

Starch-Derived Glycol and Glycerol Glucosides Prepared by Reactive Extrusion Processing

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SYNOPSIS

Previously, starch-derived glycol and glycerol glucosides were prepared by batch-reaction processes and had excellent potential as chemical intermediates for a wide range of products. However, more efficient processes for preparation of these derivatives are needed. In this present work, a modern corotating, intermeshing, twin-screw extruder with a barrel length/screw diameter (L/D) ratio of 43 : 1 was used to study the reaction of starch with ethylene glycol and glycerol in the presence of sulfuric acid catalyst at elevated temperatures. A fully continuous process was used. Variables that were investigated included temperature (140–180°C), glycol or glycerol/starch AGU mol ratio (1.5–4.0), starch feed rate (5–30 lb/h), screw speed (100–475 rpm), residence time, specific energy, and several types of commercial cornstarch and corn flour products. Rates and extents of reaction that occurred in the barrel were determined by analyzing samples that were quenched just prior to extrusion. The major glucosides were quantitated by high-performance liquid chromatography. Results of this study show that starch can be continuously, rapidly, and efficiently converted to glucosides in 90% yield at high production rates. Such processing is expected to be technically feasible for the reaction of a wide range of polyhydroxy alcohols with various starch substrates.

INTRODUCTION

Starch reacts with ethylene glycol (EG), glycerol, and other polyhydroxy alcohols in the presence of acid catalysts at elevated temperatures to yield glycosides with chemical properties of acetals. When starch is reacted essentially completely with a 3 mol excess of EG, the products are primarily the glycol glucosides shown in Scheme 1. The major starch-derived glycerol glucosides have not yet been characterized. In the 1960s, EG and glycerol glucosides were derived from starch by batch-reaction processes and evaluated as chemical intermediates for polyurethane foams, alkyd resins, surfactants and other materials.^{1–4} In particular, rigid urethane foams, prepared by reacting crude mixtures of the glucosides with isocyanates, had excellent dimensional sta-

bility, compressive strength, and insulating properties.³

Several problems are associated with preparation of these glucosides by batch-reaction procedures. For example, mixing and heat transfer are poor methods because the reaction mixtures are so viscous during much of the reaction period. Mixing can be improved by incrementally feeding starch to a mixture of acid catalyst EG or glycerol at reaction temperatures. However, additional process time, energy consumption, and handling methods are required in the latter procedure.

Because twin-screw extruders are well recognized as efficient mixers for handling the most difficult mixing requirements, the reaction of starch with EG in a small twin-screw processor by a semi-continuous process was recently investigated.⁵ In that study, glucosides were obtained in high yield, but only at inefficient throughput rates, because of the short barrel and inadequate barrel length/screw diameter (L/D) ratio (9 : 1) of the processor.

For the present work, a corotating, intermeshing, twin-screw extruder with an L/D ratio of 43 : 1 and

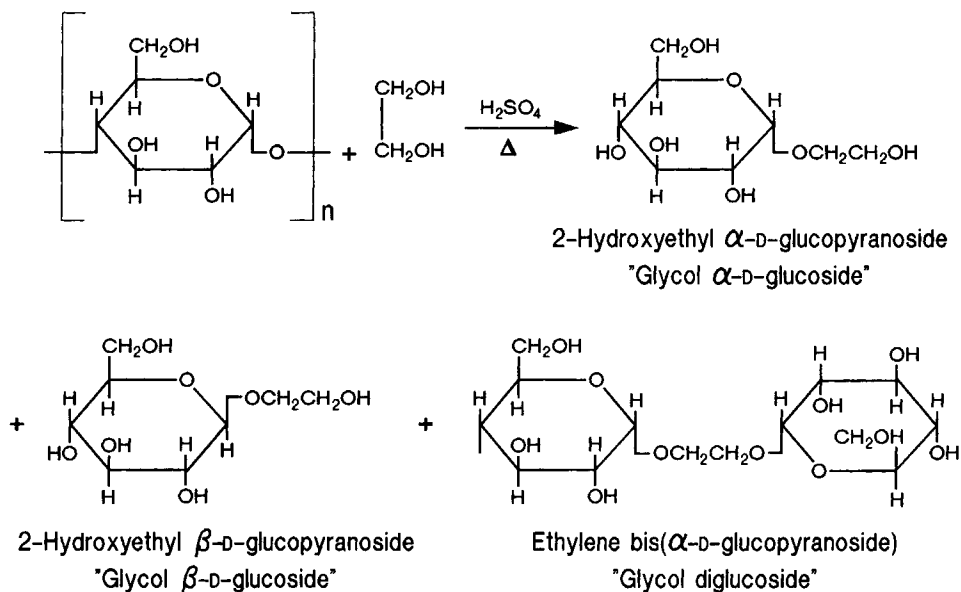
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Scheme 1 Major reaction products from starch and ethylene glycol.

a processing length of 52 in was used to extend the latter investigation. A continuous reactive-extrusion process was used. EG and glycerol were reacted with commercial cornstarches that had various contents of amylose and amylopectin and with several corn flours. Effects of extrusion processing variables on rate and extent of reaction and on composition of the extrudates were studied. Compositions were studied by high-performance liquid chromatography (HPLC).

