Chapter

Overview of Bio-Based Surfactant: Recent Development, Industrial Challenge, and Future Outlook

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Abstract

Bio-based surfactants are surface-active compounds derived from oil and fats through the production of oleochemicals or from sugar. Various applications of bio-based surfactants include household detergents, personal care, agricultural chemicals, oilfield chemicals, industrial and institutional cleaning, and others. Due to the stringent environmental regulations imposed by governments around the world on the use of chemicals in detergents, as well as growing consumer awareness of environmental concerns, there has been a strong demand in the market for bio-based surfactants. Bio-based surfactants are recognized as a greener alternative to conventional petrochemical-based surfactants because of their biodegradability and low toxicity. As a result, more research is being done on producing novel biodegradable surfactants, either from renewable resources or through biological processes (bio-catalysis or fermentation). This chapter discusses the various types, feedstocks, and applications of bio-based surfactants, as well as the industrial state-of-the-art and market prospects for bio-based surfactant production. In addition, relevant technological challenges in this field are addressed, and a way forward is proposed.

Keywords: bio-based surfactant, green surfactant, biosurfactant, renewable materials, sustainable surfactant

1. Introduction

Surfactants are surface-active agents that reduce water–oil, liquid–gas, and solid–liquid or solid–gas medium surfaces and interfacial tension [1, 2]. The surface energy is reduced by the presence of hydrophilic and hydrophobic sections of the same surfactant molecule owing to preferred interactions at surfaces and interfaces. In aqueous solution, surfactant molecules arrange themselves at the interface, where the hydrophobic part is in the air (or oil) and the hydrophilic part is in water, while at high concentration or concentrations above the critical micelle concentration (CMC), surfactant molecules self-assemble into micelles (**Figure 1**). Not only are they widely used as cleaning agents, but also other beneficial properties, such as foaming, emulsification, and particle suspension, make surfactants known for their wetting ability and effectiveness such as emulsifiers and stabilizers. Due to this characteristic, surfactants are found in a variety of products that we use every day, including food, pharmaceuticals, toiletries, detergents, automotive fluids, paints,

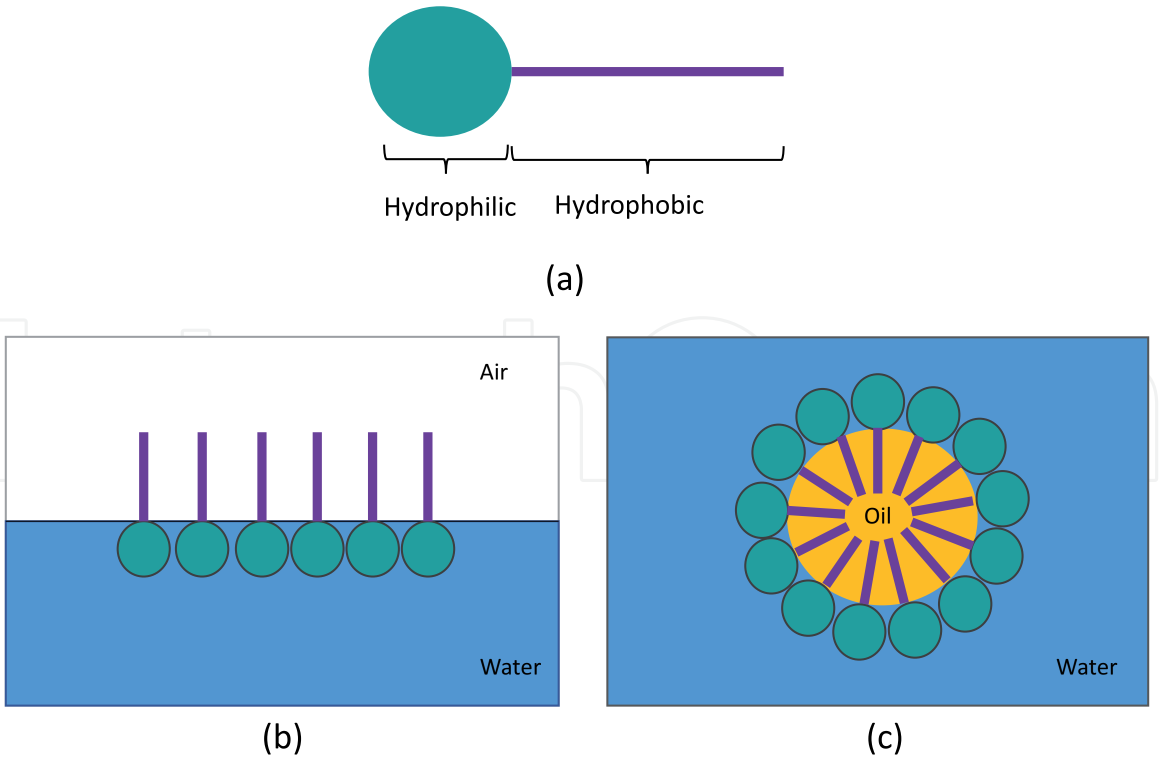

Figure 1.
(a) Simplified surfactant molecule, (b) arrangement of surfactant monomers at the water surface, and (c) micelle formation above critical micelle concentration (CMC).

and coatings [2]. Surfactants have steadily grown in popularity since their debut in the early twentieth century, and they are now among the most widely used synthetic compounds on the planet [3, 4].

