depicted in Figure 4. Biosurfactants generally possess excellent surface activity, high biodegradability, low toxicity, and high antimicrobial activity, but are expensive to prepare. Therefore, they are used for only applications where high costs are less of a factor, such as enhanced oil recovery, bioremediation, cosmetics, and pharmaceuticals. Recent research has focused upon developing more productive microbial strains, employing low-cost carbon sources such as waste cooking oils, improved bioseparations (e.g., the continuous removal of biosurfactants from the fermentation broth), and approaches to modify biosurfactants' molecular structure through *ex situ* chemical (or biochemical) reactions. In addition to several well-written chapters on biosurfactants in my co-edited book[10], several additional reviews have been recently published [11-16].

4. USE OF ENZYMES TO PREPARE SURFACTANTS: AN EXAMPLE OF GREEN MANUFACTURING

Another important life stage of surfactants

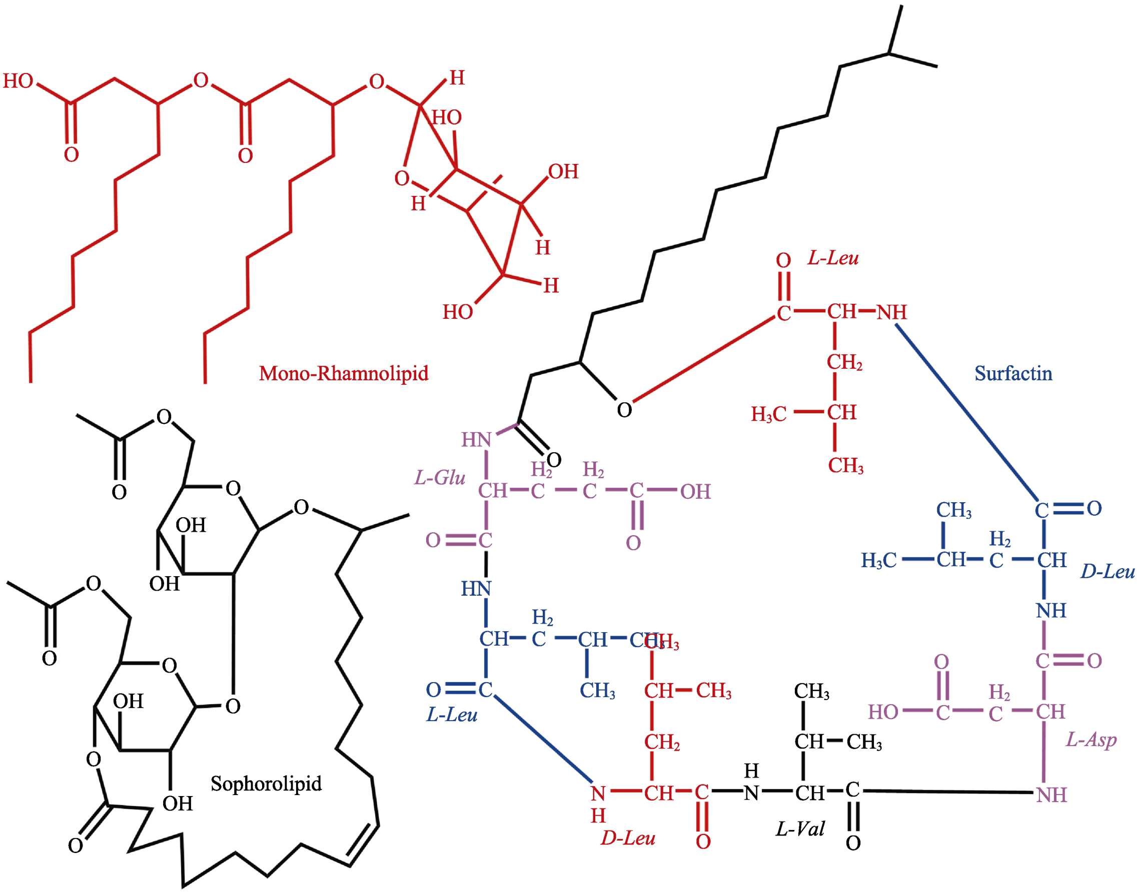

Fig.4 Molecular structure of biosurfactants. Sophorolipids and rhamnolipids are glycolipids, while surfactin is a lipopeptide.