EXPERIMENTAL

Materials

Materials included 27% amylose (ordinary) cornstarch (Buffalo 3401, CPC International, Englewood Cliffs, NJ), 50% amylose cornstarch (Amaizo 5, American Maize, Hammond, IN), 70% amylose cornstarch (Amylomaize VII, American Maize), refined waxy cornstarch (Amioca, National Starch and Chemical Corp., Bridgewater, NJ), corn flours (Regular-milled #525, Ultrafine #580A, and Pregelled #961, Illinois Cereal Mills, Inc., Paris, IL), ethylene glycol (99+% pure, 55-gal drums, Aldrich Chemical Co., Inc., Milwaukee, WI), glycerol (99+% pure, 18-L containers, Aldrich Chemical Co.), and sulfuric acid (96.4%, J. T. Baker Chemical Co., Phillipsburg, NJ).

Equipment

The extruder was a ZSK 30 twin-screw laboratory extruder with a 15 Hp DC drive and screw speeds from 50–500 rpm (Werner & Pfleiderer, Ramsey, NJ). The processing section consisted of 14 barrel sections (each 90 mm long), one barrel spacer (30 mm long), and an end plate (30 mm long), coupled by 4 tie rods. Barrel bore and screw diameters are 30.85 and 30.70 mm, respectively. The L/D ratio (43 : 1) is the processing length (1320 mm) divided by the screw diameter. Each barrel section, except the first, had an electric heater (500 W). Barrel temperature thermocouples were located at barrel sections 3, 5, 7, 9, 11, 12, and 14. Thermocouples for measuring material temperature were located at barrel section 11 and at the die head. Chilled water was circulated through the extruder barrel jackets equipped with solenoid valves and return line check valves to regulate barrel temperatures. The water was circulated constantly through jackets of unheated barrel sections 13 and 14 (zone 7) as a means of quenching the reaction so that the extent of reaction in the extruder could be studied.

The twin screw was composed of 68 individual, slip-on, mixing elements of various types on each shaft. These elements were arranged and are described in Table I. The last screw element (number 68) extends about 8 mm into the die-head assembly. Starches and flours were fed to the undercut flight screws (elements 1–3) by a twin-screw volumetric

Table I Twin-Screw Profile Screw Elements^a

| No. | Description | No. | Description | No. | Description |
|-----|-------------------------------|-----|--------------------|-----|------------------|
| 1 | UF, C, RH, 42/42 ^b | 24 | NF, C, RH, 20/10 | 47 | NF, C, RH, 14/14 |
| 2 | UF, C, RH, 42/42 | 25 | nCF, 14/14 | 48 | NF, C, LH, 20/10 |
| 3 | UF, (C)/NF, (C), RH, 42/21 | 26 | KB, C, RH, 45/5/14 | 49 | NF, C, RH, 14/14 |
| 4 | NF, C, RH, 42/42 | 27 | KB, C, LH, 45/5/14 | 50 | NF, C, RH, 14/14 |
| 5 | NF, C, RH, 42/42 | 28 | NF, C, RH, 20/20 | 51 | NF, C, LH, 10/10 |
| 6 | NF, C, RH, 28/28 | 29 | NF, C, RH, 20/20 | 52 | NF, C, RH, 14/14 |
| 7 | NF, C, RH, 28/28 | 30 | NF, C, RH, 20/20 | 53 | NF, C, RH, 14/14 |
| 8 | NF, C, RH, 28/28 | 31 | KB, C, RH, 45/5/14 | 54 | NF, C, LH, 20/10 |
| 9 | NF, C, RH, 20/20 | 32 | KB, C, LH, 45/5/14 | 55 | NF, C, RH, 14/14 |
| 10 | NF, C, RH, 20/20 | 33 | NF, C, RH, 14/14 | 56 | NF, C, RH, 14/14 |
| 11 | KB, nC, 90/9/28 ^d | 34 | NF, C, RH, 14/14 | 57 | NF, C, RH, 42/42 |
| 12 | NF, C, RH, 28/28 | 35 | KB, C, RH, 45/5/14 | 58 | NF, C, RH, 42/21 |
| 13 | NF, C, RH, 20/20 | 36 | KB, C, RH, 45/5/14 | 59 | NF, C, RH, 42/21 |
| 14 | NF, C, RH, 20/10 | 37 | KB, C, LH, 45/5/14 | 60 | NF, C, RH, 42/21 |
| 15 | KB, nC, 90/5/28 | 38 | KB, C, RH, 45/5/20 | 61 | NF, C, RH, 28/14 |
| 16 | NF, C, RH, 28/28 | 39 | KB, C, RH, 45/5/20 | 62 | NF, C, RH, 28/14 |
| 17 | NF, C, RH, 20/20 | 40 | KB, C, RH, 45/5/28 | 63 | NF, C, RH, 28/14 |
| 18 | NF, C, RH, 20/10 | 41 | KB, C, RH, 45/5/28 | 64 | NF, C, RH, 20/20 |
| 19 | nCF, ^e 14/14 | 42 | KB, C, RH, 45/5/42 | 65 | NF, C, RH, 20/20 |
| 20 | KB, C, RH, 45/5/14 | 43 | NF, C, RH, 14/14 | 66 | NF, C, RH, 20/20 |
| 21 | KB, C, LH, 45/5/14 | 44 | HF, C, RH, 14, 14 | 67 | NF, C, RH, 20/10 |
| 22 | NF, C, RH, 20/20 | 45 | NF, C, LH, 20, 10 | 68 | NF, C, RH, 20/10 |
| 23 | NF, C, RH, 20/20 | 46 | NF, C, RH, 14/14 | | |

