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Progress on the synthesis and applications of the green non-ionic surfactant alkyl polyglycosides

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Against the backdrop of deeply ingrained principles of green chemistry and sustainable development, alkyl polyglycosides (APGs), a series of green non-ionic surfactants synthesized from natural and renewable sugars and fatty alcohols, are attracting increasingly widespread attention. APGs not only exhibit low surface tension, excellent compatibility, rich and fine foaming properties, and good biodegradability, but also demonstrate low irritation to the skin and eyes, endowing them with broad application prospects. This review provides a systematic overview of the structure, properties, synthetic methods, and application research progress of APGs. Firstly, the structure–property relationships between the molecular structure of APGs and their solubility, surface activity, foaming performance, and safety are analyzed and discussed. Secondly, various synthesis routes, including glycosidation, enzymatic catalysis, and phase-transfer catalysis, are introduced. The advantages, disadvantages, and applicable scenarios of different processes are compared and analyzed, with a focused review on the various types of catalysts (inorganic acids, organic acids, solid acids, composite acids, and ionic liquids) used in the industrial glycosidation method. Their development history and catalytic performance are summarized, alongside the current technical challenges and future directions for industrialization. Finally, the practical applications of APGs in cosmetics, detergents, petroleum extraction, pharmaceuticals, and pesticides are summarized, and their future potential is discussed. This review aims to provide a valuable reference for optimizing green synthesis processes, developing high-performance APGs products, and advancing their industrialization.

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1 Introduction

Since the industrial revolution, the large-scale exploitation and utilization of fossil fuels have led to continuous environmental degradation, necessitating a transformation of the traditional model of "mass production, mass consumption, and mass disposal" to promote green and sustainable development. Against this backdrop, the development of environmentally friendly bio-based surfactants has become an inevitable trend. As a new generation of "world-class" green nonionic surfactants, alkyl polyglycosides (APGs) are synthesized from natural and renewable resources such as sugars and fatty alcohols *via* acid-catalyzed dehydration and condensation.[1–3] APGs exhibit high surface activity, low skin irritation, fine and stable foam, excellent wetting and detergency, as well as outstanding biodegradability,[4–7] making them highly aligned with current market demands for safe and eco-friendly surfactants. It was reported that the global market for APGs is projected to grow from USD 1.51 billion in 2024 to USD 3.27 billion by 2034, at a compound annual growth rate (CAGR) of 8%.[8]

The synthesis of alkyl polyglycosides (APGs) dates back to 1893, when E. Fischer developed the Fischer glycosidation method, which enabled the synthesis of short-chain glycosides with limited application potential. It was not until the 1930s that the superior surface activity of long-chain (C_8–C_{10}) APGs were recognized, spurring industrial production efforts. Current industrial synthesis primarily employs either direct glycosidation (one-step method) or transglycosidation (two-step method), both of which allow tunable control over the degree of polymerization and generate minimal by-products, making them widely adopted in commercial production.[1] The choice of catalyst significantly influences both reaction rate and product quality. Early processes used inorganic acids such as H_2SO_4, HCl, and H_3PO_4, but these have been progressively supplemented, and in many cases replaced, by organic acids (*p*-toluenesulfonic acid and dodecylbenzenesulfonic acid) and multicomponent acid systems to improve product color and reduce equipment corrosion and environmental impact. More recently, heterogeneous catalysts including solid acids and ionic liquids have been developed to facilitate catalyst

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separation and recycling. In addition to catalyst development, various synthetic routes have been explored, such as phase-transfer catalysis, the Koenigs–Knorr method, trichloroacetimidate-mediated synthesis, the Ferrier rearrangement, and enzymatic catalysis using specific enzyme preparations.[1] Among these, glycosidation remains the dominant industrial process due to its maturity, cost-effectiveness, and product quality. Despite successful commercialization, APGs production still faces challenges in industrial scaling: (1) poor mass transfer in heterogeneous reaction systems leads to slow kinetics; (2) residual fatty alcohols and by-products impair purity and color; (3) energy-intensive purification steps increase production costs; (4) thermal degradation or charring can occur at elevated temperatures. Addressing these issues through reaction system optimization, development of highly efficient catalysts, and intensification of separation processes is essential to overcome current production bottlenecks.

This review provides a systematic summary of the structure–property relationships, synthesis methods, catalytic systems, and application advances of alkyl polyglycosides. It first analyzes the influence of varying alkyl chain lengths on the solubility, surface activity, foaming performance, and safety profiles of APGs. The advantages and limitations of different synthetic routes are subsequently discussed and compared, with emphasis placed on developments in catalytic systems employed in glycosidation reactions. Furthermore, the current applications of APGs in cosmetics, detergents, petroleum extraction, pharmaceuticals and pesticides are summarized, alongside prospective potential for future utilization. The review also identifies existing challenges in industrial-scale APGs production and offers insights into future research directions, aiming to provide valuable guidance for the green manufacturing of APGs.

2 Structure and properties of alkyl polyglycosides

2.1 Structure

Alkyl polyglycosides are classified into alkyl monoglycosides, diglycosides, triglycosides, and higher-degree polymerized glycosides based on their degree of polymerization. The structural formula of alkyl polyglycosides is shown in Fig. 1. In the formula, R represents the alkyl group; n denotes the average degree of polymerization (DP) of the product, indicating the average number of sugar units attached per alkyl chain. Alkyl polyglucosides (APGs) are a class of compounds synthesized *via* the acid-catalyzed dehydration condensation between the hemiacetal hydroxyl group of a saccharide and the hydroxyl group of a fatty alcohol, forming a glycosidic linkage (C–O–C). Since the hydroxyl groups of D-glucose are unprotected, side reactions inevitably occur, leading to a mixture of APGs homologues with different degrees of polymerization (Fig. 2).[9] The structure with the lowest degree of polymerization ($n = 1$) consists of one D-glucose unit and is referred to as alkyl monoglucoside. More complex polymerization reactions ($n > 1$) yield alkyl polyglycosides (APGs). As n increases, the content of alkyl monoglycoside decreases, while that of polyglycosides increases.

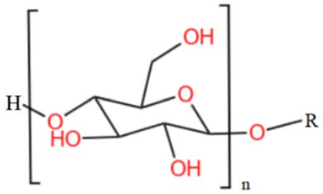

Fig. 1 Structure of APGs.

From a structural perspective of surfactants, the molecular architecture of APGs can be divided into a hydrophilic glycoside unit and a hydrophobic alkyl chain. The hydrophilic moiety typically consists of monosaccharides or disaccharides, and sometimes even carbohydrate derivatives, while the hydrophobic part is composed of linear or branched alkyl chains.[10] The composition of the reaction products depends mainly on the type of sugar. For example, D-glucose units are all polyhydroxy acetals, and their cyclic structures can be derived from five-membered furanose or six-membered pyranose rings. All D-glucose units exhibit a cyclic hemiacetal functional group formed by an intramolecular reaction. The anomeric carbon thus becomes a chiral center and can adopt two different configurations. The resulting stereoisomers are called anomers and are distinguished by the prefixes α or β. In the synthesis of alkyl polyglucosides, alkyl pyranosides exhibit greater thermodynamic stability than alkyl furanosides and are therefore the main products obtained under equilibrium conditions. In the pyranose ring, the lone pair electrons of the ring oxygen atom O-5 can stabilize a leaving group in the axial position at the anomeric carbon through orbital interactions, a phenomenon known as the "anomeric effect". For D-glucose, the most stable conformation is the $^4C_1$ chair conformation. In this conformation, an α-configured leaving group occupies the axial position and is stabilized by the anomeric effect, which makes the reaction more likely to start from an α-configured glycosyl donor and tends to produce α-glycoside products. However, in the final reaction products, the β-glycosidic bond occupies the sterically less hindered equatorial position, which itself has a thermodynamic advantage. Therefore, the anomeric effect alone is insufficient to completely suppress the formation of the β-anomer, and the reaction typically results in a mixture dominated by the α-anomer. Thus, when APGs are synthesized from D-glucose and fatty alcohols under acid catalysis, the corresponding alkyl α-furanosides (2), alkyl β-furanosides (3), alkyl α-pyranosides (4), and alkyl β-pyranosides (5) are usually produced, with alkyl α-pyranosides being the dominant product (Fig. 3).[11]

2.2 Properties

Based on the differences in alkyl chain length, alkyl polyglycosides can be categorized into short-chain and long-chain APGs. APGs with chains shorter than C_8 are classified as short-chain APGs, while those with C_8 or longer chains are considered long-chain APGs. Short-chain APGs exhibit limited performance and are unsatisfactory as surfactants, restricting their application to only a few niche areas. In contrast, C_8–C_{14} APGs demonstrate superior properties, including good solubility, low surface tension, excellent foaming characteristics, and high safety (Fig. 4). These APGs

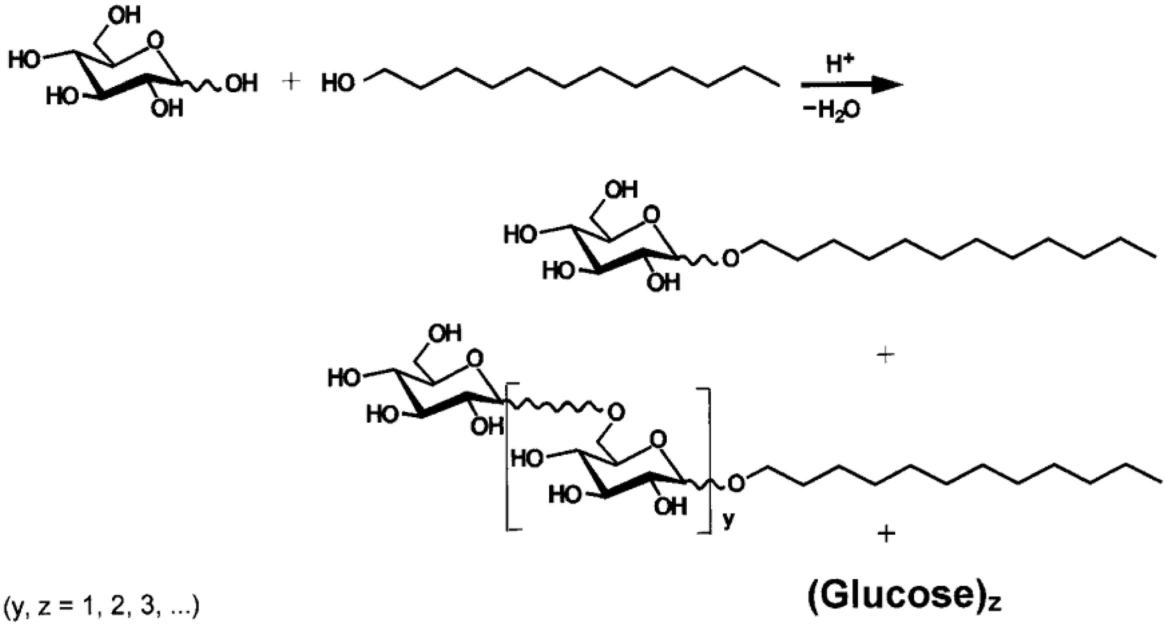

Fig. 2 Synthesis of alkyl polyglucosides *via* glycosidation of glucose with excess fatty alcohol.[9] This figure is reprinted from ref. 9 with agreement from John Wiley and Sons, copyright 1999.

are well-characterized as effective surfactants and are widely used across numerous applications.[12–14]

2.2.1 Solubility properties. APGs are readily soluble in water and soluble in polar organic solvents such as ethylene glycol and glycerol. This solubility behavior stems from the presence of multiple hydroxyl groups in their hydrophilic moieties, which form extensive hydrogen bonds with water, resulting in high hydrophilicity. At a constant degree of polymerization, the solubility of APGs in water decreases as the hydrocarbon chain length increases. This reduction occurs because the alkyl chain is hydrophobic, and its elongation enhances the molecule's hydrophobic interactions, prompting APGs molecules to either escape the aqueous environment or self-assemble into micelles rather than remain dissolved as monomolecular species. Consequently, solubility declines. In contrast, the water solubility of APGs increases with the degree of polymerization when the alkyl chain length is kept constant. This trend is attributed to the incorporation of additional hydroxyl groups with each sugar unit, which enlarges the hydrophilic portion of the molecule and increases the number of available hydrogen-bonding sites, thereby strengthening overall hydrophilicity.[15]

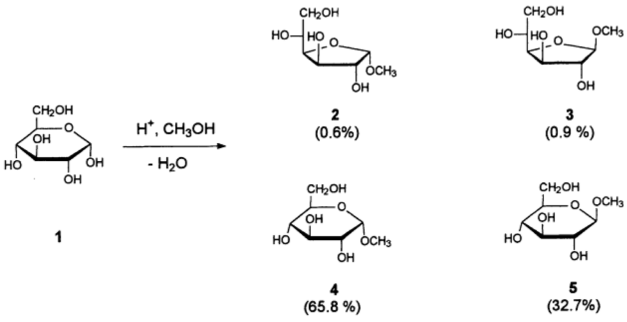

Fig. 3 Methyl D-glucosides of various configurations obtained by the Fischer process.[11] This figure is reprinted from ref. 11 with agreement from American Chemical Society, copyright 2001.

