Alkyl Polyglycosides

Technology, Properties and Applications

Edited by
K. Hill, W. von Rybinski, G. Stoll

VCH

Weinheim · New York
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Foreword

With the beginning of the development of alkyl polyglycosides more than 15 years ago, the foundations were laid for another important milestone in the history of fatty alcohol derivatives. The product concept is more relevant now than ever, embracing as it does the exclusive use of renewable raw materials, namely sugars, for example glucose from starch, on the one hand and fatty alcohol from vegetable oil on the other. The research and development work was successful in solving both the chemical and performance-related problems and also technological problems. As a result, alkyl polyglycosides have been commercially available in industrial quantities for some time. At Henkel, these surfactants are now manufactured in two production plants—one in the USA and one in Germany—in a total capacity of almost 50,000 tonnes per year and are used in a variety of products.

In recent years, scientific institutes and companies active in the alkyl polyglycoside field have published a multitude of results in the form of patent specifications, papers and articles in specialist scientific journals. However, there has never been a comprehensive account of alkyl polyglycosides as a class of substances.

We would like to fill this gap with the present book. Authors in the Henkel Group have put together results from the various fields. Scientific principles are discussed and fields of application considered. There can of course be no claim to completeness. The individual contributions intentionally show the hand of their authors to whom we express our sincere thanks. We very much hope that this compilation will lead to an even better understanding of alkyl polyglycosides and to stimulating discussions.

We would also like especially to thank Dr. Karlheinz Hill, Dr. Wolfgang von Rybinski and Dr. Gerhard Stoll who were responsible for the conception of the book and for putting the various contributions together. We deeply mourn the loss of our colleague, Dr. Stoll, who died shortly before the book was completed.

Dr. Wilfried Umbach Dr. Harald Wulff

Düsseldorf, November 1996

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1. History of Alkyl Polyglycosides

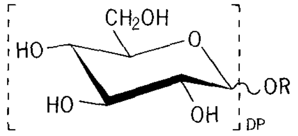
Karlheinz Hill

1. Developments in industry

Alkyl glucosides—or alkyl polyglycosides as the industrially manufactured products are widely known—are a classic example of products which, for a long time, were of academic interest only. The first alkyl glucoside was synthesized and identified in the laboratory by Emil Fischer more than 100 years ago [1]. The first patent application describing the use of alkyl glucosides in detergents was filed in Germany some 40 years later [2]. Thereafter, another 40 to 50 years went by before research groups in various companies redirected their attention on alkyl glucosides and developed technical processes for the production of alkyl polyglycosides on the basis of the synthesis discovered by Fischer.

In the course of this development, Fischer's early work, which involved the reaction of glucose with hydrophilic alcohols, such as methanol, ethanol, glycerol, etc., was applied to hydrophobic alcohols with alkyl chains from octyl (C_8) up to hexadecyl (C_{16})—the typical fatty alcohols. Fortunately, with regard to their applicational properties, not pure alkyl monoglucosides, but a complex mixture of alkyl mono-, di-, tri-, and oligoglycosides, are produced in the industrial processes. Because of this, the industrial products are called alkyl polyglycosides. The products are characterized by the length of the alkyl chain and the average number of glycose units linked to it, the degree of polymerization (Figure 1).

Rohm & Haas was the first to market an octyl/decyl ($C_{8/10}$) polyglycoside in commercial quantities in the late seventies, followed by BASF and later SEPPIC. However, owing to the unsatisfactory performance of this short-chain version as a surfactant and its poor colour quality, applications were limited to few market segments, for example the industrial and institutional sectors.



R = (fatty) alkyl group
DP = average number of glycose units/alkyl chain (R) (degree of polymerization)

Figure 1. Molecular formula of alkyl polyglycosides

The product quality of such short chain alkyl polyglycosides has been improved in the last couple of years and new types of octyl/decyl polyglycoside are currently being offered by various companies, among them BASF, SEPPIC, Akzo Nobel, ICI and Henkel.