where sustainability needs to be improved is their manufacturing (see Figure 3). Dr. Paul Anastas of Yale University, USA, has outlined the 12 principles of "green manufacturing"[17], which can be summarized as the efficient conversion of starting materials into final product using a process that requires minimal consumption of energy and water, minimal use of water of solvents, and minimal production of toxic by-products or waste products (e.g., spent metallic catalysts), and does not impose risks to the safety of employees working at the process facility, nor to consumers[18]. Traditional approaches for surfactant manufacture are often noncompliant with green manufacturing principles.

For example, polyol-fatty acid esters are traditionally prepared by reacting polyol (e.g., sugar derivatives or glycols) and fatty acid feedstocks (e.g., vegetable oils) in the presence of toxic organic solvents such as dimethylformamide or dimethylsulfoxide (to enhance miscibility of the reactants) at high temperatures (100~200 ℃) for several hours[19]. Although the product yield is high, the reaction requires significant downstream purification: removal of reactants (since usually a stoichiometric excess of sugar is employed) and recovery of solvent by molecular distillation, an energy-intensive process, and perhaps adsorption and bleaching to remove aldehydes and ketones, and agents that cause a dark color due to undesired side-reactions[19]. The use of enzymes to prepare surfactants has several inherent advantages from a sustainability point-of-view, as outlined in Table 1[20]. The table also lists the major barriers to more widespread use of enzymes, particularly their high cost and slow catalytic rates, and issues that must be addressed, including the careful control of water content in the reaction medium and enzymes' recovery and reuse.

My group and many others have developed enzymatic processing procedures to prepare sugar esters (reviewed in[21-22]), including sucrose monoesters (Figure 2). Lipase have served as the most commonly used enzymes for the preparation of sugar esters and other surfactants. Lipases have several advantages over other enzymes for surfactant synthesis: relatively high stability in the presence of elevated temperatures (e.g., 60~100 ℃) and solvents (e.g., acetone, alkanes, supercritical fluids, and ionic liquids), relatively low sensitivity to pH and ionic strength, ability to be immobilized via adsorption onto matrices, the absence of required cofactors, and relatively low

Table 1　Advantages, disadvantages and issues pertaining to the replacement of conventional syntheses of surfactants with biocatalytic syntheses

Advantages
Lower temperatures (reduced energy)
Absence of extremes in pH and ionic strength
Reduced solvent use
Improved safety for employees
Unique selectivities (e.g., enantioselectivity and regioselectivity)
Reduced production of side-reactions and by-products
Reduced production of waste products (e.g., spent catalyst)
Reduced burden for downstream purification
Disadvantages
High cost
Low biocatalyst stability
Slow reaction rate
Reactants need to be highly purified
Issues
Careful control of water
Need for recovering and reusing enzymes (e.g., via immobilization)