^a Screw elements on each shaft = 68.

^b U, undercut; F, flight; C, conveying; RH, right-handed (forwarding action); 42/42, pitch/element length (mm).

^c Undercut to normal (N) flight transition screw.

^d KB, kneading block; nC, nonconveying; 90/5/28, disc angle/number of discs/element length (mm).

^e RH conveying element superimposed on an LH (left-handed or reverse pitch) screw element.

feeder (Model T20, K-TRON Corp., Pitman, NJ). Mixtures of either EG and acid or glycerol and acid were metered into barrel 2 (element 4) by reciprocating positive displacement pumps (Model EK-3 and FC-3/V, American LEWA, Inc., Holliston, MA). Instrumentation, process control, and monitoring (temperature, torque, pressure, power consumption, screw speed, and feed rate) were all done from the remote control panel for the extruder.

Reaction Process

The procedure for converting starch substrates to glucosides is exemplified as follows: Process temperatures were set at 125°C (zone 1, barrels 2 and 3), 160°C (zones 2–5, barrels 4–11), 125°C (zone 6, barrel 12), and 25°C (zone 7, barrels 13 and 14). Temperature was kept relatively low in zone 1 to allow mixing to occur prior to high-temperature contact. Temperature at zone 6 was lowered to facilitate reaction quenching in zone 7. After the set

barrel temperatures were reached, the screw was started and quickly adjusted to 200 rpm. Immediately upon starting the screw, the EG–acid mixture was pumped into barrel 2, through a drilled port plug, at the rate of 39 mL/min (0.567 g H₂SO₄/39 mL solution). About 5 sec later, granular starch with 10% moisture was fed into barrel 1 (30°C) by the twin-screw feeder at the rate of 84.0 g/min. These feed rates represent an EG/starch AGU mol ratio of 1.5, a starch concentration of 59.3%, and an acid addition level of 0.75% (dry starch basis). After maintaining a steady-state condition for 15 min, 1-L samples of extrudate were collected for analyses, and process data were recorded. Process data included barrel and materials temperatures, torque, die-head pressure, extruder power consumption, and residence time (RT). To determine the RT, finely powdered carbon black (0.1 g) was dropped into the starch feed port directly onto the extruder feed screw. The time periods that were required to see the beginning and the end of black material discharged from the die-head assembly was recorded.

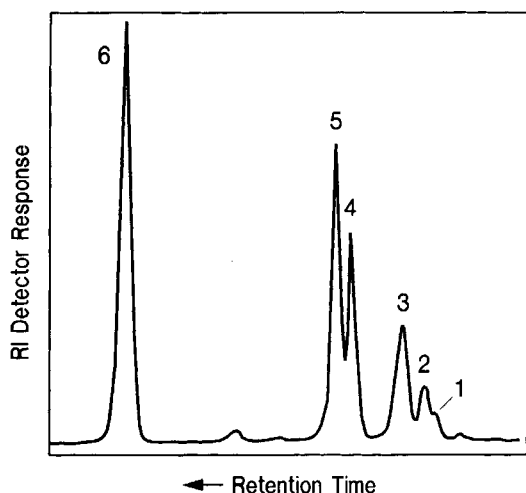


Figure 1 HPLC chromatogram of starch-ethylene glycol-acid extrudate (2.389 g extrudate diluted to 100 mL with water).

Analyses

The extrudates were analyzed for viscosity (Model LVT Brookfield viscometer, Brookfield Engineering, Inc., Stoughton, MA), dextrose equivalent,⁶ pH (10 g extrudate/50 mL distilled H₂O dilution), and glucoside composition by HPLC.