At the beginning of the 1980s, several companies started programs to develop alkyl polyglycosides in a longer alkyl chain range (dodecyl/tetradecyl, $C_{12/14}$) with a view to making a new surfactant available to the cosmetics and detergent industries. They included Henkel KGaA, Düsseldorf, Germany, and Horizon, a division of A. E. Staley Manufacturing Company of Decatur, Illinois, USA.

Using both the know-how of Horizon, which it had acquired in the meantime, as well as experience from research and development work at Henkel KGaA, Düsseldorf, Henkel Corporation built a pilot plant to manufacture alkyl polyglycosides in Crosby, Texas. The pilot plant had a capacity of 5000 t p.a., went on line in 1988/1989 and was mainly intended to determine process parameters, to optimise product quality under industrial production conditions and to prepare the market for a new class of surfactants.

During the period from 1990 to 1992, other companies announced their intention to manufacture alkyl polyglycosides with dodecyl/tetradecyl chains, including Chemische Werke Hüls, Germany, ICI, Australia, Kao, Japan, and SEPPIC, France.

New peaks in the commercial exploitation of alkyl polyglycosides were reached in 1992 with the inauguration of a 25,000 t p.a. production plant for APG® surfactants by Henkel Corporation in the USA and in 1995 with the opening of a second plant of equal capacity by Henkel KGaA in Germany [3].

2. Chemistry

Besides technology, science has always been interested in the synthesis of glycosides since this is a very common reaction in nature. The broad synthesis potential range has recently been reviewed in articles by Schmidt and Toshima and Tatsuta [4] as well as in a number of references cited there.

In the synthesis of glycosides, a polyfunctional sugar component is combined with a nucleophile, such as an alcohol, a carbohydrate or a protein. If a selective reaction with one of the hydroxyl groups of the carbohydrate is required, all other functions have to be protected in a first reaction step. In principle, enzymatic or microbial procedures, by virtue of their selectivity, can replace complicated chemical protection and deprotection steps where regioselective formation of glycosides is required. Nevertheless, the use of enzymes in glycoside synthesis has not yet been widely enough investigated and applications are presently limited to the laboratory [5]. Owing to problems of avail-

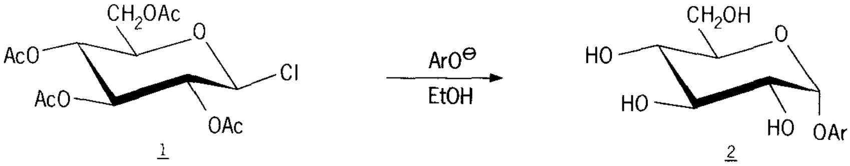


Figure 2. Synthesis of aryl glucosides according to Michael

ability of suitable enzyme systems and the high manufacturing costs anticipated, enzymatic syntheses of alkyl glycosides are not yet ready for upgrading to the industrial level, chemical procedures being preferred.

The history of synthetic routes eventually leading to glycosides began in 1870 when M. A. Colley [6] reported the synthesis of "acetochlorhydrose" (1, Figure 2) by reaction of dextrose (glucose) with acetyl chloride.

Tetra-O-acetyl-glucopyranosyl halides (acetohaloglucoses) were later found to be useful intermediates for the stereoselective synthesis of pure alkyl glucosides. In 1879, Arthur Michael [7] succeeded in preparing well-defined, readily crystallizable aryl glucosides starting from Colley's intermediate and phenolates (ArO$^-$, Figure 2).

The crucial application of Michael's synthesis to a broad range of carbohydrates and hydroxylic aglycons occurred in 1901, when W. Koenigs and E. Knorr introduced their improved stereoselective glycosidation process [8] (Figure 3). The reaction involves an S_N2 substitution at the anomeric carbon and proceeds stereoselectively with inversion of configuration, producing for example the α-glucoside 4 from the β-anomer of the acetobromoglucose intermediate 3. The Koenigs-Knorr synthesis takes place in the presence of silver or mercury promotors.