Petrochemical and renewable sources are the two primary feedstock groups used in the manufacture of surfactants [5, 6]. The development of petrochemical processing led to the acquisition of hydrophobic structures of surfactant molecules through polymerization of alkenes, such as ethylene or propylene. Although ethylene has been employed as a carbon chain-building block, its increased applicability in industrial production has resulted from the production of an intermediate or precursor, ethylene oxide [7]. Natural surfactants are usually derived from triglycerides found in vegetable oils or animal fats. The surfactant industry was focused on the saponification of oils and fats prior to petrochemical processing [8, 9]. Surfactants infiltrate water bodies after usage, where they can create issues if they remain for a long time, resulting in the buildup of potentially toxic or otherwise hazardous substances causing significant environmental concerns [10–12]. Synthetic surfactant-related water contamination has increased in recent years because of its widespread usage in domestic, agricultural, and other cleaning activities. This occurrence has caused global concern, forcing establishment of a series of new rules governing its usage and disposal [13, 14]. In addition, experts relate the production of petrochemical-based surfactants to the high net output of CO_2, a greenhouse gas linked to climate change and global warming. By switching to renewable feedstock, this rate can be minimized. A previous study shows that using renewable resources instead of petrochemicals for surfactant synthesis would cut CO_2 emissions by 37% in the EU [15]. Beside environmental concerns and regulations, growing consumer awareness and market pressures have prompted considerable R&D into bio-based surfactants as potential substitutes for synthetic surfactants.

The term “bio-based surfactant” refers to a surfactant produced by a chemical or enzymatic process that uses renewable substrates as raw materials [16, 17]. According to ISO/DIS 21680, a bio-based surfactant is defined as a surfactant

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Surfactant class	Bio-based carbon content X% (*m*/*m*)
Wholly bio-based surfactant	≥ 95
Majority bio-based surfactant	$95 \geq X > 50$
Minority bio-based surfactant	$50 \geq X \geq 5$
Non-bio-based surfactant	$X < 5$

Table 1.
Bio-based surfactant classes according to CEN/TS 17035 [19].

wholly or partly derived from biomass (based on biogenic carbon) [18]. Most applications need further processing of bio-based feedstocks to incorporate functional groups that can give the surfactant's functional characteristics, resulting in a variety of anionic, cationic, nonionic, and amphoteric products. Many of these processes require the use of petroleum-based feedstocks or moieties that are not always environmentally friendly. The European Commission of Standardization has created categories for biosurfactants, including >95% completely bio-based, 50–94% majority bio-based, 5–49% minority bio-based, and 5% non-bio-based to assist in analyzing the bio-based surfactants' sustainability criteria (**Table 1**) [19].

The hydrophobe, hydrophile, or both, which are derived from natural sources, can be used in the production of bio-based surfactants. Plant oil, fatty acids, and animal fat are examples of natural hydrophobes, while glycerol, glucose, sucrose, and amino acids (aspartame, glutamic, lysine, arginine, alanine, and protein hydrolysates) are examples of natural hydrophiles. They can be either directly utilized in their original form or produced from complicated sources, such as vegetable oil, sugarcane, sugar beets, and starch-producing crops. As for biosurfactants, they consist of hydrophilic sugar or peptide component and hydrophobic saturated or unsaturated fatty acid chains that are naturally produced by bacteria, yeast, and fungi. Hence, a biosurfactant is classified as a wholly bio-based surfactant since all its raw materials are considered natural [20–22].

The hydrophobic part of bio-based and biosurfactant feedstock is mostly from fatty acyl groups. The fatty acyl groups are generally obtained from oilseeds in the form of triacylglycerol, but they may also be derived from oleochemical by-products such as free fatty acid or phospholipids. Fatty acyl groups are generally utilized as lipophilic building blocks for surfactants in the form of free fatty acids or fatty acyl esters, which are produced *via* hydrolysis or alcoholysis of triacylglycerol [23, 24]. This fatty acyl group conjugates hydrophilic and lipophilic compounds *via* an ester bond. This bond makes the fatty acid-based surfactants suitable for foods, cosmetics, personal care, and pharmaceutical product applications, but not for laundry detergents since the ester bonds are unstable. More stable bonds, such as ether, amides, and carbonate bonds, can be produced by converting the fatty acid groups to fatty alcohols, fatty amines, or fatty acid chloride [25–27].