HPLC was performed with a Model M-6000A pump, a WISP 710 automatic injector, an R401 differential refractometer (Waters Associates, Milford, MA), an Aminex HPX-87H column (Bio-Rad Laboratories, Richmond, CA), and water as the mobile phase. Injection volume was 10 μ L, and aqueous eluent was pumped at the rate of 0.6 mL/min. Duplicate 2-g subsamples of extrudate were weighed to the nearest mg, diluted to 100 mL with distilled water, filtered through 0.45-micron filters (Millipore, type HA), and analyzed quantitatively by HPLC

for the major glucosides. Glycol glucosides were separated on an activated carbon column by the method of Otey et al.⁷ and used as reference compounds. Glycerol glucosides were separated only on the HPX-87H analytical column.

RESULTS AND DISCUSSION

HPLC

The complete reaction of starch with EG and sulfuric acid catalyst in the extruder produces a mixture of glucosides, low-molecular-weight starch, reducing sugars, and degradation products. The latter products imparted yellow to dark brown colors at intensities dependent upon reaction conditions. Most of the color can be removed by carbon black treatment. Figure 1 shows a typical HPLC chromatogram of a crude extrudate, obtained by essentially complete reaction of ordinary cornstarch with EG. The reaction was carried out at a 4.0 EG/starch mol ratio, 0.75% acid (dry starch basis), a starch feed rate of 10 lb/h (11.11 lb/h with moisture), a screw speed of 200 rpm, and a maximum temperature of 160°C (zones 2-5, see Experimental). The reaction was quenched, as done in the entire study, by lowering product temperature to about 50°C, using the barrel-jacket cooling system in zone 7. Chromatogram peaks 3, 4, 5, and 6 are the glycol diglucoside, glycol β -D-glucoside, glycol α -D-glucoside, and EG, respectively. Constituents of the other peaks have not been identified. Based on relative areas of peaks 1-5, about 40% of the starch was converted to the α -D-glucoside, 27% to the β -D-glucoside, and 23% to the diglucoside (Table II). Using pure glucoside reference compounds, the conversion values were 37, 25, and 24%, respectively. These two quantitative

Table II HPLC Data of Ethylene Glycol-Starch Extrudate

| Peak No. | Retention Time (min) | Relative Peak Area | % Starch Converted (Yield) | |
|----------|----------------------|--------------------|-----------------------------|-------------------------------|
| | | | Based on Relative Peak Area | Based on Reference Glucosides |
| 1 | 6.6 | 2,771 | 2.1 | — ^a |
| 2 | 6.9 | 9,973 | 7.8 | — ^a |
| 3 | 7.7 | 29,061 | 22.6 | 24.3 |
| 4 | 9.4 | 35,067 | 27.3 | 25.3 |
| 5 | 9.9 | 51,766 | 40.2 | 37.4 |
| 1-5 | 6.6-9.9 | 128,638 | 100.0 | NA |
| 3-5 | 7.7-9.9 | 115,894 | 90.1 | 87.0 |

^a No reference materials (unknown constituents).

methods indicate that about 87–90% of the starch was converted to the glucosides under peaks 3, 4, and 5. About 5% of the starch was converted to reducing sugars.⁶ Subsequently, the percentage of starch converted to the three major glucosides, in total, is referred to as glucoside yield.

Rate and Extent of Reaction

The most significant variables that affected the rate and extent of reaction in converting starch to the three major glucosides in the extruder were temperature, time, mol ratio of reactants, and acid catalyst concentration. Screw speed and material feed rates were less important with the exception of starch feed rate at the lowest rate investigated. Certain expressions should be defined before these variables are discussed.

The term “rate of reaction” is defined as the percent of starch that was converted in the extruder to the three major glucosides per second. The average length of time that the reactants were in the extruder is defined as the residence time (RT). The RT was determined by a test in which the lengths of time required to see the first and last traces of a carbon black adjuvant in the extrudate were averaged. Since the reaction was quenched in the last barrel zone of the extruder (see Experimental), the RT gives a good estimate of the reaction time. The terms “extent of reaction,” “percent conversion,” and “yield” are used interchangeably to refer to the percent of starch that was converted to the three major glucosides in total as determined by the HPLC analysis.

In the preceding HPLC example, the percent of starch converted to the three major glucosides was 87–90 (average 88.5%); the RT was 65 sec (beginning/end of carbon black, 40/90 sec); and the rate of reaction was 1.36%/sec (88.5% ÷ 65 sec).