2.2.2 Surface properties. A fundamental characteristic of surfactants is their ability to significantly reduce the surface tension (γ_{CMC}) of a solvent. The critical micelle concentration (CMC) refers to the minimum concentration at which surfactant molecules associate to form micelles, at which point the surface tension reaches its lowest value. The surface activities of APGs are influenced not only by temperature but also by its molecular structures, including the sugar headgroups, alkyl chain lengths, and stereochemistry of the alkyl functional groups. Experimental studies have demonstrated that longer alkyl chains in APGs lead to lower CMC values and reduced surface tension in aqueous solutions (Table 1).[16,17] The presence of hardness ions in water can further decrease the CMC of APGs, though it has a minimal effect on γ_{CMC}. Angarten and Loh[18] employed isothermal titration calorimetry to monitor the micellization of two homologous series of alkyl polyglycosides surfactants, monoglucosides from heptyl to nonyl and diglucosides from octyl to dodecyl, over a temperature range of 15–65 °C. They investigated a series of thermodynamic parameters (ΔG, ΔH, and ΔS) and influencing factors including temperature, hydrocarbon chain length, and glycone type. Their study revealed that the micellization thermodynamics of APG adhere to the enthalpy–entropy compensation mechanism: ΔH and ΔS exhibit opposing trends with temperature variation, effectively canceling each other out and resulting in a relatively stable ΔG with low temperature dependence. At lower temperatures (approximately 15 °C), ΔH is positive, and micellization is primarily entropy-driven. At elevated temperatures (approximately 65 °C), ΔH becomes negative, and the process shifts to

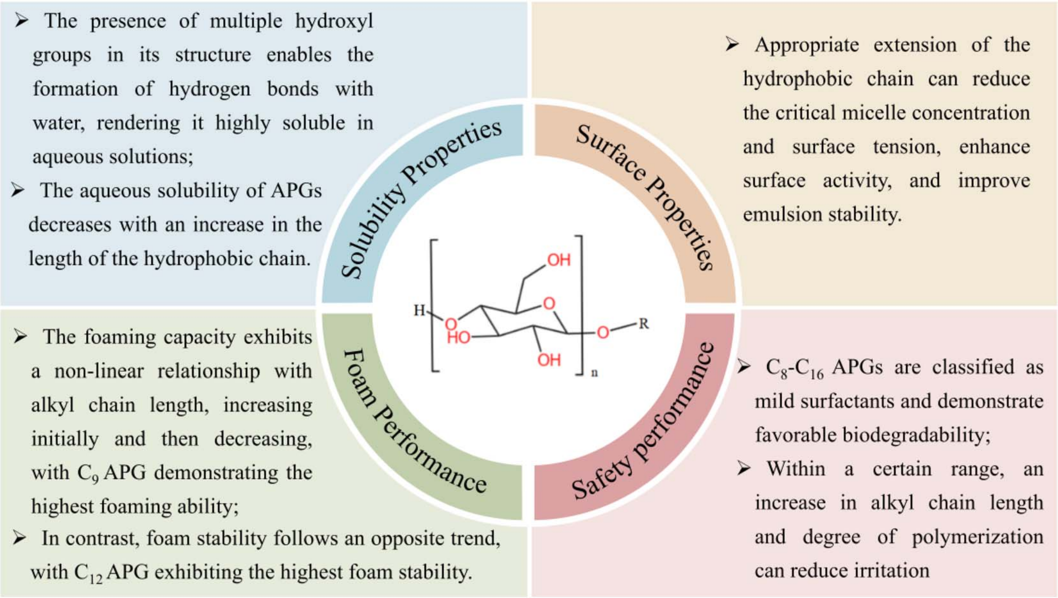

Fig. 4 Relationship between the carbon chain length of APGs and their properties.

enthalpy-driven, with the transition occurring near 55–65 °C. The hydrocarbon chain, as the hydrophobic moiety, consistently contributes a negative ΔG, serving as the primary driving force for micellization, and this contribution is slightly enhanced with increasing temperature. In contrast, the glycone head group, whether mono- or diglucoside, exerts nearly identical and minimal influence on the thermodynamic parameters, indicating that the micellization process is predominantly governed by the hydrophobic tail, while the nature of the hydrophilic head group plays a negligible role.

During emulsion preparation, interfacial tension exists between two immiscible liquids, leading to their tendency to separate. When one liquid is dispersed into the other, the contact area between the two phases increases significantly, resulting in a substantial rise in interfacial free energy. Consequently, emulsions are thermodynamically unstable systems and always exhibit a spontaneous tendency to reduce the interfacial area and revert to phase separation. Owing to their excellent surface activity, APGs can adsorb at the liquid–liquid interface to form a stable, oriented molecular film, effectively reducing interfacial tension and thereby significantly enhancing emulsion stability.[17] Therefore, APGs serve as effective emulsifiers, providing excellent emulsification performance and maintaining good emulsion stability. Higher APGs concentrations and longer carbon chains lead to lower surface tension and stronger emulsifying performance. As shown in Table 1, the stability of the formed emulsion increases with alkyl chain length. This is because longer alkyl chains enhance the solubility of the surfactant in the oil phase, promoting the formation of highly stable emulsions.[17,19]

2.2.3 Foam performance. The foam generated by APGs typically exhibits spherical bubbles with a fine and stable structure. Its foaming capacity and foam stability are significantly influenced by the molecular structure of the surfactant and the solution system. The foaming ability of a surfactant primarily depends on the rate and amount of molecular adsorption at the air–water interface. As the solution concentration increases, more molecules rapidly diffuse to the interface and achieve saturated adsorption, thereby quickly reducing surface tension and forming a robust liquid film that traps gas to produce large number of fine bubbles. For APGs, the carbon chain length has a dual effect on foaming performance. On one hand, APGs with shorter carbon chains (C_{6-8}) diffuse more rapidly, enabling them to cover newly formed interfaces quickly, which favors initial foam formation. On the other hand, excessively short chains weaken the cohesive forces between molecules, resulting in insufficient liquid film strength and reduced foam stability. Foam stability is jointly determined by

Table 1 Surface properties of APGs with different alkyl chain lengths[a]

APG	CMC (mmoL L^{-1})[17]	γ_{CMC} (mN m^{-1})[19]	Emulsion stability (s)[17]
C_8 APG	1.71	30.5	230
C_9 APG	1.23	—	210
C_{10} APG	0.78	27.8	288
C_{12} APG	0.30	27.3	310
C_{14} APG	0.03	—	426

[a] "—" indicates that no data are available.

Table 2 Foam performance of APGs with different alkyl chain lengths[17]

APG	Foam height (mm)	Foam half-life (min)
C_8 APG	20	31
C_9 APG	60	19
C_{10} APG	36	15
C_{12} APG	30	210
C_{14} APG	18	90

the mechanical properties of the interfacial film and drainage dynamics. During foaming, molecules must rapidly adsorb to the nascent interface to reduce surface tension and form initial foam; after foam formation, its stability is challenged by gravitational drainage and gas diffusion (Ostwald ripening), at which point the strength of the interfacial film becomes critical. An increase in hydrophobic chain length enhances molecular packing density, cohesion, and chain entanglement, forming a denser and tougher monolayer that significantly improves interfacial elasticity and resistance to drainage, thereby suppressing bubble coarsening and coalescence. The carbon chain length of APGs plays a decisive role in this process: long-chain APGs (C_{12-14}) pack more tightly at the interface, and the stronger interchain cohesion and entanglement result in a dense, strong, and extensible interfacial film. This not only effectively slows liquid drainage but also inhibits gas diffusion, significantly delaying bubble coarsening and coalescence, thereby yielding more stable foam. Thus, long-chain APGs enhance the long-term stability of foam mechanically by forming a tougher interfacial film.[20] For instance, El-Sukkary *et al.*[17] investigated the foaming ability and foam stability of APGs with different alkyl chains and found that the foam performance of APGs does not exhibit a linear correlation with hydrocarbon chain length. Foaming ability initially increases and then decreases with increasing hydrocarbon chain length, peaking at C_9 APG. In terms of stability, the opposite trend is observed: C_{8-10} APGs produce high initial foam but decay rapidly, whereas C_{12-14} APGs generate less initial foam but are more stable, with C_{12} APG exhibiting the optimal stability (Table 2). Furthermore, although C_{10} APG has the shortest foam half-life, it still reaches 15 minutes. This phenomenon fully demonstrates that C_{8-14} APGs generally possess excellent foam persistence, highlighting their potential as highly efficient surfactants.

2.2.4 Safety performance

2.2.4.1 Toxicity and skin irritation. To ensure the safety of alkyl polyglycosides, toxicological and irritation tests are routinely conducted. Studies have shown that C_8–C_{16} APGs exhibit low acute toxicity and are classified as mild surfactants. Hill *et al.*[21] performed a series of toxicological tests on C_8–C_{14} APGs in accordance with relevant standards: oral median lethal dose (LD_{50}) was assessed in rats, skin irritation was evaluated in rabbits, and sensitization and mutagenicity were examined using the Guinea Pig Maximization Test (GPMT) and the Ames test (*Salmonella typhimurium* reverse mutation assay). The results indicated that the oral LD_{50} values of C_8–C_{14} APGs in rats

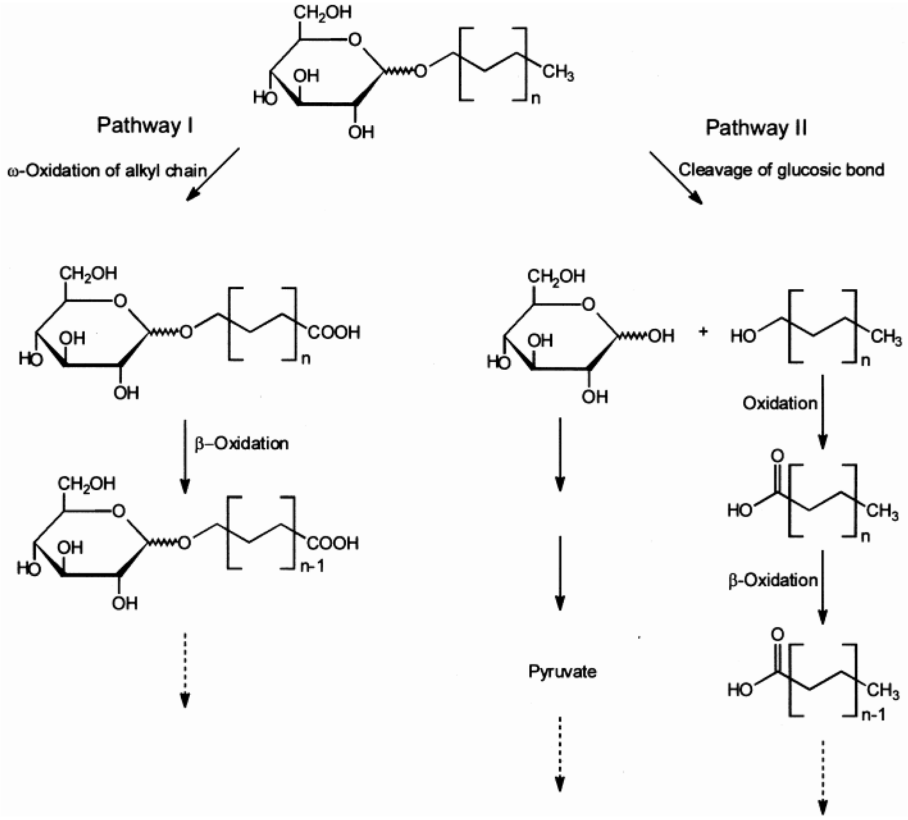

Fig. 5 Degradation pathways of APGs.[24] This figure is reprinted from ref. 24 with agreement from Elsevier, copyright 1999.

were all above 5000 mg kg^{-1}, demonstrating no acute toxicity. APGs did no irritate concentrations up to 30%, and no sensitization or mutagenicity was observed. The skin compatibility of APG was found to depend primarily on alkyl chain length and the degree of polymerization of the glucose units. Fiume *et al.*[22] conducted a safety assessment of APGs with different chain lengths. Using an occlusive patch test in rabbits, they evaluated skin irritation of C_8–C_{16} APGs at concentrations ranging from 15% to 70%. It was found that C_{12}–C_{16} APGs showed lower irritation than C_8/C_{16} APGs, and that irritation was largely concentration-dependent rather than influenced by the degree of polymerization. Cho *et al.*[23] evaluated the ocular irritation potential of five C_6–C_{16} APGs products using the Hen's Egg Test-Chorioallantoic Membrane (HET-CAM) and Bovine Corneal Opacity and Permeability (BCOP) assays. They observed that APG formulations with a higher proportion of C_{10} APG caused stronger irritation. This effect was attributed to the stronger degreasing capacity and higher skin penetration of shorter-chain APGs. In summary, APGs demonstrate low toxicity and irritation within certain concentration ranges, along with an absence of sensitization and mutagenicity. Within the C_8–C_{14} chain length range, mildness generally improves with slightly longer alkyl chains and higher degrees of polymerization. Therefore, APGs type and concentration can be selected based on application requirements to ensure both safety and performance.

2.2.4.2 *Biodegradability.* The environmental fate of surfactants is closely linked to their biodegradation behavior, with rapid and complete biodegradability being a critical requirement for environmentally compatible surfactants. Alkyl polyglycosides undergo structural breakdown and mineralization *via* microbial action, ultimately transforming into harmless small molecules such as CO_2 and H_2O. Eichhorn and Knepper[24] investigated the degradation pathways of APGs using liquid chromatography-electrospray mass spectrometry (LC-ES-MS). They proposed two distinct routes for APG degradation. One pathway involves initial hydrolysis of the glycosidic bond, yielding glucose (or sugar units) and fatty alcohols. The glucose is subsequently metabolized *via* the pyruvate cycle, while the fatty alcohols are converted to fatty acids through β-oxidation and further metabolized within the cell. The other pathway proceeds *via* ω-oxidation of the alkyl chain, forming the corresponding carboxylic acid, which then undergoes continued breakdown by β-oxidation (Fig. 5).

