

Glycol Glucosides from Starch by Continuous Twin-Screw Extruder Processing

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ABSTRACT

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Acid-catalyzed transglycosylation of starch with ethylene glycol yields a mixture of glycol glucosides that have potential as chemical intermediates for urethane foams, alkyd resins, surfactants, and other products. This reaction was carried out continuously, rapidly, and efficiently in a corotating, intermeshing twin-screw extruder. Rate, extent, and conditions of reaction as well as composition of the crude extrudates were studied. Effects of temperature, acid concentration, screw speed, feed rate

(throughput), and residence time were evaluated. Quantitation of the major glucosides in the crude extrudates was carried out by high-performance liquid chromatography. Under optimum reaction conditions 88% of the starch was converted to a mixture of glycol α -D-glucoside, glycol β -D-glucoside, and a diglucoside in a ratio of 1.0:0.6:0.6. This was accomplished in a reaction period of less than 1 min compared with about 20 min for small batch reactions also studied.

There is great potential for chemically and physically modifying cereal substrates in extruders for nonfood industrial applications. Corn starch continues to be an abundant, readily available, and low-cost source of polymeric carbohydrates suitable for chemical modifications. Twin-screw extruders are well recognized in the food and plastics industries as versatile and highly efficient continuous-type mixers for handling the most difficult mixing and compounding requirements (El-Dash 1981, Linko 1981, Mielcarek 1987). Twin-screw extruders are now being recognized as excellent in-line reactors for carrying out polymerization reactions (Eise 1986, Wielgolinski and Nangeroni 1982) and for creating new and unusual resins and thermoplastics (Sneller 1985). Corotating, intermeshing twin-screw extruders are inherently better mixers than single-screw extruders and are particularly suitable for reactive extrusion processes (Frund 1986). An excellent analysis of twin-screw extruder mechanisms has been reported (Eise et al 1981).

Although the literature on starch chemistry and technology is abundant, relatively little attention has been given to the use of extruders as reactors for converting starch to either polymeric derivatives or basic building-block chemicals. Starch extrusion studies have been limited mainly to reactions of starch with water, acid, alkali, and/or enzymes (Mercier et al 1979, El-Dash 1981, Linko 1981, Korn and Harper 1982, Colonna et al 1983, Hakulin 1983, Diosady et al 1985, Kervinen et al 1985). Currently, there is considerable interest in biodegradable films blown from extruded blends of starch and synthetic polymers such as polyethylene (Swanson et al 1987). There appears to be considerable opportunity for developing new reactive extrusion technologies to improve efficiency of starch processing and to create new starch-based products.

One reaction of interest for reactive extrusion study is the acid-catalyzed transglycosylation of starch with ethylene glycol. This reaction yields a mixture of glycol glycosides whose composition is primarily mono- and diglucosides. Preparation and use of these products have been studied considerably in batch reaction processes (Otey et al 1965a,b; Otey et al 1968; Leitheiser et al 1966; McKillip et al 1970). Mixtures of these glycosides were reacted with propylene oxide and then diisocyanates to form rigid urethane foams with excellent properties (Otey et al 1963; 1965a,b; 1969). Based on previous studies, glycol glucosides have potential for becoming industrial chemical intermediates for a variety of products including alkyd resins, surfactants, and urethane foams. However, methods to improve reaction efficiency may be necessary to generate industrial interest in these products.

Currently, methyl glucoside is a well-accepted industrial polyol initiator for preparation of rigid urethane foams.

In our work we studied the acid-catalyzed starch/ethylene glycol transglycosylation reaction in a small, corotating, intermeshing twin-screw extruder. Although this reaction was previously investigated in a single-screw plastics extruder (Roth 1967), little or no information was reported on reactive extrusion processing variables, capabilities, or extent of starch converted beyond 60%. Objectives of our study were to assess the capability of the twin-screw extruder as a reactor for converting starch to glycol glucosides, to study the rate, extent, and conditions of reaction as well as the composition of the crude extrudates, and to optimize reaction conditions to achieve complete conversion of starch in the extruder within a small fraction of the time required in batch reaction processes.

MATERIALS AND METHODS

Chemicals

Materials included ordinary corn starch (Buffalo 3401, general purpose, thick-boiling food grade, pH 5.3, CPC International, Englewood Cliffs, NJ), ethylene glycol (99% purity, 55-gal drums, Aldrich Chemical Co., Milwaukee, WI), and H₂SO₄ (96.4%, J.T. Baker Chemical Co., Phillipsburg, NJ).

