Subcritical Methanolysis of Starch and Transglycosidation to Produce Dodecyl Polyglucosides

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ABSTRACT: Biosurfactants based on carbohydrates are of special interest because of their production from renewable resources, nontoxicity, biocompatibility, and environmental friendliness. Dodecyl polyglucosides, a type of nonionic surfactant synthesized with methyl polyglucosides obtained from the eco-friendly subcritical methanolysis of renewable resource of starch, is no doubt good for ecosystem. With the subcritical methanolysis of starch, the methyl polyglucosides were obtained without any catalyst. Under the reaction condition of the weight ratio of methanol to starch of 7.5, temperature of 220 °C, and reaction time of 2 h, the yield of methyl polyglucosides was 85%. Dodecyl polyglucosides were synthesized by transglycosidation with methyl polyglucosides, and the green nonionic surfactant has excellent surface activity. The critical micelle concentration and hydrophilic lipophilic balance are 0.022 wt % and 12, respectively.

INTRODUCTION

Because of the nontoxicity, excellent biocompatibility, and environmental friendliness, biosurfactants have broad applications. The biosurfactants based on carbohydrates are of special interest because of their production from renewable resources and sound ecological effects.1−6 One type of biosurfactant is alkyl polyglucosides (APGs) with a glucose unit.7 They are nonionic surfactants produced from renewable resources such as corn, potatoes, and wheat.8−11 Owing to their antibacterial activity, high surface activity, low toxicity, dermatological compatibility, and biodegradability, they are widely used in many fields including washing, cleaning, and cosmetics.12−16

In recent years, the common material used for the synthesis of APGs is glucose, which is traditionally produced from starch and cellulose with complex processes.17−22 Therefore, the direct utilization of starch or cellulose to produce APGs is no doubt an advantageous process. It is known that β-glycosidic linkages of sugar molecules contained in the cellulose chain are strongly protected by the intra- and intermolecular hydrogen bonds, whereas the corresponding linkages in starch are weaker. The direct chemical conversion of cellulose as treated in supercritical methanol resulted in complex products.23 Therefore, APGs are easier to produce with starch as the raw material rather than cellulose.

Up to now, the main method to synthesize APGs from starch is the Fischer method, which includes direct glycosylation and transglycosidation.24,25 Zou et al. synthesized isoctyl polyglucosides directly from starch as raw material.26 However, for the synthesis of longer-chain APGs, the direct synthesis is very difficult due to the compatibility between sugar and long-chain alcohol. The transglycosidation method with methyl polyglucosides is an important method, that is to say it should first obtain methyl polyglucosides from starch. The traditional methanolysis of starch should adopt acid or alkali as a catalyst, and the process will result in environmental pollution and difficulty in separation of products.

RESULTS AND DISCUSSION

Methanolysis Products. Owing to the high activity of the subcritical methanol, the first reaction occurs between alcohol and the terminal units of starch, with the release of water and then hydrolysis of water to starch. The general methanolysis process should be the reaction of the hydroxyl group of starch with that of methanol to condense into an ether linkage (C−O−C). The Fourier transform infrared (FTIR) spectra of the methanolysis products are given in Figure 1. The characteristic absorption in the range of 1120−1170 cm−1 gives the ether linkage, and the peak at about 1146 cm−1 is the characteristic absorption peak of alkyl polyglucosides resulting from ether linkage,27,28 which indicates OH condensation.

The structures of the methanolysis products were determined by the 1H nuclear magnetic resonance (NMR) spectrum as given in Figure 2. The chemical shift of H2O is 4.790 ppm. The peak of δ 3.383 ppm shows the presence of three protons of methyl group (A1) and one proton of the glucose ring (B2). The peaks ranged from δ 3.511 to 3.849 ppm, indicating that the three protons of the glucose ring (B1, B3, B4) and the two protons of the methylene group (B5) are

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The one proton of the glucose ring (B6) linked to the hydroxyl group of methanol is shown in the peak of $\delta 5.186$ ppm. The hydroxyl groups could not be observed obviously because of the hydrogen–deuterium exchange. The $1H$ NMR spectrum is in accordance with the molecular structure of methyl polyglucosides.