cost. The molecular biochemistry of lipases is among the most deeply understood for enzymes. We used metastable solvent-free suspensions of sugar microparticles (e.g., of sucrose, fructose or xylose) in liquid-phase acyl donor (free fatty acid) at ~65 ℃ as reaction medium to prepare sugar esters. For neat acyl donor solvent, the amount of sugar that can be suspended was small: <0.1 wt%; but, as the reaction proceeded, the formation of sugar ester greatly increased the allowable sugar concentration, to ~1%~3%. Immobilized thermostable lipases were employed either in stirred batch mode or as a packed column (~65 ℃). Removal of water, a co-product of esterification, was a key consideration when operating the reaction. During the initial phase of the reaction, free evaporation was effective for its removal. However, when the conversion approached ~60%, the reaction rate greatly slowed due to the approach of thermodynamic equilibrium. A stronger means of water removal was needed to achieve further conversion (e.g., evaporation, bubbling of nitrogen gas or use of molecular sieves). Other groups have also utilized metastable suspensions in the preparation of sugar esters, particularly when using ionic liquids, a unique series of nonvolatile solvents consisting of molten salts that are liquid at or near room temperature. We were able to achieve up to 90%~95% conversion, and the final product nearly met standardized specifications for purity without the need of downstream purification, and lipase was used for a month of operation without significant loss of activity. However, the approach needs improvement to be robust for industrial operation, particularly an increase of the rate of reaction and improved ability to use cruder, less purified, starting materials.

Lipases have been employed to prepare other ester-based surfactants, including polyglycerol polyricinoleate (using castor oil as a starting material) and monoacylglycerols (MAG), both of which are common food emulsifiers[23-24]. Lipases' ability to form amide bonds has been used for the preparation of N-acylated alkanolamines[25]. The versatility of lipases has been very transformative in the preparation of amino acid surfactants (reviewed in[26-27]). Amino acid surfactants have found many uses in personal care and cosmetic products not only due to their strong performance in lowering interfacial tension but also due to their high antimicrobial activity. Amino acids are useful biobased polar groups for surfactant synthesis due to their a-amino and a-carboxylic acid groups as well as the functional groups present in their "R" moieties (e.g., e-amine, e-carboxylic acid and e-thiol groups of arginine, glutamic acid and cysteine, respectively). These groups allow for ester, amide, and thioester linkages to be formed using fatty acids, fatty amines, or fatty alcohols as co-substrates. For example, lipase-catalyzed amidification can be used to prepare sodium lauroyl sarcosinate (Figure 5), which is employed in personal care products (e.g., shampoo, skin cleansers, and oral care products), from lauric acid and sarcosine's a-amine group. In addition, the tryptophan amide of Figure 5, which can serve as a gelator, is formed through amide bond formation between hexadecamine and tryptophan's a-carboxylic acid group. One of the most innovative biocatalytic syntheses involving the conjugation between MAG or diacylglycerols (DAG) and arginine through ester bond formation between the free OH groups of the glycerol backbone of MAG or DAG and the a-COOH group of arginine (Figure 5).

Alkyl glycosides have also been prepared from disaccharides and hexanol using glycosidases [28]. The reaction yields were lower than achieved for most lipase-catalyzed reactions, and the disaccharide acetal linkages were cleaved, with no disaccharide-hexanol acetals formed. Glycosidases are very sensitive to water content, and in contrast to lipases, cannot catalyze efficiently in nearly-anhydrous nonaqueous media. Water must be present in large amounts for

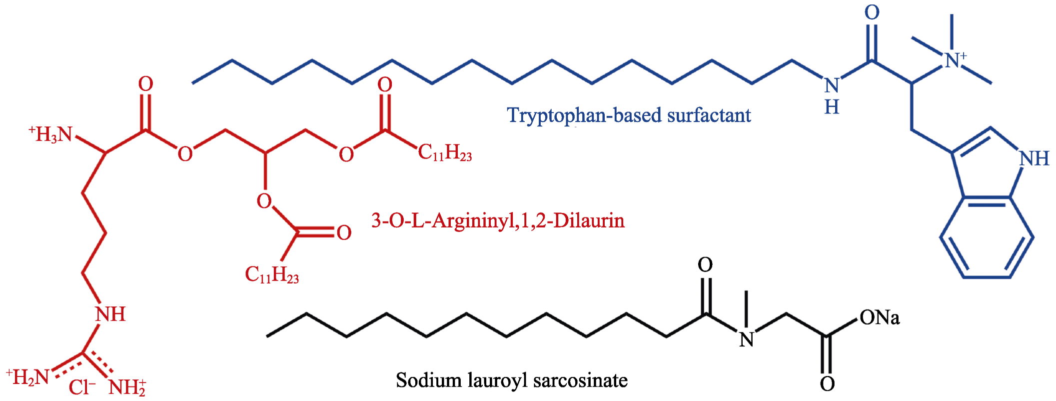

Fig.5 Examples of amino acid surfactants that can be prepared using enzymes. Sodium lauroyl sarcosinate is a commercially available surfactant that is mainly synthesized using chemical catalysts, but can be prepared using enzymes.