Algae are another potential renewable source of fatty acids. It has been an active research area in recent years due to its potential for high oil production per acre and the ability to leverage on nonarable soil [28–30]. Previously, Unilever has partnered with Solazyme, a microalgae firm, with the aim of finding a palm-oil-free replacement for its soaps and surfactants. Solazyme used the advantage of its intellectual property in the areas of recombinant DNA expression in algae and algae bioprocessing to create oils with specific fatty acyl compositions [31]. Solazyme, later renamed as TerraVia, was acquired by Carbion in 2017 to focus on delivering innovative and high-value ingredients for food, personal care, and industrial applications [32]. Lignin has also been used as a feedstock in surfactant production due to its hydrophobic aromatic structure. Lignin-based surfactants are usually made by grafting hydrophilic groups or monomers onto the lignin to enhance its surface properties [33–35]. Extensive investigations are necessary to expedite the commercialization of lignin-based surfactants to the market since information on connecting performance and characteristics of lignin-based surfactants for their optimal usage is still lacking.

Among the most significant feedstocks for renewable hydrophile sources are vegetable oils (for glycerol), sugarcane and sugar beets (for sucrose), and starch-producing crops, such as maize, wheat, potato, and tapioca (for glucose) [4, 23, 36]. The use of glycerol as an alternative hydrophilic building block to replace ethylene oxide in the synthesis of nonionic surfactants is a feasible option. The major glycerol-based surfactants in the market are ester-based mono- and diglycerides, which are made by transesterifying triglycerides with excess glycerol and a base catalyst [4, 26, 37]. Carbohydrates, such as sugar and sucrose, are another useful biorefinery feedstock that make up as surfactant hydrophiles. The discovery of sucrose monoesters, or long-chain fatty acid esters, was one of the first major achievements of the Sugar Research Foundation (SRF) and led to their use as nonionic surfactants, food additives, and emulsifiers [38]. The global sucrose esters market amounted to $71.9 M in 2018 and is expected to reach $137.85 M by 2027 [39]. However, selectivity in the synthesis of these esters remains a challenge where acylation with a single fatty acid can yield many different isomers with various degrees of substitution [40]. One of the solutions to tackle the selectivity problem is by using lipases and proteases for regioselective sucrose ester production [41, 42]. Further improvement *via* lipase and protease protein engineering might increase the regioselectivity and yield of the catalysis processes. The biotransformation of sucrose to sucrose esters utilizing whole-cell fermentation methods might also give a new path to sucrose-based surfactant production.

Glucose is utilized as a hydrophile in the manufacture of a variety of surfactants, both directly and indirectly. It can react directly with fatty alcohol in a glycosidation process to produce alkyl polyglucosides (APGs), a nonionic surfactant class with growing production and popularity. Indirectly, glucose may be chemically converted to sorbitol, sorbitan, N-methyl glucamine, and O-methylglucoside, or enzymatically converted to amino, lactic, and citric acids, all of which can be leveraged to produce surfactants (**Figure 2**) [4].

Sugar-derived surfactants have a higher market demand than synthetic chemicals and surfactants due to their low toxicity, low cost, biodegradability, good cleaning and washing abilities, environmental compatibility, and high surface activity [43, 44]. However, if the demand for sugar surfactants grows in the long run, feedstock availability will become a concern. New methods that use bacteria and microorganisms to manufacture glucose are emerging; however, the issue of scalability has yet to be solved.

The creation of new amino acid-based surfactants may be influenced by advancements in biotechnological amino acid synthesis. Other than L-glutamic acid and L-lysine, which are the two most produced amino acids in the market, alanine, aspartic acid, glycine, and arginine, as well as protein hydrolysates, are also used in the manufacture of some commercial surfactants [45–47]. Another type of amino acid surfactant, sarcosine-based surfactants, has been in the market for decades. Even though sarcosine is a naturally occurring molecule, it is mostly synthesized on a large scale by combining chloroacetic acid with N-methylamine [48–50]. Betaine, another naturally occurring molecule, is also synthesized in large scale using petrochemical-based trimethylamine and chloroacetic acid. Most betaine surfactants use an oleochemical hydrophobe precursor obtained from tropical oils as the bio-based component [51]. Glycine betaine is a promising biosurfactant that can be commercially extracted from brown algae and sugar beet molasses [52, 53].