Extrusion Equipment

A Readco 2-in. (50.8-mm) continuous processor manufactured by Read Corp. (York, PA) under U.S. patents 3,419,250 and 3,618,902 was employed as the reactor. The mixing design of the processor (extruder) is similar to that of corotating, intermeshing twin-screw extruders in that materials flow in a horizontal figure-eight-shaped pattern. Each screw shaft of the extruder was equipped with a 106-mm-long feed screw followed by 25 flat, lens-shaped, kneading paddles extending for 336 mm from the end of the feed screws to the outlet. These paddles were aligned face to face in a broken-screw arrangement at a 45° angle to each other. With each screw revolution the barrel surface is wiped twice by ends of the paddles, and the faces of the paddles are wiped once by mating paddles. Each paddle is keyed to the shaft, and the entire mixing assembly is locked together to prevent lateral motion. The extruder screws are powered by a 1-hp Polydyne-drive motor. Screw speeds are adjustable from 50 to 155 rpm. Internal dimensions of the barrel are 51 mm (diameter of each lobe) × 440 mm (length). The discharge opening is a 50 × 50-mm sideport with an adjustable slide gate (weir). The entire barrel is jacketed for circulating heating or cooling media. Steam was circulated through this jacket at pressures to 120 psi.

Ancillary Processing Equipment

Power consumption (kW) of the extruder drive motor was monitored continuously by an Esterline-Angus Graphic Wattmeter (Indianapolis, IN). Temperature was monitored continuously with a thermocouple, located internally in the barrel 80% downstream (88 mm from discharge opening), wired to a

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Foxboro Dynalog chart recorder (Foxboro Co., Foxboro, MA). Thermocouple temperatures were similar to extrudate temperatures measured with a thermometer at the discharge opening.

A model 1140 Chemcon diaphragm pump (Chemcon, Inc., Medfield, MA), with a pumping capacity of 1,500 ml/min for water, was employed to pump slurries of starch, ethylene glycol, and H₂SO₄ from a tank to the extruder feed screws. The tank was equipped with an air-driven marine-type propeller. All metal parts including internal extruder surfaces in contact with the reaction mixtures were stainless steel. The inlet and outlet of the extruder and the collection waste tank were vented to the atmosphere.

Reaction Extrusion Procedures

To 17.01 kg of ethylene glycol was admixed 85, 170, or 340 g of concentrated H₂SO₄ and then 12.47 kg (11.11 kg, dry basis) of starch, which were added slowly while mixing well. The slurry was stirred throughout the extrusion runs to keep the starch suspended. These slurries had a starch concentration of 37.6% (w/w), a glycol-to-anhydroglucose unit (AGU) mole ratio of 4.0, an acid addition level of 0.75, 1.5, or 3.0% (dry starch basis), and a water concentration of 5%. One hour after combining the reactants, the slurry was pumped into the extruder feed port at rates of 50–210 ml/min, screw speeds of 50–150 rpm, and barrel temperatures of 130–165°C. The weir was kept fully open. Samples of extrudate were collected for each set of conditions at the discharge opening after maintaining steady state operation for at least 15 min. About 150 g of each sample was collected in a 400-ml beaker which was one-quarter filled with crushed dry ice. About 2 sec elapsed before the stream of extrudate contacted the dry ice.

Small batch experiments were conducted by reacting starch (7.2 g, dry basis) with ethylene glycol (3.56–11.13 g) and H₂SO₄ (0.014–0.050 g) in 50-ml round-bottom flasks. These quantities represent a range of 37–62% starch concentrations (w/w), 1.3–4.0 mole ratios of glycol to AGU, and 0.2–0.7% H₂SO₄ (dry starch basis). The flasks were placed in an oil bath at 130–155°C for 10–180 min while keeping the contents stirred. For reaction periods longer than 30 min, the flasks were equipped with condensers. After removing the flasks from the oil bath, the reaction was quenched within 1 min by lowering the product temperature to 25°C.

Analyses

Duplicate 2-g subsamples from each crude extrudate were weighed to the nearest milligram, mixed vigorously with about 75 ml of distilled water (25°C), and diluted to 100 ml. Five-milliliter portions of the diluted subsamples were filtered through 0.45- μ m filters (Millipore, Type HA, 25-mm diameter) for high-performance liquid chromatography (HPLC) analysis. Also, 2-g subsamples were diluted to 100 ml with 95% ethanol, mixed well, filtered through tared filters (47-mm diameter), and washed with 5 ml of ethanol. Filters with material collected were oven-dried and

weighed. For HPLC analysis of constituents in the filtrates, ethanol was removed under vacuum at 50°C and replaced with distilled water to 100 ml.