A fundamentally different approach to the synthesis of alkyl glucosides was proposed by Emil Fischer in 1893 [1]. This process is now well known as the "Fischer glycosidation" and comprises an acid-catalyzed reaction of glycoses with alcohols. Any historical account should nevertheless also include A. Gautier's first reported attempt, in 1874, to convert dextrose with anhydrous ethanol

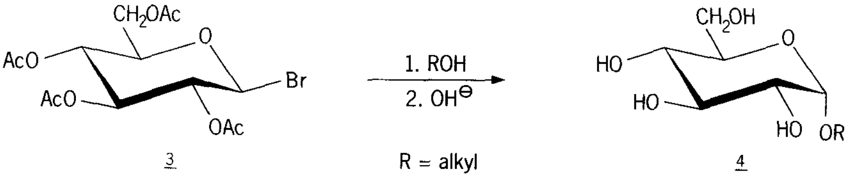


Figure 3. Stereoselective synthesis of glycosides according to Koenigs and Knorr

in the presence of hydrochloric acid [9]. Due to a misleading elemental analysis, Gautier believed he had obtained a "diglucose". Fischer later demonstrated [1] that Gautier's "diglucose" was in fact mainly ethyl glucoside (Figure 4).

The structure of ethyl glucoside was defined correctly by Fischer, as may be seen from the historical furanosidic formula ("Fischer projection") proposed. In fact, Fischer glycosidation products are complex, mostly equilibrium mixtures of α/β-anomers and pyranoside/furanoside isomers which also comprise randomly linked glycoside oligomers [10].

Accordingly, individual molecular species are not easy to isolate from Fischer reaction mixtures, which has been a serious problem in the past. After some improvement of this synthesis method [11], Fischer subsequently adopted the Koenigs-Knorr synthesis for his investigations. Using this process, E. Fischer and B. Helferich in 1911 were the first to report the synthesis of a long-chain alkyl glucoside exhibiting surfactant properties [12].

As early as 1893, Fischer had correctly noticed essential properties of alkyl glycosides, such as their high stability towards oxidation and hydrolysis, especially in strongly alkaline media. Both characteristics are valuable for alkyl polyglycosides in surfactant applications.

Research related to the glycosidation reaction is still ongoing and several interesting routes to glycosides have been developed in the recent past. Some of the procedures for the synthesis of glycosides are summarized in Figure 5 [13].

In general, chemical glycosidation processes may be divided into processes leading to complex oligomer equilibria in acid-catalysed glycosyl exchange