Biodegradation tests for APGs are conducted using internationally recognized standard methods, including the discontinuous activated sludge test, continuous activated sludge test, and the anthrone method.[12] Data show that in biodegradability assessments such as the shake-flask culture test, semi-continuous activated sludge test, and continuous activated sludge test, APGs exceed the Organization for Economic Co-operation and Development (OECD) ready biodegradability limit (60%), with a BOD_{28}/COD (Chemical Oxygen Demand/Biological Oxygen Demand) ratio of 75%.[25] Rastogi[26] also observed that C_8–C_{14} APGs meet criteria for ready biodegradability, achieving over 60% removal within 2 days. The degradation rate of APG is influenced by initial concentration, alkyl chain length, degree of polymerization (DP), and branching structure: higher concentrations (*e.g.*, 100 mg L^{-1}) inhibit degradation, while lower concentrations (*e.g.*, 15 mg L^{-1}) facilitate faster breakdown. Longer alkyl chains ($C_{12} > C_{10} > C_8$) enhance biodegradation due to improved microbial adsorption driven by higher hydrophobicity. Higher DP values slow degradation due to increased resistance to hydrolysis. Branched-chain APGs degrade more slowly than linear analogues. In summary, C_8–C_{10} APGs exhibit good biodegradability owing to their high solubility in water and microbial accessibility. C_{12}–C_{14} APGs show the highest degradation rates due to optimal hydrophobicity for microbial adhesion. APGs with chains longer than C_{16} degrade more slowly due to poor solubility and tendency to form suspensions.[12,26] Alkyl polyglucosides degrade rapidly not only under aerobic conditions but also perform excellently in anaerobic environments, which represent the rate-limiting step for their degradation. Comparative data show that the anaerobic biodegradation removal efficiencies of $C_{8/10}$ APGs and $C_{12/14}$ APGs reach 95 ± 22% and 84 ± 15%, respectively, while the degradation of linear alkylbenzene sulfonate (LAS) is significantly limited under anaerobic conditions, with a maximum removal rate of only 57%. Therefore, APGs exhibit notable advantages in environmental compatibility in terms of biodegradation, with their core strength lying in their rapid and ultimate biodegradability.[21,27]

3 Advances in synthesis methods of alkyl polyglycosides

Currently, the synthesis of alkyl polyglycosides primarily includes methods such as glycosidation, phase-transfer catalysis, enzymatic catalysis, the Koenigs–Knorr method, trichloroacetimidate-mediated synthesis, and the Ferrier rearrangement (Fig. 6). Among these, the glycosidation method remains dominant due to its well-established process, controllable reaction conditions, and cost-effectiveness. Accordingly, this review also focuses on the various catalysts employed in this method (ranging from inorganic acids, organic acids, and composite acids to solid acids and ionic liquids) systematically analyzing their characteristics to provide a theoretical basis and research insights for optimizing the synthesis and promoting the development of APGs.

3.1 Glycosidation

The glycosidation method can be classified into direct glycosidation (one-step method) and transglycosidation (two-step method). The one-step method involves the acid-catalyzed nucleophilic attack of an alcohol on protonated glucose, leading to the formation of both α- and β-anomers of alkyl polyglycosides. In contrast, the two-step method first involves the reaction of a sugar with a short-chain alcohol (typically *n*-butanol) under acid catalysis to form short-chain alkyl glycosides, which subsequently react with a long-chain alcohol to yield the desired long-chain alkyl polyglycosides.[28] A detailed reaction mechanism is illustrated in Fig. 7.

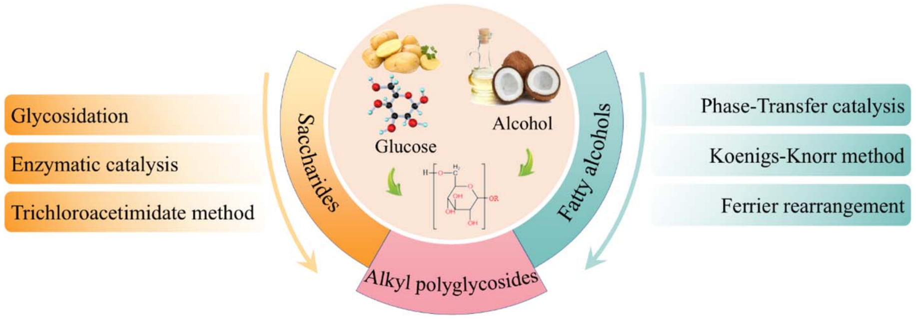

Fig. 6 Synthetic methods for APGs.

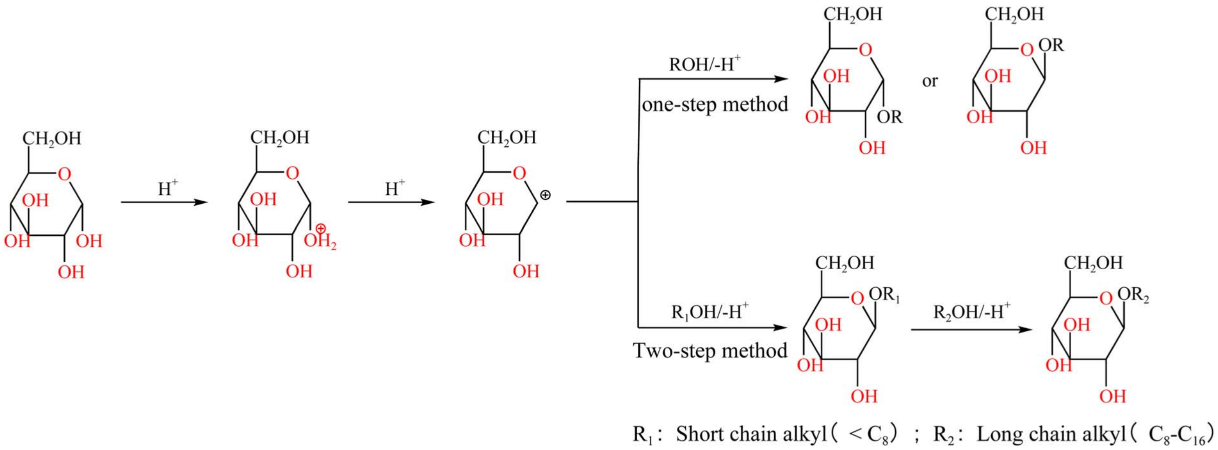

Fig. 7 Reaction mechanism of glycosidation.[29]

The direct glycosidation method eliminates the need for short-chain alcohols, offering a shorter synthetic route, operational simplicity, and lower production costs, making it the primary approach for laboratory-scale preparation of APGs. In contrast, the transglycosidation method effectively addresses issues such as phase separation caused by the poor solubility of glucose in long-chain fatty alcohols.[30] It mitigates caramelization resulting from sugar self-polymerization and provides a mild, controllable reaction process with shorter duration. From a mechanistic perspective, regardless of the synthetic method employed, the design of the catalytic system critically influences the yield and quality of APGs. Numerous researchers have conducted extensive studies on catalyst selection and process optimization for APGs synthesis. Catalysts used in glycosidation include inorganic acids, organic acids, composite acids, solid acids, and ionic liquids. Common types of catalysts are summarized in Fig. 8.

3.1.1 Employing inorganic acids as catalysts. In 1893, Fischer first synthesized ethyl glycoside using HCl as a catalyst.[31] Common inorganic acids employed as catalysts in glycoside synthesis include sulfuric acid, phosphoric acid, and hydrochloric acid, among others. Nüchter *et al.*[32] reported the synthesis of methyl glycoside with 100% glucose conversion using starch or glucose as the starting material under microwave assistance at 140 °C, 500 W power, and a reaction time of 20 minutes, with hydrochloric acid as the catalyst. Mansfield[33] reacted 210.0 g of *n*-octanol, 1.0 g of concentrated sulfuric acid, and 90.0 g of glucose at 95–100 °C for 3 hours. Gas chromatographic analysis of the reaction mixture indicated that the

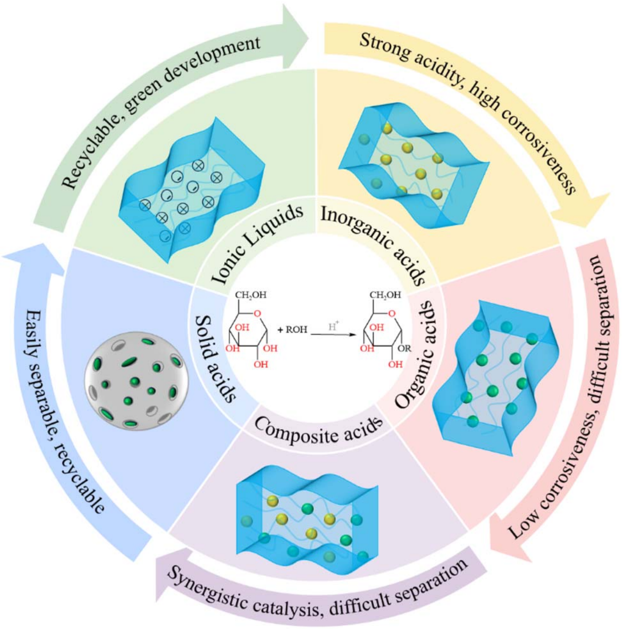

Fig. 8 Classification of catalysts used in glycosidation.

Table 3 Synthesis of APGs using sulfuric acid as catalyst (direct glycosidation)

Raw materials and ratios	Temperature and time	Result	References
Nonanol : glucose : sulfuric acid mass ratio 40 : 9 : 0.2	120 °C, 3 h	15 g nonyl glucoside	34
n-Butanol : glucose : sulfuric acid molar ratio 40 : 1 : 0.2	117 °C, 6 h	Butyl glucoside yield: 99.8%	35
Xylitol : glucose : sulfuric acid mass ratio 3.57 : 1.3 : 0.01	120 °C	Xylosyl glucoside yield: 41.8%	36

product contained 20.7% octyl glucoside and almost no residual glucose. Among the three commonly used inorganic acids, the acid strength decreases in the order: hydrochloric acid > sulfuric acid > phosphoric acid. Although hydrochloric acid exhibits the strongest acidity, its high volatility raises safety concerns during operation. Therefore, sulfuric acid is often the preferred choice among researchers using inorganic acid catalysts (Table 3).

In summary, a small amount of sulfuric acid can achieve satisfactory catalytic performance, demonstrating its strong acidity and high catalytic activity. However, the absence of universally standardized production criteria for alkyl polyglycosides has led to variations in product evaluation methods among researchers. For instance, Mansfield[33] determined glycoside yield by analyzing the reaction products using gas chromatography. Mutlu[35] evaluated the reaction outcome based on glucose conversion, defined as the percentage of glucose consumed relative to the initial amount. In contrast, Thenchartanan[37] expressed the yield of alkyl glucosides as the molar percentage of alkyl glucoside relative to the total moles of free glucose and alkyl glucoside present in the reaction. Meanwhile, Li *et al.*[38] defined alkyl polyglycosides yield as the mass ratio of glycoside products to the initial glucose mass.

Although inorganic acids such as hydrochloric acid, sulfuric acid, and phosphoric acid offer advantages including strong acidity, fast reaction rates, low cost, and ready availability in APGs synthesis, their use as catalysts also presents drawbacks such as low reaction selectivity and a tendency to cause charring or self-polymerization of sugars. These issues arise primarily for two reasons: firstly, strong acids readily promote the dehydration of glucose, leading to the formation of dark-colored furan derivatives such as furfurals. Secondly, neutralization with a strong base is required after the acid-catalyzed reaction, which can induce degradation starting from the reducing end of sugars, resulting in unavoidable coloration.[39] Furthermore, inorganic acids contribute to equipment corrosion and environmental pollution, thereby severely limiting their applicability in industrial-scale production.

3.1.2 Employing organic acids as catalysts.

When using a single organic acid as the catalyst, compared to inorganic acids, it exhibits lower corrosiveness to equipment and pipelines, yields products with lighter color and improved performance, while also reducing carbonization and polyglycoside formation. Li *et al.*[38] compared the appearance of APG synthesized under identical conditions using dodecylbenzenesulfonic acid, *p*-toluenesulfonic acid, and sulfuric acid, respectively. The results showed that the resulting products exhibited brown, light yellow, and dark brown colors, respondingly. Currently, the most commonly used organic acids are *p*-toluenesulfonic acid (PTSA) and dodecylbenzenesulfonic acid (DBSA). This preference is because PTSA possesses high catalytic activity, maintains stable reaction conditions, effectively prevents glucose agglomeration, causes no corrosion to production equipment, and yields high-quality products. On the other hand, DBSA can inhibit reactions between sugar rings, reduce the occurrence of side reactions and polysaccharide content, and exhibits high catalytic activity. Moreover, DBSA serves a dual function as both a surfactant and an acid catalyst.[40] Its emulsifying properties promote the formation of a micellar reaction system, effectively shortening the reaction time (Table 4).