Temperature and Mol Ratio

Our previous work indicated that 0.75% sulfuric acid (starch basis) was the optimum level of addition.⁵ This level was used for the present study. Figure 2 shows the effect of barrel temperature and mol ratio of reactants for ordinary cornstarch. The feed rate was 10 lb/h, and the screw speed was 200 rpm. Material temperatures at barrel 11 were similar to the set temperatures of barrels 7–11. Temperatures from 140–180°C critically affected the extent of reaction at quenching time, particularly at the higher EG/starch mol ratios. For example, a glucoside yield of about 90% was obtained with use of an EG/starch mol ratio of 4.0 at 160°C, compared to 48% at 140°C.

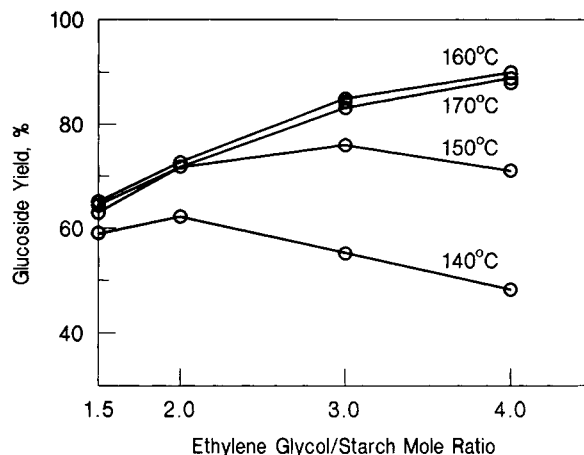


Figure 2 Effect of reaction temperature and mol ratio on yield of starch-derived glycol glucosides in extrudates. Extruder: starch feed rate, 10 lb/h; screw speed, 200 rpm.

A slight increase in glucose moiety degradation occurred at 170°C as evidenced by darker colors of the extrudates and corresponding lower glucoside yields. However, the glucosides *per se* are stable at 180°C. EG/starch mol ratios of 3.5–4.0 were required to obtain 85–90% yields. Higher yields than those shown on the 160 and 170°C curves could not be obtained by reheating the extrudates for an additional 15 min at 160°C. The maxima extents of reaction that can occur if the extrudates were not quenched were highly dependent upon mol ratio. RT and rate of reaction were also importantly affected by mol ratio. For example, the RT values for the curve end points were 120, 110, and 65 sec for 140, 150, and 160°C, respectively. The corresponding rates of reaction were 0.37, 0.65, and 1.35 %/sec. When underconverted extrudate samples (140–150°C, 4.0 mol ratio) were heated at 160°C in batches for 15 min, extents of reaction increased to 86–88%. The shapes of the curves are believed to result from a complex interrelationship of variables such as viscosity, barrel fill, shear stress, heat and mass transfer, and RT, all of which are affected by a change in temperature and mol ratio.

Screw Speed

The effect of extruder screw speed in the reaction process is shown in Figure 3. Screw speed was increased from 100 to 200 to 400 rpm at starch feed rates of 10 and 20 lb/h, EG/starch mol ratios of 2.0–4.0, and barrel temperatures of 150–180°C. These data show that the extent of reaction at quenching time was not altered significantly when

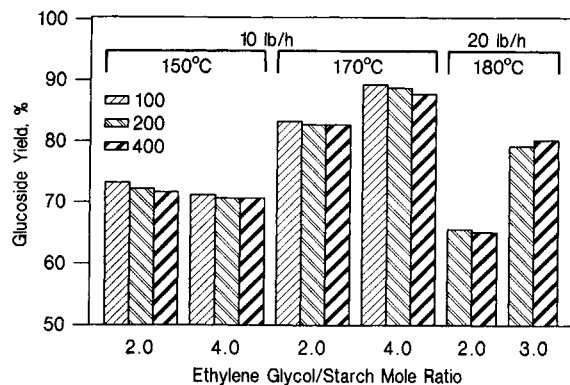


Figure 3 Effect of screw speed on yield of starch-derived glycol glucosides in extrudates. Screw speeds, 100–400 rpm. Starch feed rates, 10 and 20 lb/h. Reaction temperatures, 150–180°C.

screw speed was changed. However, since the RTs of the reaction mixtures were affected by screw speed, the reaction rates were also affected. For example, with the condition of 150°C/4.0 mol ratio, the rates of reaction were 0.49, 0.63, and 0.75%/sec for 100, 200, and 400 rpm, respectively. The effect of screw speed and other variables on RT is discussed later.