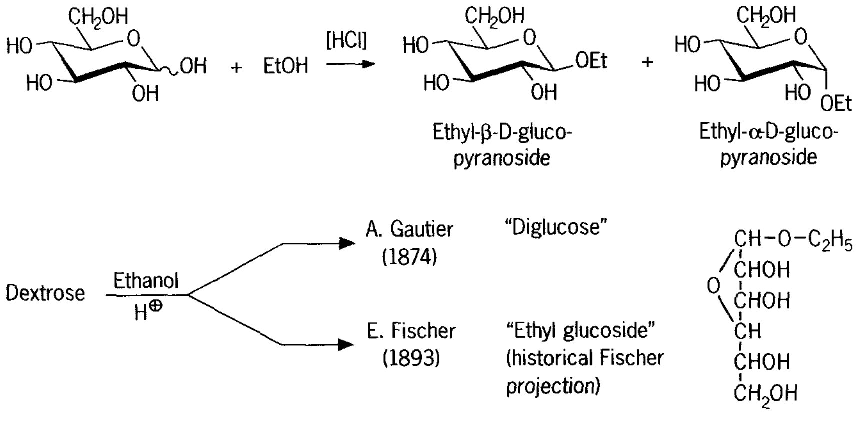


Figure 4. Synthesis of glycosides according to Fischer

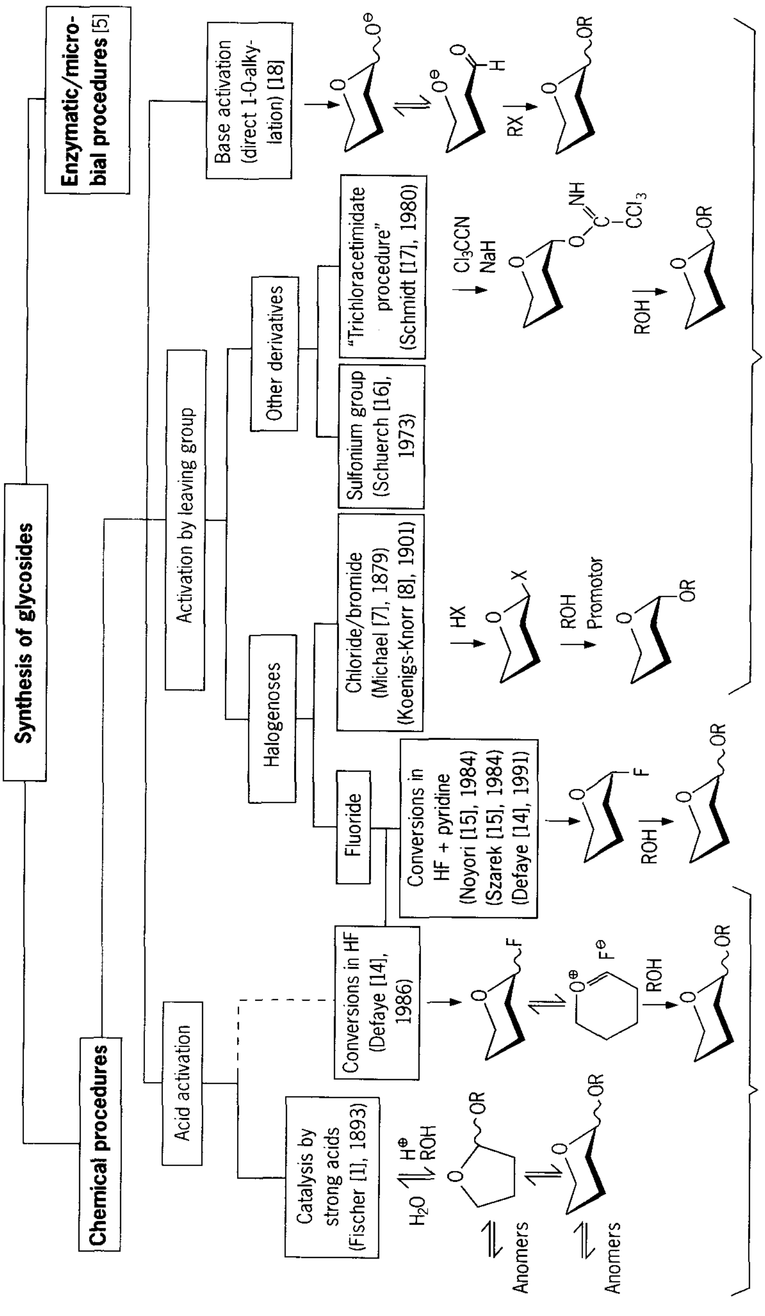


Figure 5. Summary of methods for the synthesis of glycosides [13]

reactions (Fischer glycosidation and reactions in hydrogen fluoride (HF) with unprotected carbohydrate molecules) and kinetically controlled, irreversible, mostly stereospecific substitution reactions on suitably activated carbohydrate substrates. Procedures of the second type may result in the formation of individual species rather than in complex reaction mixtures, especially when combined with protective group techniques. Carbohydrates may be activated at the anomeric carbon by leaving groups, such as halogen atoms [7,8,14,15], the sulfonium group [16], or the trichloroacetimidate group [17], or by base activation before conversion with triflate esters [18].

In the particular case of glycosidations in hydrogen fluoride or in mixtures of hydrogen fluoride and pyridine (pyridinium poly [hydrogen fluoride]) [15], glycosyl fluorides are formed in situ and are smoothly converted into glycosides, for example with alcohols. Hydrogen fluoride was shown to be a strongly activating, nondegrading reaction medium; equilibrium autocondensation (oligomerization) is observed similar to the Fischer process, although the reaction mechanism is probably different [14].