Typical high-performance liquid chromatography (HPLC) spectra are shown in Figure 3. The elution order of solutes in HPLC is governed by the degree of polymerization (DP) and alkyl chain length of APGs. Due to the use of reversed-phase C18 column, solutes with a longer alkyl chain length and bigger DP are proved to have a shorter retention time. As for the methanolysis products, there is main peak at around 3.171 min similar to the standard methyl-$\alpha$-D-glucopyranoside (DP = 1), indicating that the main methanolysis product should be methyl glucoside (DP = 1).

Except the main peak, the peaks at around 1.392, 2.349, and 2.724 min should result from polysaccharides and other methyl polyglucoside with DP = 2 and 3.

According to the normalization of peak areas, the contents of methyl polyglucosides with DP of 1, 2, and 3 are calculated on the basis of eq 1.

$$D_i(\%) = \frac{A_i}{\sum A} \times 100\% \quad (i = 1, 2, 3)$$

$A_i$ is the peak area of methyl polyglucosides with DP of 1, 2, and 3. $\sum A$ is the total area of methyl polyglucosides with DP of 1, 2, and 3. The response coefficients ($R^2$) of DP1, DP2, and DP3 were 0.9987, 0.9953, and 0.9881, respectively.

According to the normalization of peak areas, the contents of methyl polyglucosides with DP of 1, 2, and 3 are 64, 21, and 15%, respectively. Thus, the average DP of 1.51 for methyl polyglucosides can be calculated by eq 2

$$\text{Average DP} = 1 \times 64\% + 2 \times 21\% + 3 \times 15\% = 1.51$$

Yield of Methyl Polyglucosides Depending on Reaction Conditions. As for the methanolysis of starch, the first reaction occurs between alcohol and the terminal units of starch to release water; then, water hydrolyzes starch to give a low degree of polymerization of methyl polyglucosides. Methanol acts both as a reactant and a solvent in the process. Therefore, the weight ratio of methanol to starch, reaction temperature, and time should play important roles on the methanolysis of starch to obtain methyl polyglucosides. The yield of methyl polyglucosides can be expressed as $m_a/m_e \times 100\%$, where $m_a$ and $m_e$ are the experimental and theoretical weights of methyl glucoside, respectively. As for the theoretical weight, 1.1975 g of methyl glucoside can be obtained with the methanolysis of 1 g of starch.

First the reaction time of 2 h was studied to determine appropriate weight ratio of methanol to starch and reaction temperature. The yield of the methyl polyglucosides with different weight ratios of methanol to starch is given in Figure 4 at 220 °C and 2 h. It shows that with the weight ratio of
methanol/starch increasing, firstly the yield gradually increases and it attains around 85% under the weight ratio of methanol/starch 7.5 and subsequently the yield almost remains unchanged. Therefore, the weight ratio of methanol/starch 7.5 should be fit to obtain high yield of methyl polyglucosides.

Owing to that too high temperature will result in many side reactions and the temperature range of 180—260 °C was studied. Figure 5 gives the yield of methyl polyglucosides at different temperatures. It shows that the yield increases to the maximum 85% at the reaction temperature of 220 °C and with increasing temperature further, the yield decreases. It should be that the higher temperature will result in side reactions such as the carbonization of starch and the polymerization of glucose. Especially for the temperature of 260 °C, the color of products is much more yellow than that of 220 °C. Thus, the temperature of 220 °C is appropriate.

The reaction time range of 1—3 h is studied and the result is shown in Figure 6. First the yield increases with the increase of time and at the reaction time of 2 h, the yield attains the highest yield of 85%. Whereas as the reaction time further increases to 2.5 h, the yield decreases to 78%. When reaction time is too long, the side effects of hydrolysis and polymerization of methyl polyglucosides will occur, and the colored substances in products will increase and make the products dark brown. The result indicates that to ensure high yield, the reaction time of 2 h should be suitable and also temperature of 220 °C.