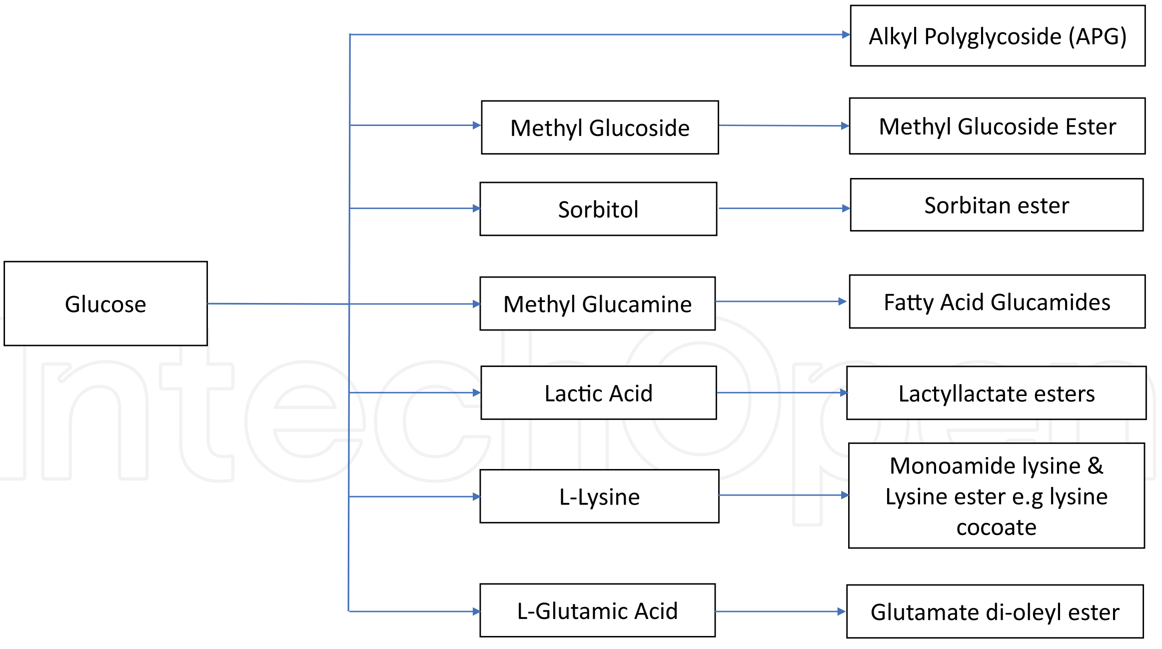

Figure 2.
Simplified transformations pathway from glucose to several surfactant building blocks and surfactants.

Glycolipids are a type of complex carbohydrate that contains both a glycan and a lipid component. They are usually the main lipids of bacterial and fungal cell walls. In an aqueous solution, glycolipids are amphiphilic substances that form stable micelles, and these molecules have the capacity to offer low interfacial tension [54, 55]. Rhamnolipids and sophorolipids are among the glycolipids that have been utilized the most as biosurfactants. Rhamnolipids are produced as one or two rhamnose sugar groups attached to one or two fatty acid chains by different bacterial species (i.e., *Pseudomonas aeruginosa*, *Pseudomonas chlororaphis*, *Burkholderia pseudomallei*) [4, 56]. Beside their favorable emulsifying, solubilizing, foaming, and antibacterial characteristics, the use of rhamnolipids is appealing due to their high production yields after relatively short incubation times [56]. Rhamnolipids are now available on a larger scale due to the optimized fermentation techniques and advanced extraction and concentration technologies. Sophorolipids, another extensively researched type of glycolipid, are biosynthesized by certain yeast strains such as *Starmerella bombicola*, *Wickerhamiella domercqiae*, and *Candida batistae* from sophorose sugar and hydroxylated fatty acid. Sophorolipids are commercially used in dish and vegetable detergents and in skin care formulations [57–60].

2. Recent progress in R&D and industrial production

Regulations on the environmental impact and hazardous chemicals are highly stringent, particularly in Europe and North America, which are the two largest markets for surfactants, especially in the home and personal care sectors. As a result, the surfactant industry is commencing to develop biosurfactants, which have lower levels of toxicity and a more environmentally friendly manufacturing process. Apart from complying with environmental regulations, the industry is seeing bio-based surfactants to achieve a sustainable competitive edge. The advent of biotechnology in the twenty-first century promoted the creation of novel bio-based and biosurfactants along with their enhanced commercial and economic viability. Extensive and significant R&D has also enabled high-quality and high-functionality bio-based surfactant formulations to evolve from the lab scale to niche applications to commercial-scale production. Some of the bio-based surfactants that are commercially available in the market, their main manufacturers, and their applications are listed in **Table 2**.