Feed Rate/Throughput

The effect of starch and EG feed rates in the conversion process is shown in Figure 4. Data are shown for a temperature of 170°C, a screw speed of 400 rpm, and EG/starch mol ratios of 3.0 and 4.0. In general, there was a surprisingly small effect over a

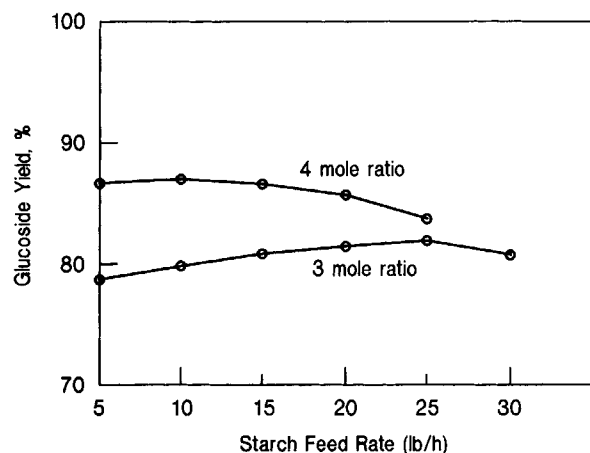


Figure 4 Effect of starch feed rate on yield of starch-derived glycol glucosides in extrudates. Reaction temperature, 170°C. Screw speed, 400 rpm. Glycol/starch mol ratios, 3.0 and 4.0.

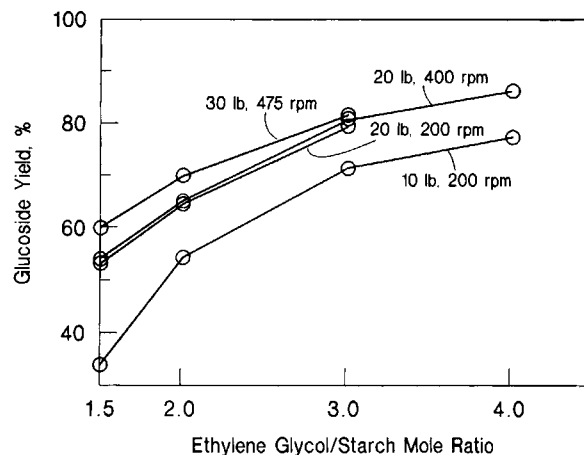


Figure 5 Yield of starch-derived glycol glucosides in extrudate at various processing conditions. Starch, 10–30 lb/h. Screw speed, 200–475 rpm.

wide range of throughputs. Glucoside yields increased from 79% at a starch feed rate of 5 lb/h to 85% at 25 lb/h, using a 3.0 EG/starch mol ratio. With the 4.0 mol ratio, there were slight decreases in yields with increases from 15 to 25 lb/h starch, which is believed to be primarily due to increases in barrel fill, sufficiently high to reduce heat transfer efficiency.

Figure 5 shows glucoside yields for selected feed rates, screw speeds, and mol ratios at a temperature of 180°C (zones 2–5). At this temperature, yields were less than maximum at all mol ratios with use of a starch feed rate of 10 lb/h, due to an increase in rate of competitive sugar degradation reaction. Less degradation occurred, and yields were improved when the starch feed rate was increased. It was necessary to increase the screw speed to 475 rpm for the screw to accept a starch feed rate of 30 lb/h (33.3 lb/h with moisture) and an EG feed rate of 34.5 lb/h (3.0 EG/starch mol ratio). With these feed rates, the heaters in zones 2–4 could not quite maintain barrel temperatures, set at 180°C. Rate of reaction increased with increases in starch feed rate. For 5, 15, 20, and 25 lb/h starch (170°C/3.0 mol ratio/400 rpm condition), the rates of reaction were 0.52, 1.25, 1.65, and 1.86%/sec.

RT

Table III shows the RT of the reaction mixtures in the extruder at various processing conditions. In general, the carbon black was most concentrated during the initial one-third of the RT. The RTs indicate that increases in screw speed, EG/starch mol ratio, temperature, and starch feed rate each in-

Table III Residence Time of Reaction Mixture in Extruder

| Reaction Temperature (°C) | Starch Feed Rate (lb/h) | Glycol/Starch mol Ratio | Screw Speed (rpm) | Yield of Glucosides (%) | RT (sec) ^a | Reaction Rate (% yield/sec) ^b |
|---------------------------|-------------------------|-------------------------|-------------------|-------------------------|---------------------------|--|
| 150 | 10 | 4.0 | 100 | 71 | 95/200 ^a (148) | 0.48 |
| 150 | 10 | 4.0 | 200 | 71 | 70/155 (113) | 0.63 |
| 150 | 10 | 4.0 | 400 | 71 | 60/130 (95) | 0.75 |
| 170 | 10 | 2.0 | 400 | 67 | 67/135 (101) | 0.66 |
| 170 | 10 | 3.0 | 400 | 83 | 39/90 (65) | 1.28 |
| 170 | 10 | 4.0 | 400 | 88 | 37/90 (64) | 1.38 |
| 170 | 5 | 3.0 | 400 | 79 | 80/220 (150) | 0.52 |
| 170 | 15 | 3.0 | 400 | 80 | 33/95 (64) | 1.25 |
| 170 | 20 | 3.0 | 400 | 81 | 30/68 (49) | 1.65 |
| 170 | 25 | 3.0 | 400 | 84 | 27/63 (45) | 1.86 |

^a Time period of beginning/end of black discharge after addition of 0.1 g carbon black to the starch feed barrel during continuous operation are averaged in parentheses.