alkyl glycoside formation to occur, leading to use of biphasic media: aqueous solutions of oligosaccharide+ glycosidase in equilibrium with fatty alcohol-rich solution. Alkyl glucosides can be converted to APGs through reactions with cyclodextrins using glucosyl transferase[29-30].

Enzymes can also be used to modify phospholipids, which are abundant naturally-occurring surfactants commonly used in foods and pharmaceuticals. Phospholipase A_1 and A_2 selectively hydrolyze or esterify fatty acyl groups into the 1- and 2-position of phospholipids’ glycerol backbone, respectively. Phospholipase A_1 derivatives are commercially available; however, robust phospholipase A_2 derivatives are not available. Alternatively, lipases can mimic the behavior of phospholipase A_1. As shown in Figure 6, phosphatidylcholine, the most commonly encountered phospholipid (e.g., in soy or egg lecithin), can be modified with unique acyl groups. In the example depicted, caffeic acid, a building block of lignin, an abundant and underutilized biopolymer found in lignocellulosic biomass, can be incorporated into the 1-position through two reaction steps: lipase-catalyzed hydrolysis at the 1-position

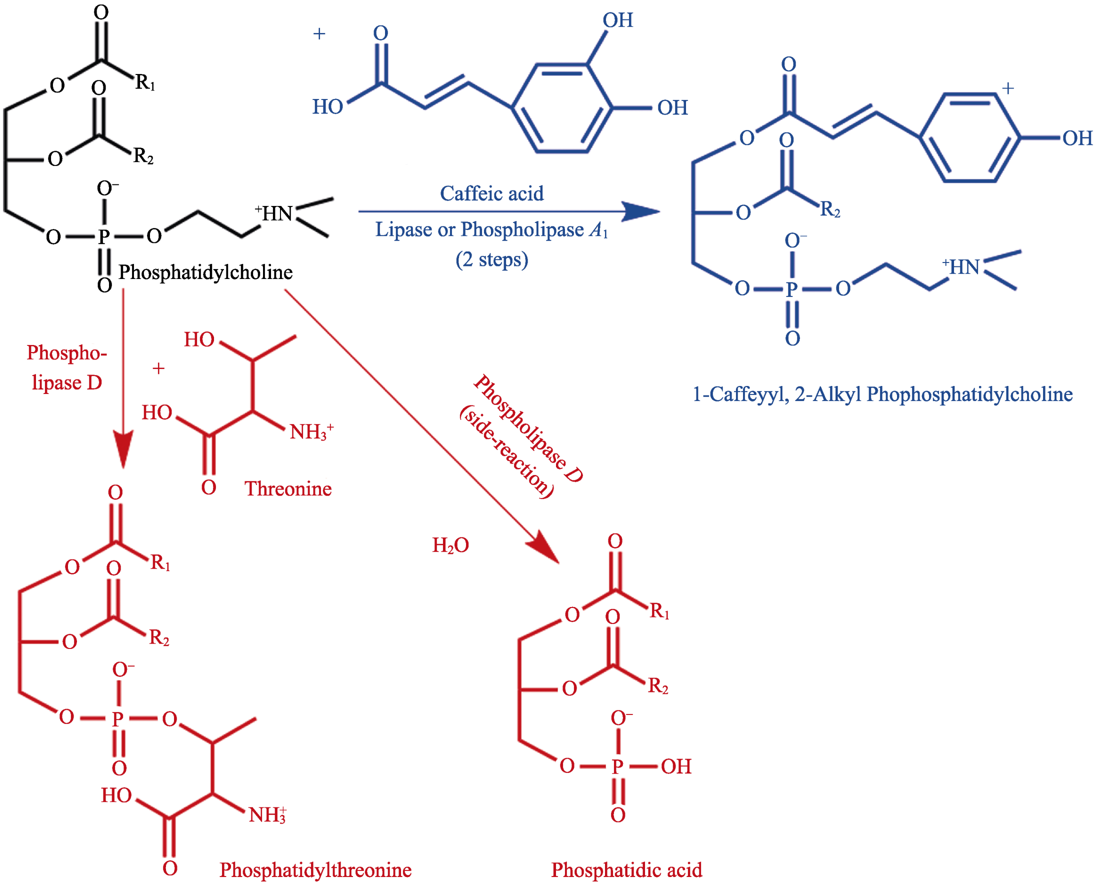

Fig.6 Enzymatic modification of phosphatidylcholine. R_1 and R_2 are *n*-alkyl chains (e.g., lauric [dodecanoic] acyl chains correspond to R_1 = *n*-$C_{11}H_{23}$). The figure is based on references[31-32].

of phosphatidylcholine, followed by lipase-catalyzed esterification (or transesterification) of caffeic acid (or caffeic acid methyl ester)[31]. The resultant derivative is a very effective antioxidant for oil-in-water emulsions due to the localization of the bioactive caffeic acyl group at the emulsions' oil-water interfaces. A second example of the enzymatic modification is the use of phospholipase D, which can be used to exchange the polar groups of phospholipids. Recently, the activity and stability of phospholipase D has been improved through protein engineering[32]. As shown in Figure 6, engineered phospholipase D can direct the replacement of the choline head group of phosphatidylcholine with unusual head groups such as the amino acid threonine via transphosphatidylation, to produce a unique phospholipid[32]. However, hydrolytic cleavage of the choline head groups by phospholipase D occurred as a side-reaction (Figure 6)[32].