In the current development of novel surfactants, there is a growing trend of utilizing nontraditional naturally occurring branching hydrophobic chains [61–63]. Nonionic surfactants based on twin tail glycerol have been synthesized and they have good oil-in-water and water-in-oil emulsifying characteristics [64]. Other

Bio-based surfactants	Selected manufacturers	Fields of applications
Anionic		
Lignosulfonate Methyl ester sulfonates Anionic derivatives of alkyl polyglucoside	Vanderbilt Minerals, LLC Huish Detergents, Inc., Lion Corp., Longkey, Stepan Cognis, Colonial Chemical	• Laundry • Food service and kitchen hygiene • Dishwashing • Hard surface cleaning • Institutional cleaning and sanitation • Vehicle and transportation care
Nonionic		
Fatty alcohol alkoxylate Fatty acid alkoxylate Alkyl polyglucoside Sorbitan ester Alkanoyl-*N*-methylglucamide Alkyl ethoxylated mono- and diglycerides Polyglycerol esters	BASF, Dow BASF, Clariant, Croda, Croda, Esterchem, Huntsman Akzo Nobel, BASF, Colonial Chemical, Dow, Huntsman BASF, Croda, Huntsman Clariant, Kao, Kerry Ingredients and Flavors BASF, Colonial Chemical, Hychem Corp., Kerry Ingredients and Flavors	• Dishwashing • Laundry • Hard surface cleaning • Food service and kitchen hygiene • Institutional cleaning and sanitation • Vehicle care • Personal care
Amphoteric		
Cocoamidopropyl betaine Cocoamidopropyl hydroxysultaine Lauryl hydroxysultaine	BASF, Colonial Chemical, Stepan Colonial Chemical, Stepan Colonial Chemical, Stepan	• Hard surface cleaning • Food and beverage processing • Personal care
Glycolipid		
Sophorolipid Rhamnolipid	BASF, Clariant, Ecover, Evonik, MG Intobio Co. Ltd., Saraya Co. Ltd., Soliance AGAE Technologies, BASF, Biotensidon GmbH, Clariant, Evonik, GlycoSurf, Henkel, Jeneil Biotech Inc., Logos Technology Rhamnolipid Companies Inc., TeeGene Biotech	• Personal care • Vegetable liquid wash • Dish washing
Amino acid surfactants		
Sodium cocoyl glutamate Sodium methyl cocoyl taurate α-Acyl glutamate and sarcosinate	Ajinomoto Co. Inc., Stepan, Zschimmer and Schwarz Clariant Schill+Seilacher	• Personal care

Table 2.
Commercially available bio-based surfactants, their manufacturers, and their applications.

structural analogs of glycerol-based surfactants have recently been created by employing heterogeneous interfacial acidic catalysts to directly etherify glycerol and dodecanol. These surfactants have been shown to be comparable with commercially available surfactants in terms of physicochemical assessment and detergency ability [37]. Another class of amphiphilic compounds with a glycerol backbone is bio-based dialkyl glycerol ethers. These compounds have good solvo-surfactant characteristics and can function as solubilizers for hydrophobic dyes in aqueous media [65].

Natural edible flavor vanillin is used to create a cleavable vanillin-based polyoxyethylene nonionic surfactant. Because it contains cleavable acetal bonds that break down quickly under acidic circumstances, this environmentally beneficial surfactant is totally biodegradable in nature. The surfactant's surface activity, wettability, and emulsifying and foaming properties are on par with nonylphenol ethoxylate surfactants, which are highly toxic to aquatic organisms and environment [66]. Several novel types of sustainable surfactant have been created in recent years by employing various types of terpenes, which are the major components of essential oils derived from a variety of plants and flowers [67–70]. The terpenes were transformed to branched hydrophobic tail containing quaternary ammonium surfactants. Natural farnesol, a 15-carbon acyclic sesquiterpene alcohol found in neroli, lemongrass, tuberose, rose, citronella, and other plant species, was used to create a new form of terpene-based sustainable surfactant, which has demonstrated excellent surfactant performance [70]. Under the trade name ECOSURF, Dow Chemical Co. is now offering a range of sustainable oilseed-based nonionic surfactants. These surfactants are claimed to have minimal aquatic toxicity and are biodegradable in nature, making them suitable candidates for paints and coatings, as well as home, industrial, and institutional cleansers and textiles [71].