Chemically pure alkyl glycosides are only suitable for very special applications. For example, alkyl glycosides have been used successfully in biochemical research for the crystallization of membrane proteins, such as the three dimensional crystallization of porin and bacteriorhodopsin in the presence of octyl β-D-glucopyranoside (further experiments based on this work lead to the Nobel prize in chemistry for Deisenhofer, Huber and Michel in 1988) [19].

During the course of the development of alkyl polyglycosides, stereoselective methods have been used on a laboratory scale to synthesize a variety of model substances and to study their physicochemical properties [2,20]. Owing to their complexity, the instability of intermediates and the amount and critical nature of process wastes, syntheses of the Koenigs-Knorr type and other protective group techniques would create significant technical and economic problems. Fischer-type processes are comparatively less complicated and easier to carry out on a commercial scale and, accordingly, are the preferred method for the production of alkyl polyglycosides on a large scale.

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2. Technology and Production of Alkyl Polyglycosides

Rainer Eskuchen and Michael Nitsche

As described in Chapter 1, there are several preparative methods which lead to alkyl glycosides or alkyl polyglycoside mixtures. The various syntheses range from stereospecific synthesis routes using protective groups, which give defined compounds with high selectivity, to nonselective processes which lead to complex isomer and oligomer mixtures.

Any production process suitable for use on an industrial scale must satisfy several criteria. The ability to produce products with suitable performance properties and process economy are the most important. There are other aspects, such as minimizing side reactions or waste and emissions. The technology used should have a flexibility which allows product properties and quality features to be adapted to market requirements.

So far as the industrial production of alkyl polyglycosides is concerned, processes based on the Fischer synthesis have been successfully adopted. Their development began about twenty years ago and has significantly accelerated in the past ten years. Development work over this period has enabled the efficiency of this synthesis route to be increased to a level where it has finally become attractive for industrial application. Optimization work, particularly in the use of long-chain alcohols, such as dodecanol/tetradecanol ($C_{12/14}$-OH), has resulted in distinct improvements in product quality and process economy. Modern production plants built on the basis of the Fischer synthesis are the embodiment of low-waste, virtually emission-free technologies. Another advantage of the Fischer synthesis is that the average degree of polymerization of the products can be precisely controlled over a wide range. Relevant performance properties, for example hydrophilicity/water solubility, can thus be adapted to meet requirements. Additionally the raw material base is no longer confined to water-free glucose [1-3].

1. Raw materials for the manufacture of alkyl polyglycosides

1.1 Fatty alcohols

Fatty alcohols can be obtained either from petrochemical sources (synthetic fatty alcohols) or from natural, renewable resources, such as fats and oils (natural fatty alcohols). Fatty alcohol blends are used in the alkyl polyglycoside synthesis to build up the hydrophobic part of the molecule. The natural fatty alcohols are obtained after transesterification and fractionation of fats and oils (triglycerides), leading to the corresponding fatty acid methyl esters, and subsequent hydrogenation. Depending on the desired alkyl chain length of the fatty alcohol, the main feedstocks are oils and fats of the following composition: coconut or palm kernel oil for the $C_{12/14}$ range and tallow, palm or rapeseed oil for the $C_{16/18}$ fatty alcohols.

1.2 Carbohydrate source

The hydrophilic part of the alkyl polyglycoside molecule is derived from a carbohydrate. Based on starch from corn, wheat or potatoes, both polymeric and monomeric carbohydrates are suitable as raw materials for the production of alkyl polyglycosides. Polymeric carbohydrates include, for example, starch or glucose syrups with low degradation levels while monomeric carbohydrates can be any of the various forms in which glucose is available, for example water-free glucose, glucose monohydrate (dextrose) or highly degraded glucose syrup. Raw material choice influences not only raw material costs, but also production costs. Generally speaking, raw material costs increase in the order starch/glucose syrup/glucose monohydrate/water-free glucose whereas plant equipment requirements and hence production costs decrease in the same order (Figure 1).