Naturally, the efficacy of the catalyst is also closely related to its loading. An insufficient amount leads to poor catalytic performance, whereas excessive loading can still cause polysaccharide aggregation and product charring. In a study by Li *et al.*[38] aimed at optimizing the mass ratio of PTSA to glucose, the reaction temperature, pressure, and molar ratio of lauryl alcohol to glucose were fixed at 120 °C, 5.0 kPa, and 6 : 1,

Table 4 Synthesis of APGs catalyzed by different organic acids (direct glycosidation)

Organic acids	Raw materials and ratios	Temperature and time	Result	References
PTSA	Dodecanol : glucose : catalyst molar ratio 6 : 1 : 0.008	120 °C 3.5 h	Yield of dodecyl glucoside: 140.2%	38
	n-Butanol : glucose : catalyst mass ratio 559 : 90 : 1.1	110–114 °C 2 h	Yield of glycoside: 67%	41
	Glucose : C_8–C_{10} alcohols : catalyst mass ratio 15 : 4.7 : 0.094	95 °C 1.5 h	Glucose conversion rate: 87.5%	42
DBSA	*n*-Decanol : glucose : catalyst mass ratio 87.83 : 50 : 1	120 °C 3 h	Glucose conversion rate: 51.6%	43
	Lauryl alcohol : glucose : catalyst	110 °C 4 h	Yield of glycoside: 25%	44
	C_{12}–C_{14} fatty alcohols : anhydrous glucose : catalyst molar ratio 3.5 : 1 : 0.03	110 °C 3 h	Yield of APGs: 99.6%	45

Table 5 Synthesis of APGs catalyzed by different composite acids

Synthetic methods	Composite acids (mass ratio)	Raw materials and ratios (mass ratio)	Temperature and time	Result	References
Direct glycosidation	DBSA : citric acid : sodium citrate (18 : 1 : 1)	*n*-Decanol : glucose : catalyst (87.83 : 50 : 1)	120 °C 3 h	Glucose conversion rate: 79.8%	43
	EDTA : phosphoric acid (molar ratio 1 : 1)	C_{14-16} fatty alcohols : glucose : catalyst molar ratio 5 : 1 : 0.05	170 °C 2 h	C_{14-16} APGs yield: 99.5%	45
	Methanesulfonic acid : phosphinic acid solution (1 : 2)	C_{14-18} fatty alcohols : glucose : catalyst (300 : 50 : 0.5)	115 °C 5 h	C_{14-18} APGs yield: 30.4%	49
Transglycosidation	PTSA : citric acid (1.6 : 10)	Starch : butanol : dodecanol (1 : 2 : 5)	120 °C 4 h	Glycoside yield: 123.25%	50
	PTSA : phosphoric acid (4 : 1)	Ethylene glycol : octanol : starch : catalyst (69.65 : 24.35 : 30.35 : 1)	120 °C 4 h	Residual alcohol content: 0.66%	51

respectively. While increasing the mass fraction of PTSA within a certain range enhanced the reaction, further increases resulted in decreased yield. This decline was attributed to excessively rapid reaction kinetics under high catalyst loadings, which prevented timely removal of water. The resulting aqueous environment facilitated the formation of viscous polysaccharides and even carbonized blocks. Alongside research on conventional organic acids, investigations into other acidic catalysts have been pursued. For instance, Obi *et al.*[46] employed sulfamic acid as a catalyst, reacting 20 g of D-glucose with 157.38 mL of octanol in the presence of 2.22 g of catalyst at 80 °C for 5 hours, achieving a glycoside yield of 91.82%. Compared to commonly used *p*-toluenesulfonic acid and dodecylbenzenesulfonic acid, this organic acid effectively promoted glycosylation at a relatively low temperature. In another study, Singh *et al.*[47] used ethanol-pretreated and heated *Lippia alba* (a species in the genus *Aloysia*) as raw material, with *p*-cymene sulfonic acid (*p*-CSA) as the catalyst. After refluxing at 180 °C for 5 hours, ethyl glucoside was obtained with good selectivity (approximately 77%).

Currently, organic acids are widely employed as catalysts in the industrial synthesis of APGs due to their effective contact with reactants, which accelerates the reaction rate and reduces sugar self-polymerization and carbonization. However, to further enhance catalytic performance, researchers have begun to explore the combination of organic acids with other acids. This composite catalyst strategy leverages synergistic effects to improve overall efficiency and effectively address issues such as deep product coloration.

3.1.3 Employing composite acids as catalysts. To overcome the limitations of both inorganic and organic single-acid catalysts, there is a growing trend toward developing multicomponent composite acid systems for APGs synthesis. These composite catalytic systems, primarily binary or ternary combinations, often integrate organic and inorganic acids to leverage synergistic effects that mitigate the shortcomings of individual acids. For example, Xu *et al.*[48] prepared a composite catalyst with a mass ratio of *p*-toluenesulfonic acid : phosphoric acid : sulfamic acid = 1 : 0.12 : 0.04. Using glucose and decanol as raw materials, the reaction was conducted at 120 °C under vacuum for 2 hours. This process achieved a glycoside yield of 155.6%, with only 0.28% residual monosaccharide and minimal by-products such as polysaccharides. The resulting product was a colorless transparent liquid. Consequently, this composite

Table 6 Synthesis of APGs catalyzed by different solid acids (direct glycosidation)

Solid acids	Raw materials and ratios (mass ratio)	Temperature and time	Result	References
TPA-SBA-15	*n*-Butanol : glucose : catalyst (40.5 : 5 : 1)	117 °C 6 h	Glucose conversion rate: >99%	35
$SO_4^{2-}/La-TiO_2-SiO_2$	*n*-Butanol : glucose : catalyst (40.5 : 5 : 1)	117 °C 6 h	Glucose conversion rate: 74.4%	35
Supported mixed acid catalyst of *p*-toluenesulfonic acid and citric acid on alumina	Dodecanol–tetradecanol mixture (2 : 1) : starch : catalyst (55.17 : 11.03 : 1)	120 °C 2 h	Residual alcohol content: 0.31%	51
H_2SO_4/SiO_2	Propargyl alcohol : glucose : catalyst (58 : 36 : 1)	65 °C 2.5 h	Yield of propargyl glycoside: 75%	55
Sulfonated ion-exchange resin (Amberlyst-15)	Propargyl alcohol, mannose	80 °C 7 h	Mannose conversion rate: 90%	56
Sulfate-functionalized niobia-based material (NbOx-DS)	Ethanol : glucose : catalyst (11.362 : 1.125 : 1)	120 °C 2 h	Yield of ethyl glycoside: 60%	57

catalyst system has attracted significant research interest (Table 5).

Although composite acid catalysts offer benefits such as synergistic enhancement, reduced corrosiveness compared to strong acids, and prevention of glucose agglomeration during reactions, most systems still rely on combinations of homogeneous catalysts like inorganic and organic acids. These liquid acid catalysts often result in APGs products with high viscosity and pose significant challenges in separation from the reaction mixture. This issue complicates subsequent steps such as alcohol removal. The difficulty in efficiently separating liquid catalysts has accelerated the development of solid acid catalysts as a more sustainable alternative.

3.1.4 Employing solid acids as catalysts. Solid acid catalysts refer to systems where liquid acid catalysts are immobilized on insoluble supports, resulting in materials containing catalytically active acidic sites both internally and externally. This structure enables the solid acid to release protons for catalytic reactions while preventing the leaching of acidic centers from the support into the reaction system. This achieves effective separation from the product and reduces side reactions caused by localized high acid concentration. Additionally, solid acids offer advantages such as reusability and ease of regeneration, addressing issues inherent to liquid acid catalysts, including difficult product separation, severe equipment corrosion, and environmental pollution. Common methods for preparing solid acid catalysts include impregnation and sol–gel methods. Compared to impregnation, the sol–gel method can form more stable structures.[35] Sheng *et al.*[52] incorporated phosphotungstic acid into mesoporous silica. They prepared solid catalysts *via* sol–gel (direct synthesis) and impregnation methods, compared their performance in the alkylation of *o*-xylene with styrene, and concluded that the directly synthesized sample exhibited higher yield and better stability.

In summary, solid acid catalysts demonstrate promising potential in APGs synthesis, owing to their unique structural properties that combine high catalytic activity, facile product separation, and recyclability (Table 6). By modulating the type of support and the structure of the acidic active sites, various solid acid catalysts can be directionally designed and constructed, offering high design flexibility and broad potential for systematic investigation. Moreover, the raw materials required for synthesizing solid acid catalysts are generally low-cost and readily available: acidic sites can be introduced using common liquid acids such as sulfuric acid, phosphoric acid, or *p*-toluenesulfonic acid, while supports may include silica, alumina, zeolites, *etc.* The preparation procedures are straightforward and easy to execute, requiring no specialized or rare instrumentation. The materials involved are typically non-toxic or low in toxicity, resulting in minimal environmental impact. Therefore, research on solid acid catalysis holds significant value, and its application in the industrial-scale production of APGs also demonstrates considerable potential for scalability. However, the catalytic efficiency and long-term stability of such catalysts have not yet been fully validated. Limited by heterogeneous reaction mechanisms, the overall catalytic performance of solid catalysts generally remains lower than that of conventional liquid acid catalysts. Moreover, most solid acid catalysts exhibit limited reusability, typically around three cycles, indicating that their cyclic stability and regeneration capacity require further improvement. To advance green and sustainable development, future catalyst selection should emphasize not only the ability to efficiently synthesize glycosides but also environmental compatibility.[53,54]

3.1.5 Employing ionic liquids as catalysts. Ionic liquids (ILs), also known as room-temperature ionic liquids, room-temperature molten salts, or liquid organic salts, are substances consisting of relatively large, structurally asymmetric organic cations and relatively small inorganic anions that exist in a liquid state at or near room temperature (generally considered as ≤ 100 °C). Owing to their extremely low vapor pressure and high thermal stability, ILs can replace volatile organic or inorganic catalysts and enable more efficient reuse.[58,59] As a green catalytic system combining the high reactivity of liquid acids with the recyclability of solid acids, ILs demonstrate unique advantages in APGs synthesis. For instance, Zhou *et al.*[60] developed hydrophobic/acidic bifunctional ionic liquids (BFILs) for catalyzing cellulose conversion, achieving yields of 93.6% for methyl glycoside and 87.3% for hexyl glycoside, with easy recovery and reuse of the catalyst. Wu *et al.*[61] designed and synthesized [PSmim][HSO_4], an SO_3H-functionalized ionic liquid catalyst. Under conditions with a molar ratio of *n*-octanol to glucose of 3 : 1 and a temperature of 75 °C for 8 hours, the sugar conversion reached 87.5%, and the [PSmim][HSO_4] catalyst could be reused more than five times.

Ionic liquids (ILs) are widely regarded as potential "green" alternatives to organic solvents,[59,62] offering mild reaction conditions and the ability to suppress side reactions. For example, Jin *et al.*[30] employed an ionic liquid catalyst synthesized from 4-pyridinesulfonic acid and chloromethane. Under conditions with a molar ratio of *n*-octanol to glucose of 1 : 2, a temperature of 80 °C, and a pressure of 3 kPa for 3 hours, the reaction resulted in only 0.08% monosaccharides and 0.33% di- and polysaccharides, with a glucose conversion rate of 99.6%. Zhang *et al.*[63] used an *N*-(2-sulfoethyl) pyridinium dihydrogen phosphate ionic liquid, achieving an APG yield of 73.5% after 6 hours at 105 °C. The ionic environment effectively inhibited sugar caramelization. Bai *et al.*[64] prepared a 1-(butyl-4-sulfonyl)-3-butylimidazolium ionic liquid from 1,3-propanesultone, 1-butylimidazole, and sulfuric acid. Catalyzing the reaction between iso-octanol and glucose at 90 °C for 4 hours, they achieved a conversion rate of 99.5% and a by-product content of 0.64%. ILs combine the high reactivity of liquid acids with the recyclability of solid acids. They enable milder glycosidation reactions (typically below 100 °C), effectively preventing issues such as sugar caramelization that occur at high temperatures. Their green solvent properties align well with the sustainable development goals. However, ionic liquid catalysts suffer from the leaching of acidic sites and the loss of active species during recycling. Moreover, the synthesis of ionic liquids often involves anions such as bis(trifluoromethanesulfonyl)imide ($[NTf_2]^-$) and cations like imidazolium or pyrrolidinium, as well as chloride-containing species. These raw materials are not only costly but also pose significant environmental risks.

Table 7 Comparative analysis of various catalysts for glycosidation methods

Item	Inorganic acids	Organic acids	Composite acids	Solid acids	Ionic liquids
Representative catalysts and their characteristics	H_2SO_4	PTSA, DBSA	Combination of inorganic and organic acids	Acidic sites supported on insoluble matrices	Composed of organic cations and inorganic anions
Reaction conditions (temperature and time)	115–120 °C 3–6 h	110–120 °C 2–4 h	110–120 °C 2–5 h	110–120 °C 2–7 h	75–100 °C 3–8 h
Performance	Butyl glucoside yield: 99.8% (ref. 35)	Yield of glycoside: 99.6% (ref. 45) (employing PTSA as catalysts)	Glucose conversion rate: 79.8% (ref. 43)	Yield of propargyl glycoside: 75% (ref. 55) (employing H_2SO_4/SiO_2 as catalysts)	Yield of methyl glycoside: 93.6% (ref. 60) (employing BFILs as catalysts)
Advantages	Strong acidity, low cost, rapid reaction	Light-colored products, low corrosivity, suppresses sugar agglomeration	Synergistic enhancement, light-colored products, minimized side reactions	Easy separation, reusability, low corrosivity	Low-temperature reaction, recyclability, green solvent
Disadvantages	Corrosion of equipment; deep-colored products; neutralization treatment required, leading to generation of saline wastewater	The efficacy of the catalyst is closely related to its dosage; an insufficient amount results in poor catalytic performance, while an excessive amount can lead to sugar agglomeration and charring. Furthermore, the catalyst exhibits poor recyclability	The process involves the use of numerous types of liquid acids that are difficult to separate, thereby complicating downstream processing	Low catalytic efficiency and poor cycling stability	High cost, and the leaching of acidic sites and loss of active components often occur after cycling
Structure–property relationship	Strong acid protonation facilitates the reaction but readily induces sugar dehydration and self-polymerization	The organic sulfonic acid structure contributes moderated acidity, which suppresses side reactions between sugar rings; meanwhile, the long-chain alkyl group enhance its compatibility within the reaction system	The combination of multiple acids modulates the acidity strength and reaction pathway	Mesoporous support-loaded acid centers enhance stability and dispersion	The part of propanesulfonic acid combined with $[CH_3SO_3]^-$ endows the quality of a Brönsted acidic catalyst, while the other part combined with $[NTf_2]^-$ facilitates the separation of BFILs from water after the reaction by enhancing the hydrophobicity of BFILs
Sustainability evaluation	High corrosivity, significant pollution, poor recyclability	Improved product quality, but poor recyclability	Improved product quality, reduced waste acid, but remains homogeneous and difficult to recycle	Recyclable, low pollution, environmentally friendly	Reusable, low volatility, green solvent

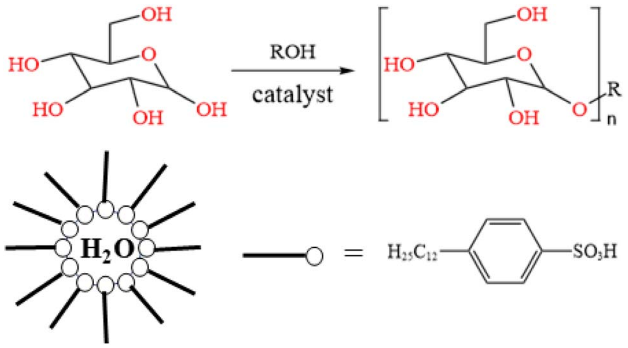

Fig. 9 Synthetic scheme for glycosides *via* phase-transfer catalysis.[65] This figure is reprinted from ref. 65 with agreement from Elsevier, copyright 2017.