HPLC was performed with a model M-6000A pump, a WISP 710 automatic injector, an R401 differential refractometer (Waters Associates, Milford, MA), an Aminex HPC-87H column (Bio-Rad Laboratories, Richmond, CA), and deionized water as the mobile phase. Injection volumes were 10 and 20 μ l, and eluent was pumped at the rate of 0.6 ml/min.

Dextrose equivalent of the crude reaction products was determined by a ferricyanide method (Farley and Hixon 1941).

Viscosities of the crude reaction products were determined with a model LVT Brookfield viscometer (Brookfield Engineering, Inc., Stoughton, MA) at 25°C, 30 rpm spindle speed, 20 hr after collection, immediately after mild stirring.

RESULTS AND DISCUSSION

Polymer mixing phenomena in corotating, intermeshing twin-screw extruders are complex (Bigio and Erwin 1985). In the acid-catalyzed reaction of starch with ethylene glycol (EG), mixing is particularly complicated because the starch and intermediate products are continuously undergoing chemical and physical changes until the reaction is quenched. Typical changes that occurred during the extrusion process in which starch is converted to glucosides were as follows. A slurry of starch, EG, and H₂SO₄ with a viscosity of 250 centipoise (cP) at 25°C was starve fed into the twin-screw extruder at a barrel temperature of 165°C, a screw speed of 100 rpm, and slurry feed rate of 100 ml/min. The starch swelled rapidly to a high paste viscosity upon entering the mixing paddle section. The material progressively thinned as it was transported downstream, and was discharged as a nearly water-thin, clear, amber solution. The extrudate thickened to the consistency of a flowable syrup at room temperature. During the more viscous stages of processing, the material was apparently transported primarily by plug flow in a laminar fluid condition. Thereafter, the extent of plug flow decreased as fluidity and backmixing increased. EG promoted rapid swelling of the starch, whereas acid promoted starch depolymerization (hydrolysis) and transglycosylation of the reducing end groups. Swelling, hydrolysis, and transglycosylation apparently occur simultaneously during early stages of reaction, and are all highly dependent upon temperature.

Processing Variables

Table I presents selected data on reaction of starch with EG in the extruder for the formulation described in Materials and Methods. The formulation was similar to that previously used in small batch reactions at an EG/AGU mole ratio of 4.0 (Otey et al 1965a,b). Feeding the extruder either a slurry substantially more concentrated in starch (lower EG/AGU mole ratio) or feeding the

TABLE I
Selected Data from Transglycosylation of Corn Starch with Ethylene Glycol in a Twin-Screw Extruder^a

Run No.	Screw Speed (rpm)	Process Temperature (°C)	Feed Rate/Throughput (ml/min) ^b	Residence Time (sec)	Sample Quenched in Dry Ice	Yield of Glucosides (%) ^c	Yield Rate (yield/sec) ^d	Brookfield Viscosity (cP) ^e
1	50	130	110	300	yes	18	0.06	7,700
2	50	150	101	124	yes	71	0.57	2,100
3	50	165	100	62	yes	84	1.35	1,360
4	100	165	100	49	yes	87	1.77	1,240
5	150	165	100	39	yes	88	2.26	1,200
6	100	165	175	61	yes	59	0.97	3,560
7	100	165	175	61	no	88	NA	1,040
8	100	165	210	67	yes	53	0.79	4,360
9	100	165	210	67	no	84	NA	1,330

^aReadco 2-in. twin-screw extruder (see Materials and Methods).

^bStarch/ethylene glycol/sulfuric acid slurry (see Materials and Methods).

^cPercent of starch converted to total mono- and diglucosides.

^dYield of glucosides \div residence time.

^eCentipoise.

extruder starch and EG separately was impossible with the feeding equipment available. At a 3.0 EG/AGU mole ratio the slurry was dilutant and could not be pumped. Samples of the extrudates were quenched with dry ice immediately upon discharge to study the rate and extent of reaction in the barrel. Unquenched samples also were selectively collected.

Yield of glucosides refers to the percentage of starch that was converted to glycol α -D-glucoside (2-hydroxyethyl α -D-glucopyranoside), glycol β -D-glucoside, and glycol diglucoside (ethylene bis [α -D-glucopyranoside]) in total. HPLC analysis of these and other constituents in the crude extrudates is discussed later. Each

yield value was divided by the amount of time the material was in the extruder (residence time, RT) to give an estimated average yield/sec. This is subsequently referred to as yield rate. The RT has been defined as the effective volume (volume of material in the barrel)/throughput rate.