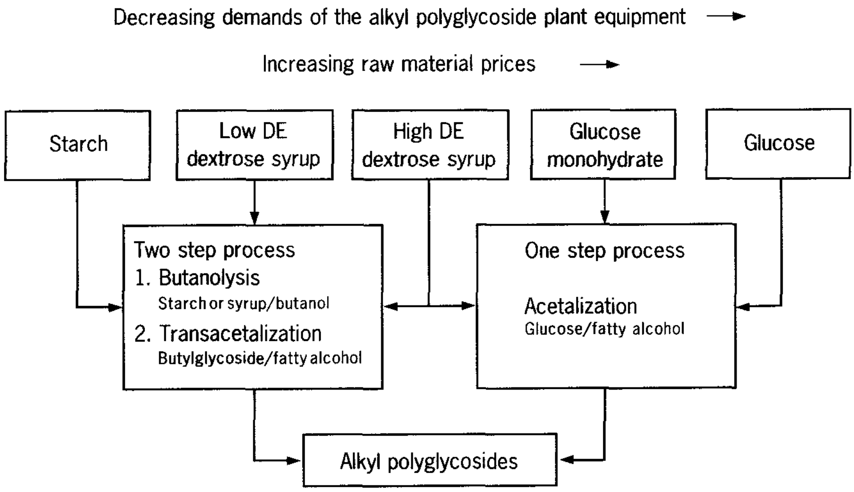

Figure 1. Carbohydrate sources for industrial-scale alkyl polyglycoside synthesis (DE = dextrose equivalent)

2. Degree of polymerization

Through the polyfunctionality of the carbohydrate partner, the conditions of the acid-catalyzed Fischer reaction yield an oligomer mixture in which on average more than one glycose unit is attached to an alcohol molecule. The average number of glycose units linked to an alcohol group is described as the (average) degree of polymerization (DP). Figure 2 shows the distribution for an alkyl polyglycoside with DP = 1.3. In this mixture, the concentration of the individual oligomers (mono-, di-, tri-, ...-, glycoside) is largely dependent on the ratio of glucose to alcohol in the reaction mixture. The average degree of polymerization (DP) is an important characteristic with regard to the physical chemistry and applications of alkyl polyglycosides. In an equilibrium distribution, the DP—for a given alkyl chain length—correlates well with basic product properties, such as polarity, solubility, etc. In principle, this oligomer distribution can be described by a mathematical model. P. M. McCurry [4] showed that a model developed by P. J. Flory [5] for describing the oligomer distribution of products based on polyfunctional monomers can also be applied to alkyl polyglycosides. This modified version of the Flory distribution describes alkyl polyglycosides as a mixture of statistically distributed oligomers. The content

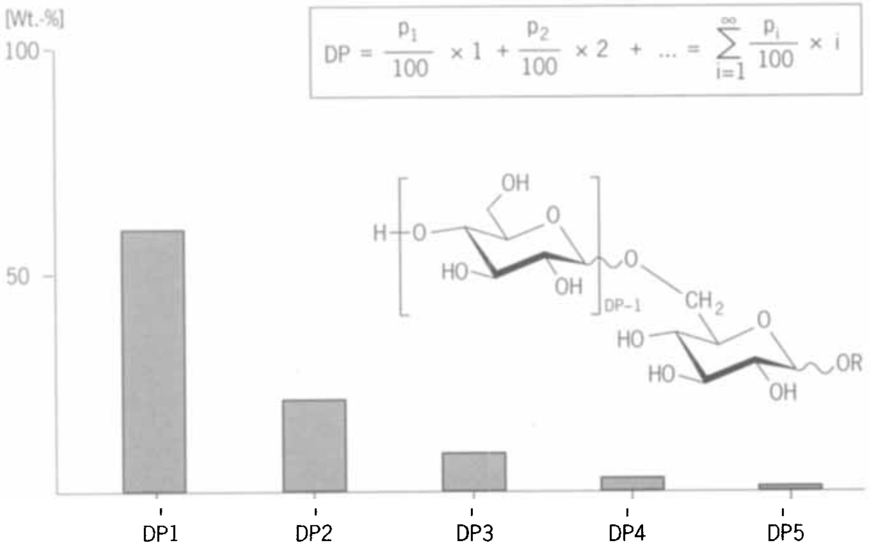

Figure 2. Typical distribution of dodecyl glycoside oligomers in a DP = 1.3 mixture (R = dodecyl)