Consequently, their scalability for large-scale industrial applications remains limited. Future research should prioritize the design of environmentally friendly, highly stable ionic liquids and the development of immobilization techniques to facilitate their industrial use in alkyl polyglycosides synthesis.

3.1.6 Comparative analysis of various catalysts. Through a systematic review and comparative analysis of the reaction conditions, structure–property relationships, and sustainability of different types of catalysts (Table 7), this review clearly reveals the evolutionary trajectory of catalysts for APGs synthesis: a shift from traditional highly corrosive and difficult-to-separate liquid acid catalysts toward efficient, green, and recyclable heterogeneous catalytic systems. The analysis demonstrates that solid acid and ionic liquid catalysts exhibit significant advantages in terms of sustainability due to their unique recyclability, reusability, and low environmental impact. Consequently, the construction of high-performance and reusable heterogeneous catalytic systems undoubtedly represents the core direction for overcoming current technical bottlenecks in APGs synthesis and achieving its green industrial upgrade.

3.2 Phase-transfer catalysis

In the synthesis of APGs, the immiscibility of glucose and fatty alcohols directly hinders the achievement of high yield and high product quality. Phase-transfer catalysis addresses this issue by facilitating the transfer of otherwise insoluble reactants into the desired phase.[62] For example, by utilizing the property that water can migrate into reverse micelles without the catalyst changing its position, the formed micelles significantly increase the interfacial area between the two immiscible phases. This greatly enhances the efficiency of reactions occurring at the interface, making it an effective strategy for the selective synthesis of various functional glucosides (Fig. 9).[65]

Nowicki *et al.*[65] employed a bifunctional catalyst (combining a surfactant and DBSA) within a micellar reaction system to investigate the feasibility of glycosidation between unprotected glucose and fatty alcohols. Compared to conventional glycosidation methods, micellar catalysis offers distinct advantages: even at relatively low temperatures, the reaction maintains high selectivity. For instance, at 60 °C, a glucose conversion rate of 96.1% was achieved, and the product was notably free of oligomers, indicating high purity. Furthermore, the process eliminates the need for energy-intensive water removal *via* distillation, thereby simplifying operation and reducing energy consumption. Additionally, Nowicki *et al.*[66] demonstrated that micellar catalysis significantly alters the selectivity of the Fischer glycosidation, yielding exclusively a mixture of α- and β-pyranosyl glucoside isomers without oligomeric byproducts. In a separate study, Wang *et al.*[67] used microcrystalline cellulose and C_8–C_{10} fatty alcohols ($C_8 : C_{10} = 52 : 48$) in a mass ratio of 1 : 7 as raw materials. A phase-transfer catalyst was prepared from deionized water, hydrous dodecatungstophosphoric acid, and dodecylbenzenesulfonic acid in a mass ratio of 9 : 0.6 : 0.3. The reaction conducted at 130 °C for 2.5 hours yielded 37.80 g of alkyl polyglycosides product. Tao *et al.*[68] investigated the synthesis of branched-chain alkyl polyglycosides using 2-butyl-1-octanol as the substrate in an acid/phase-transfer catalyst (PTC) system. Under optimized conditions, a conversion rate of 98.4% was achieved. The resulting APG functioned as a low-foaming surfactant, with a critical micelle concentration (CMC) of 5×10^{-4} mol L^{-1} and a surface tension of 25.87 mN m^{-1} for a 1% aqueous solution. However, the catalytic system of this method is relatively complex, often requiring bifunctional or composite catalysts. Their preparation, recovery, and reuse can be more challenging than those of a single-component catalyst. Furthermore, the micro-environment of the system profoundly influences the reaction outcome, necessitating intricate design and optimization, which complicates large-scale implementation.

3.3 Enzymatic catalysis

3.3.1 Types of enzymatic reactions for APGs synthesis. Conventional chemical synthesis of alkyl polyglycosides often requires harsh conditions, including strong acid catalysts, high temperature, and high pressure, leading to undesirable by-products such as polysaccharides and ethers. In contrast, enzymatic catalysis offers a green synthetic route utilizing glycosidases as biocatalysts under mild conditions. Compared to traditional methods, the most notable advantages of enzymatic synthesis include mild reaction conditions, high specificity, environmental friendliness, and low energy consumption. The core principle relies on the high specificity of enzymes to catalyze the formation of glycosidic bonds between

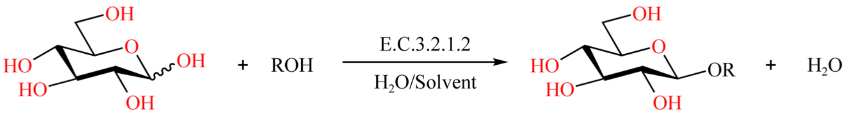

Fig. 10 Synthetic scheme for glycosides *via* reverse hydrolysis.[69] This figure is reprinted from ref. 69 with agreement from Elsevier, copyright 1992.

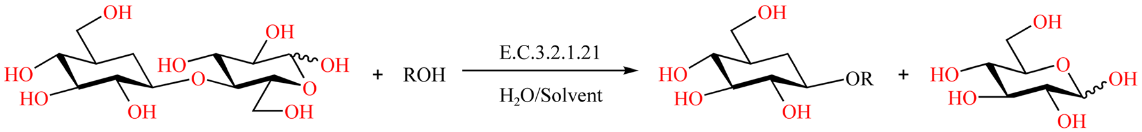

Fig. 11 Synthetic scheme for glycosides *via* transglycosylation.[69] This figure is reprinted from ref. 69 with agreement from Elsevier, copyright 1992.

glycosyl donors and fatty alcohol acceptors. This approach primarily depends on two reaction mechanisms: thermodynamics-controlled reverse hydrolysis and kinetics-driven transglycosylation, as illustrated in Fig. 10 and 11, respectively. The choice between these strategies depends on the nature of the glycosyl donor. In the former, APGs are synthesized from monosaccharides and alcohols by shifting the equilibrium toward synthesis through reduced water activity, achieved by adding cosolvents or increasing substrate concentration. The latter employs activated glycosyl donors to react with alcohols, forming new glycosidic bonds.[1,69,70] Common glycosidases used for APGs synthesis include β-glucosidase, β-galactosidase, α-glucosidase, and α-amylase. For instance, Kouptsova *et al.*[71] used β-galactosidase to catalyze the reaction between lactose and octanol, achieving 80% sugar conversion after 5 days at 60 °C to form β-D-galactoside. They also synthesized β-D-glucoside from glucose and octanol using β-glucosidase at room temperature, yielding 40% glycoside. Since environmental factors significantly affect enzyme activity, enhancing enzyme stability is a key research focus. Current strategies often employ immobilized enzymes or whole-cell systems to improve stability, reuse efficiency, and overall cost-effectiveness.[71]

3.3.2 Immobilized enzymes. Immobilized enzymes are defined as enzymes that are bound to solid supports *via* physical or chemical methods to perform catalytic reactions. This strategy enhances enzymatic stability, allows for recovery and reuse, reduces costs, facilitates the production of high-quality products, and improves economic efficiency. It is increasingly employed in glycosylation research. The primary methods for enzyme immobilization include cross-linking, encapsulation, and covalent binding (Table 8). Gargouri *et al.*[72] immobilized β-xylosidase and β-glucosidase by adsorption on ion-exchange resins (Duolite-A7 and Amberlite), diatomaceous earth (Celite), and ion-exchange chromatography media (DEAE-Sepharose), as well as by encapsulation in polyacrylamide gels or networks using glutaraldehyde. Glycosidation reactions were carried out with ethanol and sugars. The highest yields were observed when β-xylosidase was adsorbed on the anion-exchange resin Duolite-A7 and β-glucosidase was adsorbed on DEAE-Sepharose. Furthermore, the immobilization of β-glucosidase encapsulated in polyacrylamide gels increased the enzyme's half-life by 63–130%. Although the catalytic activity of immobilized enzymes may not necessarily exceed that of free enzymes, their principal value lies in enhancing enzyme utilization efficiency.

3.3.3 Whole-cell enzyme catalysis. Whole-cell biocatalysis involves the direct use of genetically engineered intact cells as catalysts, eliminating the need for enzyme purification. This approach allows enzymes to remain protected within their natural cellular environment, resulting in enhanced stability and reduced costs.[73] Jayakody *et al.*[74] employed a genetically modified strain of *Saccharomyces cerevisiae* (EJ2) expressing intracellular β-glucosidase and a heterologous cellodextrin transporter to directly convert cellulose into ethyl-β-D-glucoside at 30 °C. The EJ2 strain produced 0.06 g of ethyl-β-D-glucoside per gram of cellulose. Siziya *et al.*[75] employed a recombinant *Corynebacterium glutamicum* strain expressing amylosucrase to synthesize luteolin glycosides at room temperature. The results demonstrated that whole cells (WCs) of *C. glutamicum* exhibited efficient biocatalytic performance for glycoside derivatives, achieving a maximum conversion rate of 99% after 15 hours of reaction.

In summary, enzymatic catalysis represents a highly promising approach for APGs synthesis due to its mild and environmentally friendly characteristics. However, its slow reaction kinetics, high enzyme costs, and current technological immaturity hinder its competitiveness with economically viable chemical methods in large-scale industrial production. Future breakthroughs will depend on the discovery or engineering of enzymes with higher activity and stability, coupled with

Table 8 Comparison of different enzyme immobilization methods[1]

Method	Advantages	Disadvantages
Cross-linking method	High enzymatic activity and excellent stability	Low immobilization strength, cumbersome and time-consuming operation, high preparation cost
Encapsulation method	The operation is simple, and the tertiary structure of the encapsulated enzyme remains well-preserved	Weak immobilization strength, diffusion challenges of substrates and products, limited mass transfer
Covalent binding	Firm binding and high reaction efficiency	Enzyme leaching may lead to irreversible deactivation, cumbersome operational procedures

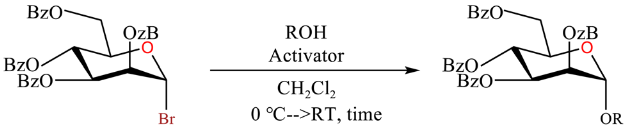

Fig. 12 Synthetic scheme for glycosides *via* the Koenigs–Knorr method.[79] This figure is reprinted from ref. 79 with agreement from John Wiley and Sons, copyright 2018.

continued optimization of immobilization and whole-cell biocatalytic processes to reduce costs.

3.4 Other methods

In addition to glycosidation, phase-transfer catalysis, and enzymatic catalysis, alternative methods such as the Koenigs–Knorr method, trichloroacetimidate method, and Ferrier rearrangement are also employed for glycoside synthesis. These approaches typically rely on the use of activated glycosyl donors to facilitate glycosylation reactions. It is noteworthy that these methods are primarily employed for the synthesis of glycosides with complex structures. Most carbohydrates found in nature exhibit structural complexity, primarily arising from monosaccharides interconnected *via* glycosidic bonds or linked to other types of aglycones. Known glycosidic bonds include *O*-, *S*-, *N*-, and *C*-glycosidic types.[76]

3.4.1 Koenigs–Knorr method. The Koenigs–Knorr method, initially developed in 1901 and also known as the "protective group approach",[77] is a classical glycoside synthesis strategy. In its conventional form, glycosyl bromides (or chlorides) are employed as glycosyl donors and coupled with glycosyl acceptors (ROH) in the presence of silver oxide (or carbonate salts) to form glycosidic bonds.[78,79] This method applies to the preparation of both aryl and alkyl glycosides and has been widely used for synthesizing glycosides bearing complex groups linked to the anomeric carbon, particularly in the context of oligosaccharides.[80] The reaction pathway is illustrated in Fig. 12.

This method offers excellent selectivity, mild reaction conditions, and high product purity. However, the process is complex: the Koenigs–Knorr reaction requires excess heavy metal salts (typically expensive silver or mercury salts) to activate glycosyl bromides for glycosylation. This results in high costs, severe environmental unfriendliness, and significant health hazards. Consequently, it is only suitable for laboratory-scale synthesis and has not been adopted industrially.[81,82] This article summarizes studies on glycoside synthesis using the Koenigs–Knorr method in Table 9.

3.4.2 Trichloroacetimidate method. The trichloroacetimidate method employs trichloroacetimidate (TCA) as a glycosyl donor in glycosylation reactions. The glycosyl donor typically acts as an electrophile, while the acceptor serves as a nucleophile. Glycosyl trichloroacetimidates (Schmidt donors) are among the most widely used glycosyl donors in the total synthesis of glycosides due to their high reactivity. These reactions predominantly involve Brønsted or Lewis acids, such as metal triflates, $AuCl_3$, $HClO_4$, carboxylic acids, and phosphoric acid. TCA glycosyl donors can be synthesized *via* base-catalyzed reaction of appropriate hemiacetals with trichloroacetonitrile. Strong bases (*e.g.*, NaH) favor the formation of α-TCA donors, whereas weaker bases (*e.g.*, K_2CO_3) predominantly yield β-anomers,[81,88] allowing selective control over glycoside synthesis (Fig. 13). This method operates under mild conditions and exhibits broad applicability, overcoming limitations such as the instability of halogenated sugars, difficult reaction control, and the use of toxic heavy metal catalysts in the Koenigs–Knorr method. However, most Lewis acids used in this process are moisture-sensitive and require low temperatures, which restricts their practical utility. Notably, some of the most complex glycosides, particularly *O*-glycosides, have been synthesized using glycosyl trichloroacetimidates. For example, Hitchcock *et al.*[89] achieved coupling between a glycosyl trichloroacetimidate and an enediyne under silver trifluoromethanesulfonate (AgOTf) catalysis during the total synthesis of calicheamicin γ_1^{I}, obtaining the desired β-glycoside in 34% yield. Li *et al.*[90] performed glycosylation using a 2-glycosyl trichloroacetimidate donor with 1,2-*cis*-diol and 1,3-diol acceptors under platinum chloride catalysis at −78 °C, successfully obtaining the target β-configured product.