TegraSurf, a range of sustainable water-based surfactants developed for energy, mining, agricultural, water treatment, and other industrial applications, was released in July 2021 by Integrity BioChem (IBC), a technology-driven business producing next-generation biopolymers. TegraSurf is made of sustainable vegetal materials and is certified Readily Biodegradable by the OECD 301B guideline. After 90 days, it is no longer present in the environment, making it safer and healthier for local populations and allowing formulators to fulfill industry sustainability criteria [72]. BASF and Solazyme Inc. recently released Dehyton® AO 45, the first commercial microalgae-derived betaine surfactant made from microalgae oils as an alternative to conventional amidopropyl betaine surfactants [73]. Following the launch of sophorolipid-based surfactants in 2020, BASF formed an exclusive partnership with Holiferm Ltd. in the United Kingdom to focus on the development of glycolipids other than sophorolipids for personal and home care as well as for industrial uses [74].

Croda expanded its commercial-scale bio-based manufacturing capabilities and technology leadership in renewable raw materials by unveiling its 100% bio-based ethylene oxide production facility as an effort to make the world's products greener. Ethylene oxide is the key raw material used to produce surfactants. Croda's Atlas Point manufacturing plant in New Castle, Delaware, is the first of its type in the United States for the manufacture of 100% sustainable, 100% bio-based nonionic surfactants [75]. Ajinomoto is increasing to 60% of its global capacity for its Amisoft range of amino acid-based liquid surfactants by building a new plant in Brazil [76]. Sironix Renewables received $645,000 in investment from the University of Minnesota Discovery Capital Investment program and investors as well as a $1.15 million grant from the US Department of Energy Advanced Manufacturing Office, to help them scale up their Eosix® production. The new renewable oleo-furans-based surfactants are 100% plant-based that offer unique and adjustable characteristics in a wide range of areas, including cleaning products, cleaners, cosmetics and personal care, agriculture and inks, and paint and coatings [77].

3. Industrial challenge on bio-based surfactant

This section covers the market performance, demand drivers, and growth prospects of biosurfactants. The market trend on bio-based and biosurfactants is discussed for the different geographic regions and in terms of changing market trends for biosurfactants in various application areas. Analysis of the industrial challenges of biosurfactants, which include the growth-restraining factors and future opportunities, is provided.

3.1 The economy and market trend of bio-based surfactant

The worldwide surfactant industry, estimated to be worth $39 billion in 2019, is expected to expand at a rate of 2.6% per year over the following five years, reaching $46 billion in 2024. Surfactants are produced in total of 17 million metric tons per year [78]. In the EU, of the 3 million metric tons of surfactants produced in 2019, roughly 50% were bio-based [79]. A market study by Market Research Future [80] indicated that the global biosurfactants' market value is around USD 2.1 billion in 2020 and predicted it to reach USD 2.8 billion by 2026, with a compound annual growth rate of over 5% from 2021 to 2026. The attractive performance of biosurfactants advances their high potential to substitute synthetic-based surfactants for drop-in applications and with unique properties that can overcome entry barriers for the emerging industrial areas. Major types of biosurfactants, such as sophorolipids, glycolipids, lipopeptides, polymeric biosurfactants, phospholipids and fatty acids, generally form the product demand application. Among biosurfactants, sophorolipids provide the largest global market demand with detergents and industrial cleaning applications. The leading demand drivers for biosurfactants comprise a growing consumer preference, increasingly stringent regulatory requirements, and rising awareness toward eco-friendly alternatives. By being environmentally compatible and with low toxicity, many studies have considered biosurfactants as the next generation of industrial surfactants [81–83]. In terms of end-user applications, biosurfactants are finding usage in household detergents, industrial and institutional cleaners, cosmetics, and personal care within the major markets in Europe and North America [80]. Recently, they have been gaining acceptance in the newer application areas such as in oil and gas as well as in agricultural industries.

Furthermore, the increasing consumer awareness of the benefits of biosurfactants and their wide range of application sectors form market drivers that increase their future growth potential. Higher growth of biosurfactants is seen in Asia-Pacific (APAC), especially in Southeast Asian countries that have slightly different demand factors that involve the increasing purchasing power of mass consumers, growing concern on environmental issues, and the generation of harmful chemical by-products. In terms of APAC market segmentation, the major sales revenue for biosurfactants resides within the home care and personal care applications, as rising urbanization becomes the dominant factor for surfactant growth. More importantly, a key growth enabler is in the innovative research on biosurfactants, especially when it can generate multifunctional and diversified products using renewable feedstock. This technological progress contributes to the desirable properties of biosurfactants to meet the changing consumer lifestyles in developing economies and consequently their increasing preference for usage in the end-user product formulation. As an example, within the home care detergent industry, the usage of biosurfactants as environmentally friendly products provides sustainable alternatives that are gaining a large market share [81, 84, 85].