Data in Table I illustrate the effect of changing screw speed, temperature, and throughput (feed rate) on yield rate. When screw speed was increased from 50 to 100 rpm at a throughput of 100 ml/min and a barrel temperature of 165°C, a very small increase in yield occurred (runs 3 and 4). However, since the RT decreased correspondingly, the yield rate was 1.3 times greater at 100 rpm (from 1.35 to 1.77). The rate was 1.7 times greater at 150 rpm (runs 3 and 5). Although the maximum yield was 88% (run 5), 87–88% yields were obtained at other conditions to be discussed.

Temperature was an extremely important variable in the reaction. When barrel temperature was increased from 130 to 150°C the yield increased from 18 to 71%, and the yield rate increased ninefold (runs 1 and 2). The yield rate was 22.5 times greater at 165°C than at 130°C (runs 1 and 3). Temperatures above 165°C could not be investigated due to equipment and safety limitations.

Throughput rate also had a very large effect on conversion rate. For example, an increase from 100 ml/min to 210 ml/min (100 rpm, 165°C) reduced the yield from 87% (39-sec RT) to 53% (67-sec RT) (runs 4 and 8). Thus, the average yield rate for the higher throughput was about one-third of that for the lower throughput.

Samples that were extruded at 165°C, but not quenched, retained sufficient heat to facilitate much of the reaction ex situ (runs 6 vs. 7 and 8 vs. 9). These samples were simply stirred in uninsulated glass beakers while cooling at ambient conditions. Thus, a number of continuous or batch post-reaction schemes could be developed that would permit higher production rates with little, if any, additional energy consumption.

Brookfield viscosities of extrudates with 84–88% yields ranged from 1,040 to 1,360 cP at 25°C (30 rpm spindle speed). Viscosities of these extrudates were 3–5 cP at 150°C.

Screw speed, temperature, and throughput rates are interrelated with respect to effect on reaction rate. For example, an increase in temperature and/or decrease in throughput caused decreases in viscosity, effective volume, and RT.

Temperature and Throughput

The effect of changing the temperature and the throughput rate on yields of the glycol glucosides is shown in more detail in Figure 1. Screw speed was constant at 100 rpm for the curves shown. Curve 1 (165°C) and curve 2 (150°C) are almost parallel, showing that the differences in yields due to changes in temperature were almost constant at various throughputs. An approximate 2% change in yield occurred for each degree centigrade for throughputs from 100–200 ml/min.

At either 150 or 165°C the relationship between throughput rate and yield was fairly consistent. The ratio of yield to throughput decreased slightly at higher throughput rates. This is particularly evident at the processing temperature of 130°C. The RTs for the entire range of conditions need additional study to warrant a definitive discussion.

Acid Concentration

The effect of acid catalyst concentration in the reaction process is shown in Figure 2. These curves reflect the effect of acid on rate of reaction until quenching. Yields generally increased as acid level was increased. For example, at 150°C and 175 ml/min yields were 40 and 60% for 1.5 and 3.0% H₂SO₄ (dry starch basis), respectively. This compares to 31% for 0.75% acid shown in Figure 1. However, the effect of acid levels was progressively less at the upper portions of the curves. These data suggest that the yield benefit at the higher acid levels would rapidly diminish with respect to time and energy required to produce the increased yield, particularly after about 80% yield is achieved. In this case it may be more energy efficient to partially react the starch and then recover and recycle (reprocess) the higher molecular weight materials. The higher molecular

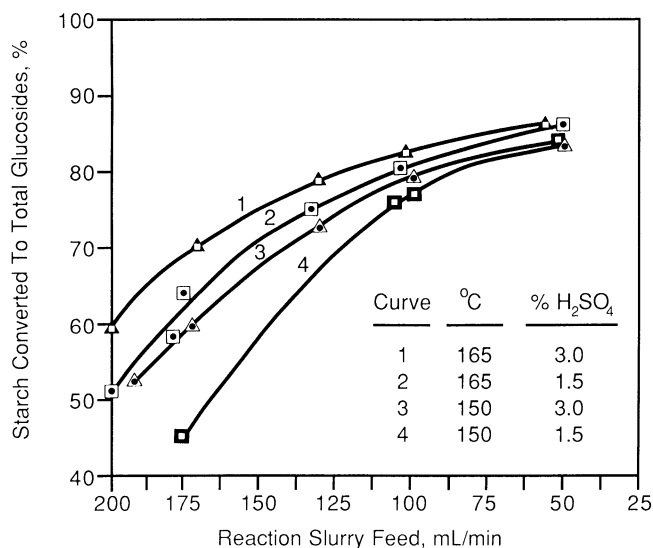


Fig. 1. Effect of changing temperature and throughput on yield of starch-derived glycol glucosides produced by twin-screw extruder processing at a constant screw speed of 100 rpm. Percent H₂SO₄, dry starch basis.