3.4.3 Ferrier rearrangement. In the presence of a nucleophile and Lewis or Brønsted acid, allylic rearrangement occurs at the C_1 position. This method is commonly referred to as the Ferrier reaction in various glycosylation processes.[91,92] Wieczorek and Thiem[91] conducted glycosylation of 3,4,6-tri-*O*-acetyl-D-glucal with various unsaturated alcohols (allyl alcohol, 1-pentenol, and farnesol) under boron trifluoride catalysis in dichloromethane, yielding the corresponding glycoside derivatives (ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-

Table 9 Synthesis of glycosides *via* the Koenigs–Knorr method[a]

Types of catalysis	Element	Catalyst	Solid-to-liquid ratio	Temperature and time	Glycoside yield (%)	References
Metal catalysis	Indium (In)	InI_3	5 : 6	25 °C, 2 h	98	83
		$In(NTf)_3$	5 : 6	25 °C, 4 h	96	84
	Fe	$FeCl_3$	—	16 h	95	85
Non-metal catalysis	Urea	Macrocyclic dithiourea derivatives	—	40 °C, 48 h	87	86
	Non-volatile solvents	Supercritical carbon dioxide	1 : 4	60 °C, 14 h	>98	87

[a] "—" indicates that no data are available.

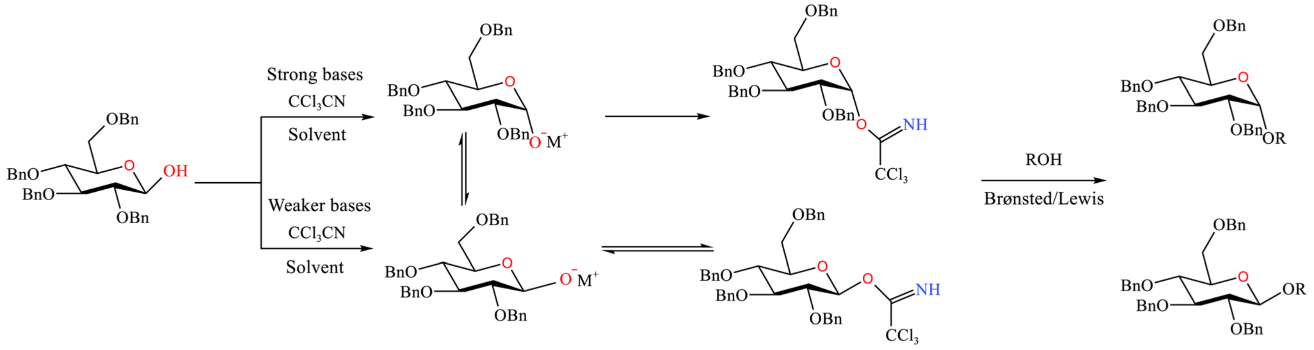

Fig. 13 Synthetic scheme for glycosides *via* the trichloroacetimidate method.[88]

enopyranosides) at yields of 91%, 89%, and 47%, respectively. The reaction process is illustrated in Fig. 14. Although this method achieves high product yields, the Ferrier reaction-based APGs synthesis involves relatively complex procedures and requires expensive catalysts, resulting in high costs that hinder its suitability for industrial production.

3.5 Comparison of synthetic methods and advances in emerging technologies

3.5.1 Comparison of various synthetic methods. Based on a systematic review of various synthetic routes for alkyl polyglucosides (APGs), this review provides a mechanistic analysis of each approach: the glycosylation method relies on the direct nucleophilic attack of an alcohol on protonated glucose under acid catalysis. While the direct method offers a concise pathway, it is constrained by the high temperatures required to overcome the low reactivity of long-chain alcohols. In contrast, the transglycosylation approach introduces short-chain alcohols as mediators to form short-chain glycoside intermediates, which lowers the reaction energy barrier but complicates subsequent alcohol separation due to the additional steps. Phase-transfer catalysis enhances the contact efficiency of heterogeneous reactants by constructing micellar/microemulsion interfaces, where the aqueous phase is confined within reverse micelles, facilitating the reaction under mild conditions. However, the challenges in recovering the composite catalyst system and the complexity of microenvironment control limit its scalability. Enzymatic catalysis utilizes the high specificity of glycosidases to form glycosidic bonds *via* reverse hydrolysis or transglycosylation mechanisms, offering excellent stereoselectivity and environmental compatibility, yet it is hindered by high enzyme costs, slow reaction rates, and immature process technology. The Koenigs–Knorr method employs glycosyl halides as donors to facilitate glycosidic bond formation with acceptors under metal salt catalysis. Glycosyl halides exhibit enhanced stability, ease of handling, and high stereoselectivity, offering attractive atom economy in glycosylation reactions. This approach enables streamlined purification, improved yields, and suitability for complex glycoside synthesis. However, the initial step necessitates the reaction of saccharides with halogenating agents. This reliance on toxic heavy metal catalysts and halogenating reagents poses significant challenges to both environmental compatibility and operational safety. Similarly, the trichloroacetimidate method involves the base-catalyzed formation of trichloroacetimidate donors from sugars and trichloroacetonitrile, followed by Lewis acid-promoted reaction with alcohols, allowing stereocontrol but suffering from tedious donor preparation, high reagent toxicity, and harsh reaction conditions. The Ferrier reaction, based on an allylic rearrangement mechanism, directly forms glycosides at the C1 position under acid catalysis. Its stepwise yet concerted pathway of rearrangement and nucleophilic attack avoids high-energy carbocation intermediates, providing strong driving force for the reaction, though it is hampered by high catalyst costs and limited applicability due to the formation of unsaturated glycosides. Furthermore, this review comprehensively compares the process conditions, environmental sustainability, and scalability of these methods (Table 10), aiming to offer systematic insights for the optimization and selection of APGs synthesis routes.

In summary, the direct glycosylation method remains the mainstream technology with the most significant industrial advantages, demonstrating outstanding performance in technical reliability, economic viability, and large-scale production capacity. Although other synthetic methods show potential in specific scenarios or certain performance metrics, they have not yet achieved the same level of industrial applicability. However, the aforementioned charts still lack a systematic analysis of the selectivity and yield of synthetic products across different methods. The systematic evaluation of product selectivity and overall yield represents an essential aspect of ongoing research. Existing literature predominantly focuses on the formation of

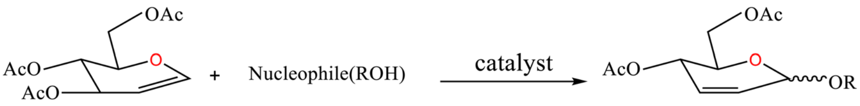

Fig. 14 Synthetic scheme for glycosides *via* the Ferrier rearrangement.

Table 10 Comparative analysis of synthetic routes for alkyl polyglycosides

Item	Glycosidation	Phase-transfer catalysis	Enzymatic catalysis	Koenigs–Knorr method	Trichloroacetimidate method	Ferrier rearrangement
Temperature (°C)	100–120	60–100	25–60	25–60	<−50	−10–40
Catalyst	Brønsted acids, lewis acids, solid acids, and ionic liquids	Phase-transfer catalyst	Enzyme preparations, immobilized enzymes, whole-cell biocatalysts	Heavy metal salts	Lewis acids	Brønsted acids, lewis acids
Solvent	Fatty alcohols	Aqueous solution	Fatty alcohols	Halides	CCl_3CN	Unsaturated alcohols
Performance	Yield of C_{12-14} APGs: 99.6% (ref. 45)	Glucose conversion rate: 98.4% (ref. 68)	Yield of β-D-galactoside: 80% (ref. 71)	Yield of glycoside: 98% (ref. 83)	Yield of β-glycoside: 34% (ref. 89)	Yield of ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosides: 91% (ref. 91)
Green metrics (atom economy, recyclability)	The process exhibits high atom economy, with water as the primary by-product; both solid acids and ionic liquid catalysts are conducive to reuse	The catalyst exhibits low recoverability and reusability	The system offers excellent recyclability and generates negligible by-products, leveraging the advantages of both immobilized enzymes and whole-cell biocatalysts	The reaction involves halogen atoms, which leads to the formation of by-products such as hydrogen halides and chloroform. Furthermore, the catalyst itself suffers from deactivation, making its recovery and reuse impractical	The process suffers from the presence of trichloroacetonitrile residues, which generate chlorine-containing waste. Furthermore, the catalyst itself is not amenable to recovery and reuse	The catalyst exhibits poor recoverability and reusability
Environmental impact	Certain acidic catalysts are corrosive; moreover, strong acids require neutralization treatment, which tends to generate salt-containing wastewater	The use of multicomponent catalytic systems often presents relatively challenging recovery and limited biodegradability compared to their single-component counterparts	Enzymes are naturally occurring, biodegradable proteins. They operate under mild reaction conditions, are virtually waste-free, and are environmentally benign	Heavy metal catalysts such as mercury and silver salts are toxic and moreover pose a potential hazard to the environment	The employment of highly toxic trichloroacetonitrile presents a major environmental and safety drawback, motivating the search for greener alternatives	Catalysts such as BF_3–Et_2O exhibit both corrosiveness and toxicity
Advantages	The well-established process enables efficient synthesis of APGs *via* direct reaction and exhibits low by-product formation	The reaction can be conducted at relatively low temperatures, while also promoting the dissolution of sugar alcohols	The reaction proceeds under mild conditions at ambient temperature and exhibits excellent reaction selectivity	The reaction proceeds under mild conditions and exhibits high stereospecificity toward APGs formation	The stereochemical outcome of glycoside formation can be regulated by employing different bases to control the reactivity of the glycosyl donor	The reaction accommodates a broad range of Lewis acids, resulting in high product yields

Table 10 (*Contd.*)

Item	Glycosidation	Phase-transfer catalysis	Enzymatic catalysis	Koenigs–Knorr method	Trichloroacetimidate method	Ferrier rearrangement
Disadvantages	Some of the acidic catalysts employed exhibit a corrosive nature; the process requires stringent pressure control to suppress side reactions, and is also prone to undesirable darkening of the product	The use of multiple catalysts poses challenges for their recovery, can compromise product quality, and complicates the subsequent purification steps	The reaction pathway requires long durations, and moreover, the cost of enzyme preparations is relatively high; genetically modified enzymes exhibit superior catalytic efficiency	The use of heavy metal catalysts presents challenges including high cost, toxicity, and environmental pollution	The Lewis acid catalysts employed are highly sensitive to moisture; consequently, the reaction must be carried out at low temperatures	The process involves a complex route and high catalyst costs, resulting in compromised economic viability
Scalability	The process achieves high atom economy; moreover, it accommodates a broad range of highly recyclable catalysts, making it suitable for large-scale industrial production	The scale-up of microemulsion/micellar systems presents more formidable challenges in reactor design, heat and mass transfer, and process control compared to conventional homogeneous reactions, thus limiting their industrial applicability	The process exhibits high product selectivity and proceeds under mild and environmentally benign conditions. However, the high preparation cost coupled with the technical immaturity of the catalyst currently prevents its large-scale implementation	The method generates significant by-products and exhibits low atom economy; furthermore, heavy metal salts such as mercury and silver pose substantial toxicity, presenting unacceptable safety and environmental risks at industrial scale. Consequently, the process lacks industrial scalability	The synthesis starting from glycosyl donors involves a complex procedure; furthermore, the catalysts employed are temperature-sensitive, necessitating stringent reaction conditions; and the solvents used are toxic and environmentally detrimental. These factors collectively render the method unsuitable for large-scale industrial production	The catalyst is expensive; moreover, the process primarily targets the synthesis of unsaturated alkyl glycosides, thereby exhibiting limited applicability and low scalability for industrial production

alkyl monoglycosides while largely overlooking the quantitative analysis of by-products such as alkyl polyglycosides, making it difficult to compare the selectivity of various methods. Furthermore, since synthetic yield is profoundly influenced by multiple variables including raw materials, catalysts, and reaction conditions and due to the absence of uniform evaluation criteria within the field yield data from different studies cannot be directly compared, preventing definitive conclusions. Clarifying these two core indicators is crucial for deeply understanding the reaction mechanisms and enabling targeted optimization of the synthesis process. Therefore, establishing a standardized analytical method for APGs yield is a key driver for the advancement of alkyl polyglycosides synthesis.