of individual species in the oligomer mixture decreases with increasing degree of polymerization. The oligomer distribution obtained by this mathematical model accords well with analytical results (see Chapter 3). In simple terms, the average degree of polymerization (DP) of alkyl polyglycoside mixtures can be calculated from the mole percent p_i of the respective oligomeric species "i" in the glycoside mixture (Figure 2).

3. Synthesis processes for the production of alkyl polyglycosides

Basically, all processes for the reaction of carbohydrates to alkyl polyglycosides by the Fischer synthesis can be attributed to two process variants, namely direct synthesis and the transacetalization process. In either case, the reaction can be carried out in batches or continuously.

Direct synthesis is simpler from the equipment point of view [6-8]. In this case, the carbohydrate reacts directly with the fatty alcohol to form the required long-chain alkyl polyglycoside. The carbohydrate used is often dried before the actual reaction (for example to remove the crystal-water in case of glucose monohydrate = dextrose). This drying step minimizes side reactions which take place in the presence of water.

In the direct synthesis, monomeric solid glucose types are used as fine-particle solids. Since the reaction is a heterogeneous solid/liquid reaction, the solid has to be thoroughly suspended in the alcohol.

Highly degraded glucose syrup (DE>96; DE = dextrose equivalents) can react in a modified direct synthesis. The use of a second solvent and/or emulsifiers (for example alkyl polyglycoside) provides for a stable fine-droplet dispersion between alcohol and glucose syrup [9,10].

The two-stage transacetalization process involves more equipment than the direct synthesis. In the first stage, the carbohydrate reacts with a short-chain alcohol (for example n-butanol or propylene glycol) and optionally depolymerizes.

In the second stage, the short-chain alkyl glycoside is transacetalized with a relatively long-chain alcohol ($C_{12/14}$-OH) to form the required alkyl polyglycoside. If the molar ratios of carbohydrate to alcohol are identical, the oligomer distribution obtained in the transacetalization process is basically the same as in the direct synthesis.

The transacetalization process is applied if oligo- and polyglycoses (for example starch, syrups with a low DE value) are used [11]. The necessary depolymerization of these starting materials requires temperatures of >140 °C. Depending on the alcohol used, this can create correspondingly higher pressures which impose more stringent demands on equipment and can lead to higher plant cost.

Generally, and given the same capacity, the transacetalization process results in higher plant cost than the direct synthesis. Besides the two reaction stages, additional storage facilities and, optionally, working-up facilities for the short-chain alcohol have to be provided. Alkyl polyglycosides have to be subjected to additional or more elaborate refining on account of specific impurities in the starch (for example proteins). In a simplified transacetalization process, syrups with a high glucose content (DE > 96 %) or solid glucose types can react with short-chain alcohols under normal pressure [12-16]. Continues processes have been developed on this basis [14].

Figure 3 shows both synthesis routes for alkyl polyglycosides.