According to the above results, the yield of methyl polyglucosides was 85% when the methanolysis condition was reaction temperature 220 °C, reaction time 2 h and the weight ratio of methanol to starch 7.5.

**Transglycosidation Products.** FTIR spectrum of transglycosidation products is shown in Figure 7. The peak of 1142 cm⁻¹ are the characteristic absorption peak of alkyl polyglucosides resulted from ether linkage.

Figure 5. Yield of methyl polyglucosides with different temperature (2 h, the weight ratio of methanol to starch 7.5).

Figure 6. Yield of methyl polyglucosides with different time (220 °C, the weight ratio of methanol to starch 7.5).

![Figure 5](image1.png)

![Figure 6](image2.png)

Figure 7. FTIR spectra of the starch and transglycosidation product.

Different from the methanolysis product, the transglycosidation product was dissolved in chloroform-d (CDCl₃) solvent, and their ¹H NMR spectrum is shown in Figure 8.

Figure 8. ¹H NMR spectrum of the transglycosidation product.

![Figure 8](image3.png)

The chemical shift of the CDCl₃ solvent is 7.260 ppm. The peaks of δ 0.876, 1.253, and 1.616 ppm belong to the three protons of the methyl group (A1), the sixteen protons of methylene group (A2, A3, A4, A5, A6, A7, A8, A9), and the four protons of the methylene group (A10, A11), respectively. The one proton of the glucose ring (B6) linked to the hydroxyl group of 1-dodecanol is shown in the peak of δ 5.076 ppm. The peaks in the range from δ 3.841 to 4.305 ppm are a result of other twelve protons (A12, B1, B2, B3, B4, B5, B1, C1, C2, C3, C4). The peaks of the ¹H NMR spectrum are in accordance with the molecular structure of dodecyl polyglucosides.

The HPLC spectra are given in Figure 9. The remain time from low to high should be residual 1-dodecanol, polysaccharide, and dodecyl polyglucosides of DP = 3, 2, and 1, respectively. The response coefficients (R²) of DP1, DP2, and DP3 were 0.9962, 0.9918, and 0.9839. According to the
normalization of peak areas, the contents of dodecyl polyglucosides with DP of 1, 2, and 3 are 67, 18, and 15%, respectively; thus, the average DP of 1.48 of dodecyl polyglucosides can be calculated by eq 3

\[
\text{average DP} = 1 \times 67\% + 2 \times 18\% + 3 \times 15\% = 1.48
\]

According to the above results, the main transglycosidation product was dodecyl polyglucosides and their yield was 83%.

Critical Micelle Concentration (CMC) and Hydrophilic Lipophilic Balance (HLB) Values of the Dodecyl Polyglucosides. The critical micelle concentration (CMC) and the hydrophilic lipophilic balance (HLB) value of the desired products dodecyl polyglucosides were studied. According to the curve of the surface tension of the aqueous solution versus the corresponding logarithm of concentrations, the related parameters can be obtained.

Figure 10 shows the general trend that the increase of the concentration of dodecyl polyglucosides first leads an obvious decrease in surface tension and then gradually becomes constant. The value of the CMC is determined from the intersection of the two dashed lines obtained by linear fitting. Thus, the CMC is 0.022 wt % and the corresponding surface tension is 32.42 mN/m. The result is in accordance with the CMC value of 0.2 wt % of isodecyl glucoside studied by Nilsson et al., who pointed out that the CMC approximately decreases by a factor of 10 when the hydrophobic chain was increased by two carbons. 32

The HLB value can be calculated by the empirical eq 4 according to the method of W. C. Griffin. 33

\[
\text{HLB} = \left( \frac{\text{relative molecular mass of the hydrophilic moieties}}{\text{relative molecular mass of the surfactants}} \right) \times 20
\]

Subcritical methanolysis of starch and transglycosidation to produce green nonionic surfactants benefits the sustainable development owing to renewable resources. Starch alcoholysis in subcritical methanol to obtain the main products of methyl polyglucosides and transglycosidation with 1-dodecanol can obtain dodecyl polyglucosides, which have the CMC of 0.022 wt % and HLB of 12. The process can use renewable starch to produce alkyl polyglucosides to avoid traditional glucose material, which first need to hydrolyze starch firstly.