3.5.2 Advances in emerging technologies. To address challenges in APGs synthesis such as poor mutual solubility of raw materials and sugar self-polymerization induced by excessive temperatures, research frontiers have shifted from conventional process parameter optimization to process intensification technologies utilizing novel reactors and external field assistance. These approaches actively create advantageous reaction environments, providing new perspectives for APG synthesis optimization. For instance, Mi *et al.*[93] employed microwave-assisted transglycosylation of wheat bran with butanol as the transglycosyl agent to synthesize butyl glycosides of glucose, xylose, and arabinose. Using H_2SO_4 as catalyst at 90 °C for 3 h, the reaction achieved a combined biosurfactant yield of 29%. Under identical conditions, microwave heating increased yield by 53% and reduced reaction time by 72% compared to conventional heating. Life cycle assessment and techno-economic analysis demonstrated that microwave heating reduced energy consumption by 42%, CO_2 emissions by 56%, with corresponding reductions in equipment, operational, and production costs of 44%, 35%, and 30%. Microwave irradiation represents an efficient heating technology for biomass depolymerization and conversion, offering advantages in reaction yield and efficiency particularly at relatively lower temperatures. This enhancement arises from microwave energy directly interacting with polar groups on sugar molecules, activating hydrogen bonds within carbohydrate polymers and improving energy efficiency during carbohydrate hydrolysis. Zeng *et al.*[94] utilized *n*-decanol and glucose as raw materials with a composite catalyst (molar ratio of DBSA acid–phosphoric acid–sulfuric acid = 1 : 0.3 : 0.3) in an impinging stream-rotating packed bed (IS-RPB). The high-speed rotation of the packed bed effectively simulated supergravity conditions, enabling APG synthesis *via* direct glycosylation at 100 °C with an alcohol-to-sugar molar ratio of 3 : 1 and supergravity factor of 130.67. This approach significantly increased the contact area between glucose and fatty alcohol, enhanced interphase mass transfer rate, intensified micromixing, accelerated reaction kinetics, and suppressed glucose self-polymerization. The novel method achieved over 70% glucose conversion within 30 minutes, reduced the *n*-decanol-to-glucose molar ratio to 2 : 1, and maintained reactivity below 90 °C. When water vapor generated during the reaction (which promotes glucose self-polymerization) was removed by gas stripping, glucose conversion exceeded 90%. High-gravity technology leverages unique flow behaviors of multiphase systems under high-gravity conditions to enhance relative velocity and interfacial contact between phases, thereby promoting effective mass/heat transfer and chemical reactions. This technology demonstrates broad applicability and offers advantages over conventional equipment including compact size, reduced energy consumption, operational safety, and strong environmental adaptability.

The advancement of synthetic methodologies for glycopolymers offers considerable insight. Carbohydrate-functionalized synthetic polymers can feature a central sugar unit or incorporate sugar moieties within the polymer side chains or backbone. In the preparation of glycopolymeric materials, modern polymerization techniques enable precise control over molecular weight, molecular weight distribution, chemical reactivity, and polymer architecture. The primary synthetic strategies include the polymerization of glycomonomers and the chemical modification of preformed polymers using sugar-based reagents. Polymerization of glycomonomers involves copolymerizing sugar-containing monomers with other monomers, while the modification of preformed polymers with carbohydrate reagents facilitates the production of glycopolymers with identical macromolecular backbones by conjugating diverse sugar units to a predefined polymeric scaffold. From the perspective of polymer materials science, the key challenge lies in developing straightforward and practicable synthetic routes to introduce the essential sugar motifs required for molecular recognition.[95] These sophisticated polymerization methods provide novel perspectives for the controlled synthesis of APGs structures. By enabling precise molecular design and customization of APGs, they allow for the efficient development of high-performance target products, thereby advancing APGs synthesis from conventional processes toward molecular-level precision engineering.

4 Recent advances in applications of alkyl polyglycosides

As a class of green and highly efficient non-ionic surfactants, alkyl polyglycosides exhibit numerous advantages, including excellent compatibility, strong biodegradability, high detergency, rich and stable foam, mildness to skin, non-toxicity, tolerance to acids and alkalis, and low environmental impact. They can function as emulsifiers, thickeners, dispersants, wetting agents, and foaming agents. Consequently, APGs are widely used in various fields such as cosmetics, detergents, petroleum extraction, pharmaceuticals, and pesticides (Fig. 15).[5,6,96]

4.1 Application in cosmetics

APGs possess a molecular structure that combines the hydrophilicity of natural sugar moieties with the hydrophobicity of alkyl chains, endowing them with remarkable surface activity and interfacial properties. This makes them particularly suitable for high-end cleansing and skincare formulations. Owing to their superior performance, APGs demonstrate broad application prospects in cosmetics and cleaning products (Table 11).

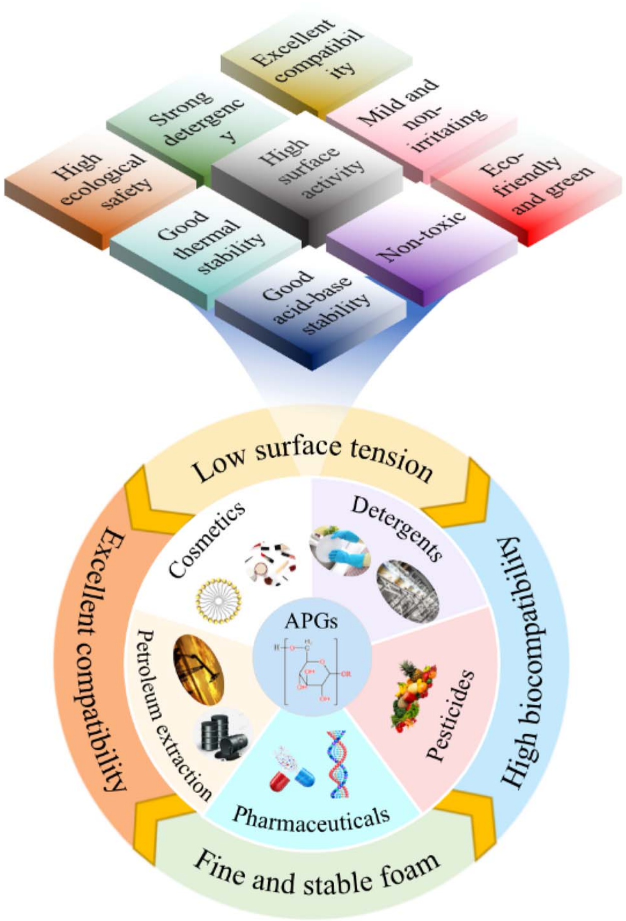

Fig. 15 Performance and applications of APGs.

As a class of mild surfactants, APGs are well-suited for cosmetic formulations. When used in such products, they exhibit reduced penetration into the epidermis and dermis, thereby lowering the overall potential for skin irritation.[15] Additionally, APGs offer good compatibility, emulsifying capacity, and functions such as moisturizing, softening, and conditioning. Compared with conventional cosmetic formulations, those incorporating APGs exhibit enhanced biodegradability, aligning with the trend toward environmental sustainability in the cosmetics industry. APGs can serve as key surfactant components in creams, gels, microemulsions, and other products.[97,98]

4.2 Application in detergents

APGs exhibit low surface tension, excellent foaming properties, good compatibility, low irritancy, and high biodegradability, making them suitable for designing highly efficient and environmentally friendly detergents.[97,98] In household cleaning formulations, APG-based products effectively remove soil and grease with strong degreasing capacity while remaining mild on the skin. When used as the main component in laundry detergents, APGs provide anti-shrinkage, softening, and antistatic properties, and maintain performance in hard water conditions. Their ready biodegradability prevents surfactant accumulation in the environment. As a result, APGs have been widely adopted as key active ingredients in dishwashing liquids, laundry detergents, and metal cleaning agents (Table 12).

4.3 Application in petroleum extraction

Surfactants can enhance oil fluidity and modify the wettability of rock formations. The process of injecting surfactant-containing fluids into reservoirs, commonly employed to boost production in mature oil fields, is known as enhanced oil recovery (EOR).[105] EOR refers to technologies used in the oil and gas industry to maximize extraction of residual oil after primary and secondary recovery methods have been applied. The ultimate recovery rate of crude oil rarely exceeds 50% of the original oil in place. However, following primary and secondary recovery processes, over two-thirds of the original crude often remains trapped in rock pores due to factors such as high viscosity, reduced mobility, and oil retention in porous media. Injecting surfactants capable of reducing the interfacial tension between oil and rock surfaces into reservoirs facilitates improved oil recovery and offers significant economic benefits.[106] APGs significantly reduce solution surface tension and exhibit excellent emulsification capacity and biodegradability. They can effectively enhance oil recovery while minimizing environmental impact, demonstrating broad application prospects in petroleum extraction. Furthermore, APGs display interfacial/phase behavior that is largely independent of temperature and salinity. Their incorporation into drilling fluids can extend the operational temperature range, positioning them as potential EOR agents (Table 13).

4.4 Application in pharmaceuticals

In the pharmaceutical field, alkyl polyglucosides (APGs) are widely used in drug loading and delivery systems due to their excellent compatibility, wetting capacity, emulsifying ability, skin mildness, non-toxicity, and strong biodegradability. As functional excipients or carrier materials, APGs demonstrate unique advantages: their mild properties, excellent biocompatibility, and structural tunability contribute to enhanced drug stability and delivery efficiency. These surfactants can form micelles, liposomes, or nanoparticles as drug carrier systems, serving to solubilize poorly soluble drugs, promote drug penetration across biological barriers, and improve stability and targeting accuracy during delivery, thereby enabling efficient drug utilization (Table 14).

4.5 Application in pesticides

In the field of agrochemicals, APGs also play a significant role as key adjuvants in pesticide formulations such as emulsions and nanoemulsions due to their excellent emulsifying and wetting properties. Nanoemulsion systems constructed with APGs can significantly enhance the penetration, solubility, and physicochemical stability of pesticides, modulate their release kinetics, and effectively prevent premature degradation of active ingredients, thereby improving overall pesticide efficacy. Moreover, the outstanding wetting capability of APGs ensures effective spreading and adhesion of pesticide solutions on target surfaces, further guaranteeing efficient pesticide utilization (Table 14).

Table 11 Applications of APGs in cosmetics and cleaning products

Formulations and product categories	Type and dosage of APG	Product performance	References
Microemulsion	9% $C_{8/10}$ APGs	APGs exhibit a low critical micelle concentration, enabling reduced surface tension and facilitating the formation of nanoscale microemulsion droplets. This enhances product stability with low sensitivity to storage temperature variations	3
Liquid soap	C_{10-16} APGs	The combination of APGs and an anionic surfactant formed a gel network, imparting higher viscosity, greater stability, and a balanced pH to the formulation, leading to low skin irritation	97
Sunscreen microcapsules	5% APG	Acting as a co-emulsifier, it synergistically emulsifies and solubilizes lignin, significantly reducing the capsule size to approximately 100 nm. This process ensures product stability, prevents leakage during storage, and achieves a shelf life of over one year	99
O/W cream	5% C_{16} APG	It can form lamellar liquid crystal emulsions, which exhibit superior physical stability, rheological properties, and skin feel compared to classical emulsions	100
Shampoo	8.8% C_{10} APG	It exhibits excellent foaming and wetting capacities, demonstrates low cytotoxicity toward human keratinocytes and retinal cell lines (compared to SLES), and is highly efficient and mild	101

Table 12 Applications of APGs in detergents

Product	Type and dosage of APG	Product performance	References
Foaming detergent	1% APG	It exhibits excellent foaming properties and anti-residue characteristics, with strong cleaning efficiency on surfaces including stainless steel and glass	5
Fabric detergent	C_{10} APG	APG reduce surface tension, enhance textile wetting, remove and separate stains from fibers, and form micelles to solubilize insoluble substances. When synergistically blended with other surfactants, they further enhance solubilization efficacy. The color difference between the cleaned sample and the unstained reference was only 3.81, accompanied by a significant reduction in iron content, demonstrating high efficiency in removing iron oxide compounds	102
Fabric detergent	APG	Graft copolymerization was performed on polyester macromolecules to enhance the moisture absorption and detergency of the polyester fibers. The improvement was evidenced by a detergency index of 63.66% against carbon black oil	103
Cleaning agent	8% C_{12} APG	It reduces aquatic toxicity pollution by more than 60% while maintaining sufficient cleaning performance	104

Table 13 Applications of APGs in petroleum extraction

Types of APG	Product performance	References
C_{12} APG	The hydrogen bonding, van der Waals forces, and micellization facilitated by APG enhance their adsorption onto sandstone surfaces. Furthermore, APG can reduce interfacial tension and alter wettability even at very low concentrations (0.01%), contributing to enhanced oil recovery. Demonstrating temperature and salt tolerance, APG adsorption on solid surfaces remains relatively stable across a broad temperature range (20–115 °C)	105
C_{12} APG	APG significantly reduce solution surface tension, improve oil fluidity, and alter rock formation wettability. A 2% C_{12} APG-supplemented brine solution achieved an oil recovery rate of 52.1%. Additionally, APG inhibit the activity of sulfate-reducing bacteria (SRB), thereby mitigating acidification	107
C_{10} APG	When formulated with hydrophobically associating water-soluble polymer (HAWP), the foam stability of APG is strengthened through hydrogen bonding and hydrophobic interactions. This polymer-enhanced foam successfully alters the oil–water interface and significantly improves oil displacement efficiency in porous media	108

4.6 Summary

In summary, alkyl polyglucosides (APGs), as green and efficient nonionic surfactants, have demonstrated significant value across diverse fields such as cosmetics, detergents, petroleum extraction, pharmaceuticals, and pesticides, owing to their excellent mildness, ecological compatibility, and outstanding interfacial properties. In the personal care and household industry, APGs are widely used in various skincare cosmetics and daily cleaning products, not only improving formulation stability and efficacy but also significantly reducing skin irritation and environmental impact. In petroleum extraction, APGs effectively reduce oil–water interfacial tension under extreme temperature and salinity conditions, enhance crude oil recovery, and exhibit both antibacterial and eco-friendly characteristics. In pharmaceuticals and pesticides, serving as drug carriers, APGs significantly improve the stability, permeability, and targeting performance of active ingredients by constructing delivery systems such as micelles, liposomes, and nanoemulsions, thereby enhancing the efficacy of corresponding drugs. Consequently, APGs hold broad development potential in high-performance functional cosmetics, high-efficiency cleaning agents, green oil and gas extraction technologies, and drug loading and delivery systems, particularly in premium, child-friendly, and environmentally sustainable product lines, offering important directions for innovative formulation design in related industries.