The highest adoption of bio-based and biosurfactants is in Europe and North America, which dominate bio-based surfactant market share in terms of revenue and volume. Increasingly stringent regulatory requirements enable a wider acceptance of biosurfactants in the place of synthetic surfactants. For example, the imposed government regulations, such as CEN/TC-276, define the standards for surface-active agents and detergents to enhance the EU bio-based economy, detergent regulation (EC) No 648 that require surfactants used in detergents to be biodegradable under aerobic conditions as per OECD 301 test series. In addition, the COVID-19 pandemic results in a sharp increase in the bio-based surfactant product demand for household detergents, personal care, and industrial cleaners due to the rising trend for sanitation.

3.2 The industrial challenges of bio-based surfactant

Bio-based surfactants are synthesized *via* a chemical reaction, which is usually carried out under harsh conditions. The use of hazardous solvents and toxic acid or base catalysts sometimes creates undesired waste or by-products that are detrimental to the environment. Enzymes have the potential to play a significant role in the production of numerous bio-based surfactants, although they are not currently used on a large basis. Enzymes provide several advantages over chemical processing, notably in terms of improving process sustainability. The main drawbacks of enzymes are their relatively higher price compared to chemical catalysts as well as their slower reaction speeds. However, since energy costs are expected to rise, the need of sustainability (lower operating energy, less waste, and safer operating condition) is crucial. Despite the growing demand for bio-based surfactants, several challenges exist that restrain their further market growth and wider adoption. The main challenge is in the higher pricing of bio-based and biosurfactants as the biggest hurdle in meeting the requirement of priced sensitive Asian customers. Higher complexity and low-efficiency microbial fermentation process in biosurfactant manufacturing contribute to the high production cost and expensive capital cost investment. For example, the average price of sophorolipids is USD 34 per kilogram as compared to sodium dodecyl sulfate and amino acid surfactants that are priced at USD 1–4 per kilogram [86]. Nevertheless, a lower operating cost of USD 2530/ton for sophorolipids' production is attainable through technological improvement such as integrated separation, which places sophorolipid surfactants at similar prices to other specialty surfactants [87]. Increased sustainability of biosurfactant alone without significantly higher performance is not well accepted, as the usual consumers will not be willing to pay a "green" premium for bio-based products. Therefore, lower cost improvement in biosurfactant manufacturing is fundamentally important to attain an economically sustainable process and assure future market continuity [85].

A second challenge is the dependency of biosurfactant demand on the volatility and economic downturn of downstream end-user industries. Industries that are applicable for biosurfactant applications, such as oil and gas, enhanced oil recovery, food industry, construction, textiles, paints, pharmaceutical, and detergents, are known to be susceptible to general macroeconomic performance. In addition, the COVID-19 pandemic further leads to disruption in the end-user industrial demand and sustainability concern on the raw material supply. The sustainability of raw materials is a major concern as these contribute up to 50% of the glycolipid production cost and 10–30% of the overall cost for other biosurfactant products. Purification accounts for 60% of the production cost, but this can be minimized for the case of biosurfactant application in crude forms, such as in an industrial environment [88]. However, for high-purity applications, improvement in downstream processing methods is needed to attain a competitive cost of production. Opportunity exists in developing a new technology solution that utilizes a low-cost raw material such as industrial wastes for biosurfactant production. However, this needs to consider the overall production impact factors that include the availability, stability, and variability of each component [88]. The economic viability criteria for biosurfactant production, therefore, include microorganism performance, bioreactor design, target market, purification process, product properties, production condition, fermentation cycle time, and production yield [89].

Additionally, several operation and control factors provide important handles to minimize biosurfactant production costs. Batch cycle optimization on the fermentation and purification process can reduce the idle time between batches and minimize chemical usage for equipment cleaning and energy use during sterilization. Productivity is the most important factor in the manufacturing economics of biosurfactant production at commercial scales [8]. Optimum batch-sequencing campaign minimizes startup and shutdown frequency to lower the production downtime that improves productivity. Lastly, biosurfactant product development will need to fulfill time-consuming and expensive legislative requirements, which restrain market growth [90]. These add a high cost of compliance to the product development cost that is incurred by biosurfactant manufacturers. Other market entry requirements include the biosurfactant products that are tested for long shelf life and the ability to maintain stable properties in the industrial environment [91].

4. Future outlook and prospect

The development of bio-based surfactants from renewable feedstocks is an attractive alternative to fossil-based surfactants with a significantly growing market attributed to their performance, biodegradability, biocompatibility, and nontoxicity [22, 33]. Additionally, advances in renewable technology, increased environmental concern, consumer awareness, and stringent regulatory requirements provide a continued push toward the demand of bio-based surfactants. Potential areas for use are growing fast, and valuable outcomes depend on whether the bio-based surfactants can be customized for specific applications along with if they can be produced at a price that will make them attractive alternatives to the fossil-based surfactants. The simultaneous design of bio-based surfactants for functional, economic, and environmental benefits will be taxing, but it will ensure the replacement of conventional fossil-based surfactants provided they can offer comparable or superior performance and a unique value proposition.