^b Percent yield of glucosides ÷ average RT values shown in parentheses.

creased the reaction rate. However, synergisms do not necessarily occur. The sharp increase in reaction rate by increasing the starch feed rate from 5 to 10 lb/h is particularly interesting, showing the importance of barrel fill/shear interaction. The effect of EG/starch mol ratio is believed to be primarily a chemical rather than physical effect on reaction rate. At the higher screw speeds, reaction was improved as a result of better mixing and heat transfer. As opposed to extent of conversion, the maximum rate of conversion was 84% in an RT of 45 sec (1.86%/sec) at the 25 lb/h starch feed rate. Although the RT distribution (RTD) of the material mass in the

extruder was fairly broad, the glucosides that are formed early in the reaction are quite stable at these high-temperature conditions. A quantitative RTD study was not done but would be considerably more important to follow for reactions in which constituents were unstable during the later stages of the RTD.

Starches and Flours

Table IV shows yields and percentage distributions of the three major glucosides in the extrudates for waxy and high-amylose cornstarches, and for the

Table IV Cornstarch and Corn Flour Reacted with Ethylene Glycol at 170°C^a

| Type of Cornstarch Substrate | Glycol/Starch Substrate mol Ratio | Yield of Glycol Glucosides | | | |
|------------------------------|-----------------------------------|----------------------------|----------------------|-------------------------|-------|
| | | α -D Glucoside | β -D Glucoside | α -D Diglucoside | Total |
| Waxy | 4 | 41 | 26 | 26 | 93 |
| | 3 | 37 | 23 | 30 | 90 |
| | 2 | 26 | 19 | 31 | 76 |
| 50% amylose | 4 | 41 | 25 | 25 | 91 |
| | 3 | 34 | 22 | 27 | 83 |
| 70% amylose | 4 | 40 | 25 | 26 | 91 |
| | 3 | 36 | 22 | 27 | 85 |
| | 2 | 26 | 17 | 31 | 74 |
| Corn flour | | | | | |
| Regular | 4 | 0.4 | 0.6 | 0 | 1 |
| Ultrafine | 4 | 0.5 | 0.5 | 0 | 1 |
| Pregelld | 4 | 1.1 | 1.2 | 0.7 | 3 |

^a See Experimental for source of products. Starches and flours were fed to the extruder at the rate of 10 and 15 lb/h, respectively. Screw speed was 200 rpm.

Table V Specific Mechanical Energy

| Starch Feed Rate (lb/h) | Glycol/Starch mol Ratio | Reaction Temperature (°C) | Screw Speed (rpm) | Glucoside Yields (%) | Extrudate | | |
|-------------------------|-------------------------|---------------------------|-------------------|----------------------|-----------------------------|--------------------------------|---------------|
| | | | | | Viscosity ^a (cp) | Production ^b (lb/h) | SME (kw-h/kg) |
| 10 | 4.0 | 140 | 200 | 49 | 6,460 | 26.4 ^c | 0.033 |
| 10 | 4.0 | 150 | 100 | 71 | 1,944 | 26.4 | 0.017 |
| 10 | 4.0 | 150 | 400 | 71 | 1,230 | 26.4 | 0.108 |
| 10 | 2.0 | 160 | 200 | 73 | 5,960 | 26.4 | 0.058 |
| 10 | 4.0 | 160 | 200 | 87 | 600 | 26.4 | 0.075 |
| 10 | 4.0 | 170 | 400 | 89 | 548 | 26.4 | 0.108 |
| 25 | 4.0 | 170 | 400 | 86 | 600 | 66.1 ^c | 0.023 |

^a Brookfield, Model LVT, 30 rpm, 25°C.

^b Total starch, glycol, and acid feed rate/h.

^c 26.4 and 66.1 lb/h = 12.0 and 30.0 kg/h, respectively.

corn flours, which were reacted at a feed rate of 15 lb/h, a screw speed of 200 rpm, and a barrel temperature of 170°C (zones 2–5). Rate and extent of reaction were both slightly greater for waxy cornstarch than for the other starches. Glucoside yields for the waxy cornstarch were 90 and 93% with use of EG/starch mol ratios of 3.0 and 4.0, respectively, compared to 85 and 91% for the 70% amylose cornstarch. The percentage distribution of the glucosides was primarily a function of the EG/starch mol ratio used in the reaction and of the extent of reaction. The distribution was not significantly affected by either reaction time, temperature, shear stress, and other physical conditions or by starch substrates containing widely different proportions of amylose and amylopectin.