5 Industrial scale-up challenges

In industrial practice, the synthesis of alkyl polyglycosides primarily employs the glycosidation method. The production process is mainly divided into three stages: synthesis, dealcoholization, and decoloration,[73] with the process flow illustrated in Fig. 16. The glycosidation reaction must be carried out in an excess of fatty alcohol to ensure complete conversion of sugar, resulting in crude APGs products containing significant amounts of unreacted alcohol. Simultaneously, heat-sensitive substances such as glucose are prone to caramelization during the reaction and subsequent treatments. Moreover, under alkaline conditions, by-products can easily cause APGs to develop color, necessitating decoloration treatment to meet product appearance and performance requirements.[40,114] Therefore, the industrial scale-up of APGs production faces core challenges such as low reaction efficiency, high by-product formation, and high energy consumption during purification. Addressing these issues requires integrated solutions to key problems including mass transfer, catalysis, and separation. Dealcoholization and decoloration are critical refining steps to ensure product purity and appearance, ultimately enabling efficient, low-cost, and high-quality production.

The dealcoholization process aims to remove excess fatty alcohols, with its challenges originating directly from the reaction stage. The low solubility of glucose in higher alcohols leads to limited initial conversion and high unreacted alcohol content. Meanwhile, temperature and equipment during purification require precise control to prevent thermal degradation of APGs, thereby increasing process complexity. Current dealcoholization techniques include distillation, adsorption, extraction, and supercritical fluid extraction. Among these, adsorption offers high purity but poor continuity; liquid–liquid extraction introduces issues such as solvent removal and secondary pollution, along with complex procedures that raise production costs; while supercritical fluid extraction requires high-pressure equipment, increasing both capital and operating expenses. Therefore, distillation remains the predominant method, including conventional distillation, vacuum distillation, falling film evaporation, and thin-film evaporation. Vacuum distillation is widely used in laboratory-scale APGs purification due to its operational simplicity and low cost. In industrial practice, combined separation methods are commonly adopted, such as falling film evaporators coupled with short-path evaporators or wiped film evaporators. These systems utilize high vacuum to lower boiling points and mitigate thermal damage. For example, Zhai *et al.*[114] employed a two-stage series connection evaporation unit, where a falling

Table 14 Applications of APGs in pharmaceuticals and pesticides

Field	Product	Types of APG	Product performance	References
Pharmaceuticals	Micellar hydrogel	C_{10} APG	The hydrophobic drug indomethacin (IND) is solubilized in APG micelles, maintaining drug stability and enabling delivery; the hydrogel exhibits good compressive properties and shape recovery performance, as well as pH and temperature sensitivity, providing effective drug release	109
	Novel dihydroartemisinin liposome	C_8 APG	Glycosides containing glucose moieties exhibit high affinity for the unidirectional transporter (GLUT1) and possess favorable lipophilicity, enabling integration into the lipid bilayer of liposomes. Liposomes modified with APG-based glucose fragments demonstrate significantly enhanced targeting specificity toward human hepatocellular carcinoma cells (HepG2)	110
	Nanoemulsion	C_{12} APG	As a cosurfactant, APG acts synergistically with the primary surfactant to reduce the system's hydrophilicity and enhance its lipophilicity, enabling effective loading of ibuprofen. The resulting particles, with sizes ranging from 20 to 200 nm, maintain the stability of the incorporated ibuprofen	111
Pesticides	Nanoemulsion	$C_{12/14}$ APGs	When formulated with polyoxyethylene lauryl ether, the system exhibits the smallest droplet size (113.5 nm), thereby enhancing product stability. The low critical micelle concentration cmc and γ_{CMC} values indicate favorable micelle formation in water, which improves the solubilization of β-cypermethrin and facilitates pesticide loading. Additionally, the superior wetting ability of APG enhances the wetting and spreading of the pesticide solution on leaf surfaces	112
	O/W emulsion	APG	When formulated with an amphiphilic sodium alginate derivative, the system effectively increases the interfacial layer thickness of emulsion droplets formed through hydrophobic interactions, thereby significantly enhancing the stability of the O/W emulsion. Additionally, it greatly improves the wetting behavior and adhesion of the pesticide solution on banana leaf surfaces	113

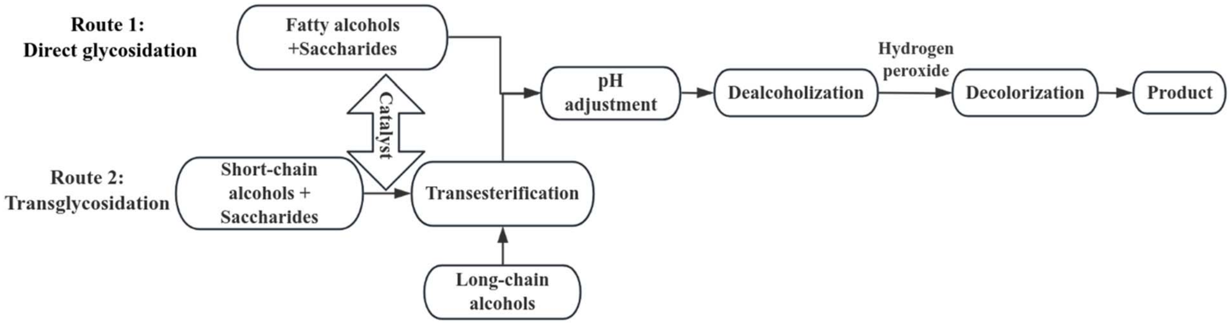

Fig. 16 Industrial process for APGs synthesis *via* glycosidation.

film evaporator was used as the first stage to remove the majority of fatty alcohols, followed by a wiped film or short-path evaporator as the second stage to eliminate residual alcohols. Jin *et al.*[115] applied a two-stage series connection system consisting of a falling film evaporator and a wiped film evaporator for APGs dealcoholization. Their results indicated that the alcohol content in crude APGs was reduced from approximately 68% to 30% after the first stage and further to below 1% after the second stage. This combined separation approach offers three major advantages: first, efficiency and energy consumption are optimized. The combination effectively integrates "rough separation" with "fine separation," enhancing both separation rate and alcohol removal efficiency. It alleviates the inherent trade-off between processing capacity and separation accuracy in single-unit operations and enables energy cascade utilization, resulting in lower overall energy consumption compared to using a single device for complete dealcoholization. Second, product quality is ensured (thermal damage is reduced). Through this hybrid process, particularly with the second stage employing short-path/wiped film evaporators that operate under high vacuum with short material residence times, the temperature and duration of heat exposure for APGs materials are reduced. This effectively suppresses thermal degradation and the formation of colored by-products, which is critical for guaranteeing the purity, color, and performance of the final product. Finally, a balance between process feasibility and economic viability is maintained. This integrated approach successfully meets both the requirements of high-throughput production and high product standards. Although the initial equipment investment may be relatively high, the overall production cost, product yield, and quality demonstrate that its economic and practical performance is significantly superior to other methods. It represents a core enabling technology for achieving efficient and high-quality industrial production of APGs.

The decolorization process focuses on removing colored impurities generated by coking, side reactions, and thermal treatment during dealcoholization. The challenges in this step are directly linked to poor reaction selectivity, the tendency to form by-products with varying degrees of polymerization, and the control of operating parameters. These factors collectively determine the content and nature of impurities, thereby influencing the difficulty and cost of decolorization.[4,44,116] Decolorization methods for APGs are mainly categorized into physical and chemical decolorization. Physical adsorption primarily relies on adsorbents such as activated carbon, bentonite, zeolite, and macroporous resins to remove colored substances. While this method is simple and low-cost, its decolorization efficiency often fails to meet industrial requirements. Therefore, chemical decolorization *via* oxidation is currently the predominant approach. Oxidation decolorization uses oxidizing agents like H_2O_2 to convert colored substances into colorless compounds. This method offers high decolorization rates and effectiveness. However, due to the high viscosity and poor fluidity of concentrated APGs solutions, product loss or incomplete decolorization can easily occur. To address this issue, researchers have made improvements in decolorization equipment. For example, Feng[117] developed a high-speed low-foam decolorization device for APGs. This device introduces air into the system during stirring, causing foam to rise. Defoaming spike balls are employed to facilitate the rapid movement of foam toward a three-way defoaming screen. The addition of an oily liquid effectively reduces the surface tension of the foam, accelerating its rupture. Meanwhile, volatilized oil components fill the space between the liquid and the defoaming screen, causing the foam to break prematurely upon contact with the oil phase before reaching the screen. Compared to conventional methods, this device allows operation at higher stirring speeds, significantly improving decolorization efficiency. Jin[118] developed an efficient APGs decolorization equipment comprising a container barrel, a driving mechanism, and a scraping and cleaning system. An electric motor is mounted above the barrel to drive a rotating rod that controls the stirring paddles. The equipment primarily operates by using an electric push rod to lower an external circular plate, inflating an annular air bag. This expansion pushes an annular scraping ring tightly against the inner wall of the barrel, effectively removing residual material and significantly improving discharge efficiency and inner wall cleanliness. Additionally, the equipment incorporates a foam suppression function, which effectively eliminates foam during stirring through optimized structural design, thereby enhancing the overall decolorization efficiency of APGs. To address the current challenges in APGs decolorization, efforts should focus on both process optimization and equipment innovation, particularly through precise control of reaction conditions to minimize impurity generation at the source. Future research should deepen the understanding of impurity formation mechanisms and structure–activity relationships, and promote the integrated innovation of continuous and intelligent decolorization processes and equipment.

In summary, the industrial production of APGs primarily encompasses three core stages: synthesis, dealcoholization, and decolorization. The overall process faces key challenges including low reaction efficiency, significant by-product formation, and energy-intensive purification with suboptimal results. During the synthesis stage, the low solubility of glucose in higher alcohols necessitates the use of excess fatty alcohol, resulting in crude products containing substantial unreacted alcohol. This makes the dealcoholization step a major separation difficulty. The decolorization process primarily addresses colored impurities formed by coking and side reactions, with hydrogen peroxide-based chemical oxidation being the current mainstream method. However, the high viscosity of the system often leads to uneven decolorization and product loss. To address these challenges, successful industrial scale-up relies on optimizing reaction conditions, such as improving mass transfer and controlling parameters, to reduce impurities at the source. For dealcoholization, multi-stage series connection distillation systems, such as those combining falling film evaporators with short-path or wiped film evaporators, can be adopted. This approach integrates "rough separation" with "fine separation", enhancing alcohol removal efficiency while minimizing thermal degradation, thereby ensuring product purity. For decolorization, innovative designs such as low-foam decolorization devices and wall-scraping cleaning systems can be implemented. These improvements enhance mixing and suppress foam formation, thereby increasing the overall decolorization efficiency.

6 Conclusion and outlook

A close relationship exists between the structure of alkyl polyglucosides (APGs) and their performance characteristics. Analysis of the correlation between APGs structure and properties such as solubility, surface activity, foaming behavior, and safety reveals that APGs with alkyl chain lengths of C_{8-14} exhibit superior performance, leading to their wide application in cosmetics, detergents, petroleum extraction, pharmaceuticals, and pesticides. Synthetic methods for APGs include direct glycosylation, enzymatic catalysis, phase-transfer catalysis, and the Koenigs–Knorr reaction. Among these, the glycosylation method remains the most commonly used for industrial-scale APGs production due to its mature technology, controllable reaction, and low cost. However, ongoing process investigations have spurred the development of novel strategies utilizing process intensification technologies, such as advanced reactors and external field assistance, to proactively create favorable reaction environments. Regarding catalysts, the evolution has progressed from highly corrosive inorganic acids to less corrosive organic and composite acids that improve product color, and further to easily recyclable solid acids and environmentally friendly ionic liquid acids. Currently, organic acid catalysts are commonly employed in industrial production to save time and costs. From a sustainability perspective, however, the homogeneous acid catalysts used in conventional chemical synthesis of APGs could be replaced by practical, stable, and recyclable heterogeneous catalysts, such as solid acid catalysts, ionic liquid catalysts, and immobilized enzymes. Concurrently, key challenges persist in the industrial production of APGs, including low reaction efficiency, significant by-product formation, and energy-intensive purification with suboptimal results. In the purification stage, conventional distillation for dealcoholization and oxidative decolorization still have room for optimization. To enhance purification efficiency and ensure product quality, multi-stage series connection distillation systems, such as those combining falling film evaporators with short-path or wiped film evaporators, can be adopted for alcohol removal. This approach integrates "rough separation" with "fine separation," improving alcohol removal efficiency while minimizing thermal damage to safeguard product quality. For decolorization, innovative designs such as low-foam decolorization devices and wall-scraping cleaning systems have emerged. These systems enhance mixing and suppress foam formation, thereby improving overall decolorization efficiency.

Looking forward, research on alkyl polyglucosides (APGs) will continue to focus on three key areas: synthesis, purification, and application. In synthesis, the systematic evaluation of product selectivity and overall yield constitutes a core component of current research; advancing this will be a key driver for propelling the field forward. Process intensification technologies, such as microwave heating and high-gravity rotating packed beds, can effectively lower reaction temperatures and suppress side reactions, enabling efficient and green synthesis in optimized reaction environments. The strategy of proactively creating favorable reaction conditions through novel reactors, external field assistance, and new energy inputs to enhance product yield and quality represents a promising new direction in APGs synthesis. In purification, equipment innovation should be emphasized. Examples include multi-stage series connection dealcoholization systems, low-foam decolorization devices, and wall-scraping cleaning systems. The optimized design and innovation of such equipment are effective approaches to improving APGs purification outcomes. Regarding applications, building on existing uses in cosmetics, detergents, petroleum extraction, pharmaceuticals, and pesticides, efforts should expand into emerging markets such as premium cosmetics, child-specific products, and environmentally friendly product lines. This will promote the broader use of APGs and enhance their application value.

Author contributions

Bo Zhang: conceptualization, investigation, writing – original draft, funding acquisition. Chaolin Yang: investigation, data curation, writing – review & editing. Shuting Liao: investigation, writing – review & editing. Xiangqin Lai: investigation, writing – review & editing. Yang Zhang: visualization, writing – review & editing. Binbin Chen: visualization, writing – review & editing. Wuwan Xiong: conceptualization, funding acquisition, writing – review & editing.

Conflicts of interest

The authors declare that they have no competing interests.

Data availability

No primary research results, software or code have been included, and no new data was generated or analysed as part of this review.

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