Presently, fossil-based surfactants are less expensive than bio-based surfactants [4, 92, 93]. However, this trend will likely change in the future, thereby increasing the prospects of bio-based surfactants. Feedstocks and how the bio-based surfactants are produced are the two key factors governing final product costs [4, 36, 94, 95]. To use renewable feedstock in the industry, they should be cost-effective, available in large quantities, and can effectively be converted to value-added surfactants [95]. Renewable feedstocks used as starting materials to produce surfactants usually face severe economic competition from their fossil-based counterparts. Surfactants comprised of hydrophilic head group and hydrophobic tail group, which are linked by a chemical bond generating an amphiphilic molecule that can be used directly or further modified. Surfactant design requires careful selection of the hydrophile and hydrophobe pair so that they can be easily synthesized with minimum purification and provide the desired properties for the intended application [4, 16, 92, 96]. Triglycerides, fatty acid methyl esters, fatty alcohols, fatty acids, and fatty amines are common examples of renewable hydrophobes used to produce bio-based surfactants. Sustainable hydrophilic headgroups can be designed using several molecules such as glycerol, carbohydrate feedstocks such as sucrose, glucose, organic acids, and amino acids [4, 36, 94, 95]. Additionally, the use of renewable feedstock for surfactant manufacturing also helps reduce CO_2 emissions because once the bio-based surfactants degrade, they only release back the quantitative amount of the carbon used by the plant to produce the surfactants [36]. Other than the starting material mentioned above, the use of alternative substrates, such as agro-based industrial wastes or other suitable simple waste substrate, is gaining a lot of research interest and can lead to significant cost reduction [97].

Researchers are continually improving the cost-effectiveness of production methods as well as enhancing the current technologies with green manufacturing principles to convert renewable feedstocks into valuable and new biobased surfactants. Some of the key focus areas include developing biobased surfactants from cheaper feedstocks, higher performance catalysts, green solvents, optimized reaction processes, and effective downstream purification could entice the industry players and end-use customers to make the switch from fossil-based surfactants to biobased surfactants. Catalyst design is also crucial to ensure high selectivity of the processes to limit or eliminate the formation of by-products and to help push the reaction forward towards completion faster [98–100]. Other than that, researchers are looking into equipment miniaturization such as continuous reactors to help reduce the raw material consumption and effluent production. Process intensification is another aspect that could help to reduce the investment costs [99]. Research focusing on alternative or green solvents dedicated to the conversion of renewable feedstock to value-added products has led to several publications. Among those being researched include bio-based ionic liquids, deep eutectic solvents, bio-based solvents, CO_2-switchable solvents and supercritical fluids [101–103].

In terms of market penetration of bio-based surfactants, customers tend to choose cost-effective surfactants. Despite much progress in technical knowledge, the large-scale production of bio-based surfactants using the methods described above is still limited. The commercial production of bio-based surfactants still faces many challenges that must be addressed for them to be economically viable. One major obstacle is the homogeneity and consistency of the feedstock, which can lead to inconsistency in the final bio-based surfactants. Variation in the surfactant properties and performance could lead to unsatisfactory properties. Thorough testing on the use of bio-based surfactants in place of fossil-based ones will also be needed to provide enough and convincing data on the merits of bio-based surfactants. It is hoped that these efforts will lead to broader use of bio-based surfactants in the future, offering enormous benefits such as excellent physicochemical properties, biodegradability, lower risk to human health, and minimum harm to the environment.

5. Conclusions

Surfactant manufacturers have introduced numerous new eco-friendly surfactant-based products to the market in the past few years. Increased consumer awareness, along with a responsibility for sustainable development, has resulted in the creation of several novel surfactant types based on renewable building blocks. These surfactants have improved biodegradation characteristics and low toxicity, making them a preferred alternative for innovative formulations in the industrial and consumer markets. However, these "drop-in" surfactant molecules, which aim to directly replace their petrochemical-based equivalents, face a huge challenge since prices must be as competitive as their fossil counterparts. Moreover, while several personal care and consumer product businesses have shown interest in 100% bio-based surfactants, only a few green premium products have been accepted into the market. More assessments and surveys need to be done to gauge consumer willingness to pay premium prices for other than commodity products. With increasing innovative formulations to meet consumer, legislative, and sustainability demands, it is obvious that the global demand for both petroleum- and bio-based surfactants will continue to grow, while manufacturers are challenged to balance cost-effective formulations with efficient performance.

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