The corn flours were surprisingly resistant to conversion. Glucoside yields were only 1–3%, due primarily to slow reaction rates. The pH values of the flour extrudates were higher than those of the starches (3.0–3.3 vs. 2.4–2.6), probably due to protonation of protein constituents. However, when the acid level was doubled (1.5% flour basis) to give an extrudate pH in the same range as for the starches (pH 2.4–2.6), the rate of reaction was still impractically slow in the extruder. In batch work, the ultrafine cornflour was converted to glucoside yields of 80–85% when 1.5% acid was used at 150°C for 2 h (4.0 EG/starch basis mol ratio).

Specific Energy

Table V shows the specific mechanical energy (SME) that was required to convert ordinary cornstarch to glycol glucosides at selected conditions. In general, the SME values are indicative of low to

moderate shear systems. Large differences in values were primarily due to starch feed rates and screw speeds. The lowest SME consumption resulted from a high production rate (30 kg/h of starch/glycol/acid). Higher production rates are possible since zones 6 (125°C), 7 (barrel cooling only), and 8 (unheated die head) were used for quenching the reaction. Most twin-screw processes use various extents of starved-barrel systems, i.e., the barrel is less than completely full. The optimum SME efficiency in this reaction tended to be with relatively high barrel fills. Considerably more study is needed to optimize total energy consumption, production rate, and extent of conversion. However, the continuous conversion of starch to glycol glucosides in the twin-screw extruder appears to be a practical and efficient approach.

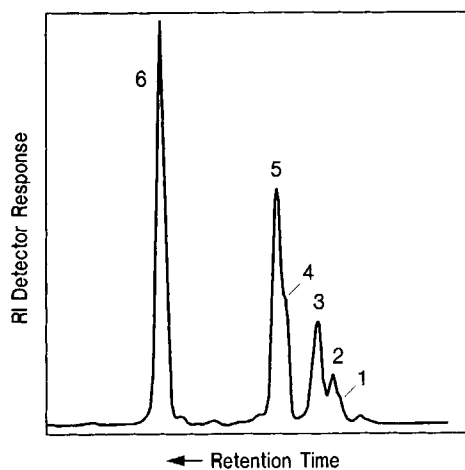


Figure 6 HPLC chromatogram of starch/glycerol/acid extrudate (2.112 g extrudate diluted to 100 mL with water).

Table VI HPLC Data of Starch-Glycerol Extrudate

| Peak No. | Retention Time (min) | Relative Peak Area | % Starch Converted (Yield) Based on Relative Peak Area |
|----------|----------------------|--------------------|--|
| 1,2 | 6.6, 6.8 | 13,826 | 10.8 |
| 3 | 7.4 | 31,109 | 24.3 |
| 4, 5 | 8.9, 9.0 | 83,072 | 64.9 |
| 1-5 | 6.6-9.0 | 128,007 | 100.0 |

Glycerol

Glycerol was reacted with ordinary cornstarch in the extruder at starch feed rates of 10–20 lb/h, glycerol/starch mol ratios of 2.0–4.0, screw speeds of 200–400 rpm, and a temperature of 170°C. With a 3.0 mol ratio (20 lb/h, 400 rpm), starch was converted completely to water-soluble constituents. The extrudate was less colored, slightly more viscous, and more completely converted than with use of an EG/starch mol ratio of 3.0. An HPLC chromatogram of this extrudate is shown in Figure 6. Corresponding HPLC data are in Table VI. The pattern of peaks is quite similar to that exhibited by the glycol glucosides and may suggest that the mixture of major constituents is much less complex than theoretically possible for a trihydroxy alcohol. Peak 6 is glycerol. Based on the relative peak areas, about 65% of the products are under peaks 4 and 5, 24% under peak 3, and 11% under peaks 1 and 2. The major constituents are believed to be primarily anomeric glycerol mono- and diglucosides, but they have not been characterized. The study indicates that starch is as readily converted to glucosides in the extruder with use of glycerol as with EG and suggests that reactive extrusion processing could be effectively adapted to the conversion of starch to many other types of polyhydroxy glucosides.

CONCLUSIONS AND FUTURE WORK

The present work is the first to establish the feasibility of converting the high polymer starch directly to glycol and glycerol glucosides in high yields, high production rates, and short reaction periods of 45–60 sec by a continuous twin-screw reactive process. These glucosides have excellent potential as chem-

ical intermediates for urethane foams and a wide range of other products. However, one major objective of this work was to demonstrate the suitability of the twin-screw extruder for the specific type of reaction investigated so that the principles and techniques of the study can be applied to similar types of reactions and materials. Future studies may include the reaction of starch with higher molecular weight polyhydroxyalcohols and hydroxyl-containing fatty acids. Viscous systems that cannot be handled in batch systems are of particular interest. Currently, other types of systems in the twin-screw extruder are also being investigated, such as starch-graft polymerization and encapsulation reactions.

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