5. CONCLUSIONS

The scientific community has made significant progress in the enhancement of ecological sustainability in the preparation of surfactants. Consumer motivation for increased sustainability will lead to continued interest in eco-friendly products. For example, many consumers are willing to pay a higher price for environmentally-sustainable products compared to conventional products[33-34]. Green manufacturing of surfactants is at its initial development phase, but is expected to impact commercial-scale processing in the years to come. Enzyme-catalyzed synthesis of biobased surfactants and biosurfactants derived from microbial fermentations will continue to make progress.

REFERENCES:

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Author Profile

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A Professor of Department of Bio-systems Engineering and Soil Science (BESS) at the University of Tennessee (UT), USA, and is a UT-Oak Ridge National Laboratory Joint Faculty member. He also serves as a Guest Professor at Wuhan Polytechnic University and Jinan University, a Member-at-Large for the Governing Board of the American Oil Chemists' Society (AOCS), and as Editor-in Chief of *Journal of Surfactants and Detergents*. He also is on the Editorial Board of *Journal of Oil Palm Research* and *Grain & Oil Science and Technology* and previously served as Senior Associate Editor for *JAOCS*.

Dr. Hayes received his B.S. and PhD degrees in Chemical Engineering from Iowa State University (1986) and the University of Michigan (1991), respectively.

Dr. Hayes has published 85 articles in peer-reviewed journals, 23 book chapters and 3 co-edited books. He has received several awards for his research work, including the John J. and Dorothy G. McDow Faculty Excellence Award (BESS Department, UT, 2019), the Gamma Delta Sigma Team Award (UT Institute of Agriculture, 2019), and the UT Agricultural Research Impact Award (2017). His research interests include surfactant self-assembly systems, enzymology in nonaqueous systems, biobased and biodegradable polymers, micro- and nanoplastics, and small-angle scattering analysis of colloids.

(Organized/Translated it into Chinese by TAN Hongzhuo)