The yield of methyl glucoside can reach 85% at the temperature of 220 °C and reaction time of 2 h in the subcritical methanolysis of starch. Owing to no need of any catalyst such as a strong acid in the methanolysis process, the method is eco-friendly and quite efficient in separating the main methanolysis products. The residual starch is separated by filtration and excess methanol is removed with distillation; the methanolysis product is used to synthesize dodecyl polyglucosides, and the yield of the main transglycosidation products of dodecylglucopyranoside is 83%.

EXPERIMENTAL SECTION

Materials. Reagents including starch, 1-dodecanol, methanol, p-toluene-sulfonic acid, and 30 wt % hydrogen peroxide (H₂O₂) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Standard methyl-α-D-glucopyranoside (degree of polymerization, DP = 1) and dodecyl glucopyranoside (DP = 1) were purchased from Crystal Pure Industrial Co. Ltd (Shanghai, China). All reagents were used as purchased without further purification.

Subcritical Methanolysis. Some weight ratio of starch and methanol were mixed under ultrasonic dispersion. Subcritical methanolysis of the mixed sample was carried out in a stainless steel batch type autoclave reactor with an inner volume of 20 mL, and the total volume of all samples put into the vessel was about 15 mL to maintain appropriate pressure and keep a relatively smooth reaction. After the desired reaction temperature and time were achieved, the reactor was taken out from the furnace and quenched in ice-water bath to stop the reaction immediately in ambient temperature. The solid including residual starch and liquid after reaction were separated by filtration. The liquid product was distilled to remove excess methanol, and it was used to synthesize dodecyl polyglucosides.

Synthesis of Dodecyl Polyglycosides. The liquid product of the above methanolysis was put into a three-necked flask containing about 1.0% weight ratio of p-toluene-sulfonic acid as catalyst. After heating to 110 °C, 1-dodecanol,
with twice the weight of the liquid product of methanolysis preheated to 60 °C, was added slowly for 30 min. The mixtures were then stirred at 110 °C to react for about 1 h, and methanol produced during the process of the transglycosidation of 1-dodecanol was removed by distillation.

After the reaction, the excess 1-dodecanol was removed by distillation at 150 °C under 1000 Pa vacuum degree. Then, the residual liquid products underwent oxidative decoloration with 30 wt % hydrogen peroxide (about 5% weight ratio in all liquids) at the temperature of 85 °C and for 2.5 h to give light-yellow products. Finally, the product of dodecyl polyglycosides was obtained after sodium borohydride was added to decompose excessive hydrogen peroxide and the pH adjusted to 8.

**Analysis of the Products.** Methanolysis and transglycosidation products were quantitatively and qualitatively analyzed by Fourier transform infrared spectroscopy (FTIR), 1H-nuclear magnetic resonance (NMR), and high-performance liquid chromatography (HPLC). FTIR spectra were recorded on an Avanter 370 FTIR spectrograph (Nicolet Co.). 1H NMR spectra were recorded by an AVANCE 500 MHz (Bruker Co., Germany) digital spectrometer operating at 500 MHz with the products dissolved in deuterium oxide (D2O) and chloroform-d (CDCl3).

The HPLC was carried out with Agilent 1200, which is coupled with reversed-phase C18 column (250 mm × 4.6 mm × 5 μm), and a UV–vis detector was employed to determine the wavelengths of 205 and 216 nm, respectively. The mobile phase was a mixture of methanol/water (50:50, v/v) at a flow rate of 1 mL/min and methanol/water (60:40, v/v) at a flow rate of 0.5 mL/min, respectively. The autosampler with the injection volume was set to 1 μL and the column temperature was maintained at 25 °C.

The critical micelle concentration (CMC) values of the prepared APGs were determined using surface tension and interfacial tension methods. The surface and interfacial tensions of the final product solutions were measured using the video optical contact angle measuring instrument at temperature of 25 ± 1 °C.

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**Notes**

The authors declare no competing financial interest.

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