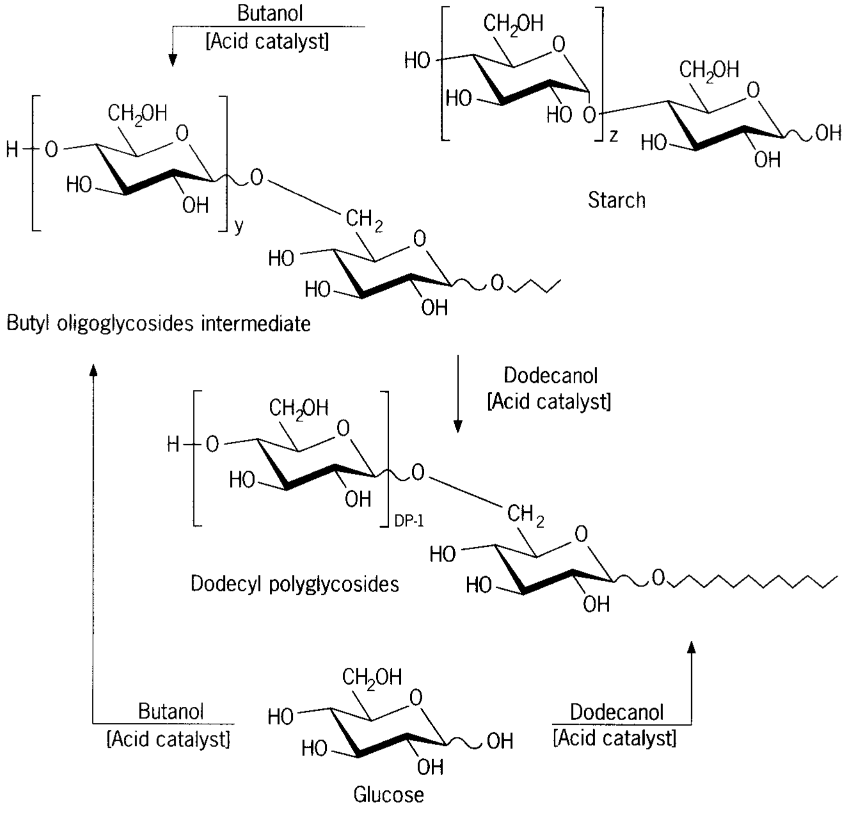

Figure 3. Alkyl polyglycoside surfactants—industrial synthesis pathways

4. Requirements for the industrial production of water-soluble alkyl polyglycosides

The requirements for or rather the design of alkyl polyglycoside production plants based on the Fischer synthesis are critically determined by the carbohydrate types used and by the chain length of the alcohol used. It is intended here to describe first the production of water-soluble alkyl polyglycosides on the basis of octanol/decanol ($C_{8/10}$-OH) and dodecanol/tetradecanol ($C_{12/14}$-OH). Alkyl polyglycosides which, for a given DP, are insoluble in water on account of the alcohol used (number of C atoms in the alkyl chain ≥ 16) are dealt with separately (*see 5. in this chapter*).

Under the conditions of the acid-catalyzed syntheses of alkyl polyglycoside, secondary products, such as polydextrose [17,18], ethers and colored impurities, are formed. Polydextroses are substances of undefined structure which are formed in the course of the synthesis through the polymerization of glycoses. The type and concentration of the substances formed by secondary reactions are dependent on process parameters, such as temperature, pressure, reaction time, catalyst, etc. One of the problems addressed by development work on industrial alkyl polyglycoside production over recent years was to minimize this synthesis-related formation of secondary products.

Generally, the production of alkyl polyglycosides based on short-chain alcohols ($C_{8/10}$-OH) and with a low DP (large alcohol excess) presents the fewest problems. Fewer secondary products are formed with the increasing excess of alcohol in the reaction stage. The thermal stress and formation of pyrolysis products during removal of the excess alcohol are reduced.

The Fischer glycosidation may be described as a process in which, in a first step, the dextrose reacts relatively quickly and an oligomer equilibrium is reached. This step is followed by slow degradation of the alkyl polyglycoside. In the course of the degradation, which consists of dealkylation and polymerization steps, the thermodynamically more stable polydextrose is formed substantially irreversibly in increasing concentrations. Reaction mixtures which have exceeded an optimal reaction time may be described as over-reacted. If the reaction is terminated too early, the resulting reaction mixture contains a significant amount of residual dextrose.

The loss of alkyl polyglycoside active substance in the reaction mixture correlates well with the formation of polydextrose, the reaction mixture in the case of over-reacted systems gradually becoming heterogeneous again through precipitating polydextrose. Accordingly, product quality and product yield are critically influenced by the time at which the reaction is terminated. Starting with solid dextrose, alkyl polyglycosides low in secondary products are obtained, providing other polar constituents (polydextrose) are filtered off to-