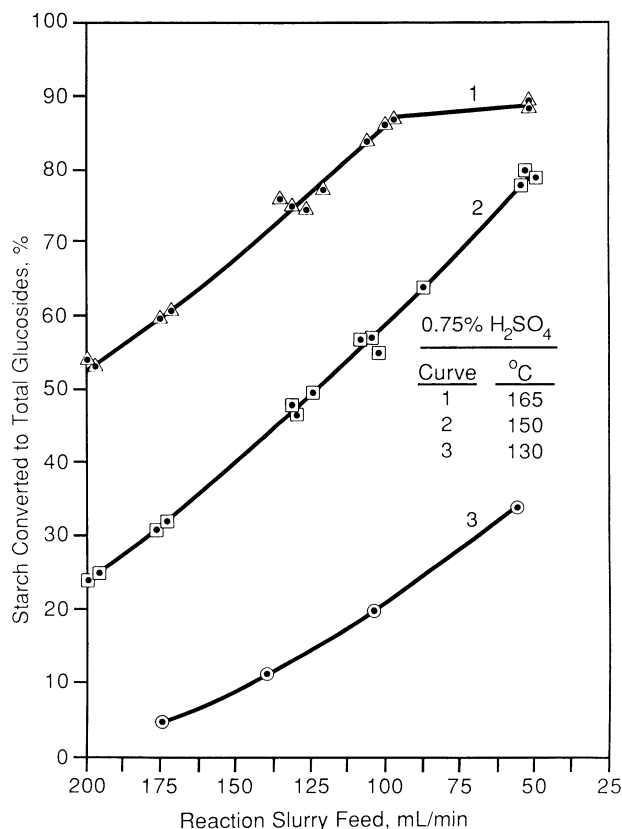


Fig. 2. Effect of H₂SO₄ concentration at various temperatures and throughputs on yields of starch-derived glycol glucosides produced by twin-screw extruder processing at a screw speed of 100 rpm.

weight materials readily precipitated in 95% ethanol, whereas the glucosides were soluble. As an alternative to recycling, the higher molecular weight materials could be studied for other uses. Conceivably, crude mixtures with 85, 80, 75% or lower yields could be investigated as polyols for a series of rigid urethane foams varying only in composition of the polyalkoxylated polyol initiators. Several other schemes are possible.

Specific Energy

Table II shows the specific energy consumed for selected extruder runs with the formulation described for Table I. Specific energy is defined as net kilowatt-hours per kilogram of glucosides produced. The net kilowatts for each condition is the kilowatts used under extruder load minus the kilowatts used under no load at the same screw speed and barrel temperature. The specific energy values are low and not substantially different from each other for high reaction yields. Values were slightly greater at 150 rpm and slightly lower at 50 rpm. Since the temperature was 165°C in these runs, low viscosities were rapidly reached. Thus, this temperature minimized the mechanical energy consumption at the expense of increased thermal energy used to heat the extruder barrel. We believe that excess ethylene glycol in the reactive system may serve as a lubricant to reduce frictional forces, contributing to the low net electrical power consumption.

HPLC

The three major products derived by batch reaction of starch with EG have been previously separated on a carbon column, identified to be the glucosides discussed earlier, and quantitated by a gas-liquid chromatography procedure (Otey et al 1965a,b). We repeated their batch reaction exactly as reported and analyzed the crude mixture by our HPLC procedure. The chromatogram was the same in all respects as that exhibited by our "88% yield" extrudate, except for minor differences in relative peak areas. Use of pure glycol β -D-glucoside (supplied by Otey) as a reference compound gave the same percentages of glycol glucosides as reported for the gas-liquid chromatographic procedure. Based on these results, this reference compound was used to quantitate the glycol glucosides in the extrudate.

Figure 3 shows HPLC chromatograms (C-1 through C-5) of the crude extrudates for glycol glucoside yields from 5 to 88%. Peaks 3, 4, and 5 were produced by the glycol diglucoside, glycol β -D-glucoside, and glycol α -D-glucoside in order of increasing retention time shown. Only peaks 3, 4, and 5 were used in calculating total yields (percentage of starch converted to glucosides). Peak 2 may contain a diglucoside anomer since three diglucoside anomers (α - α , β - β , and α - β) are theoretically possible. However, the identity of the products generating areas prior to peak 3 have not been established yet. Peak 1 probably contains low molecular weight starch products that were gradually converted to the glycol glucosides or other water-soluble products as extent of reaction increased (C-1 through C-5). Such constituents may include sugar glycosides as well as reducing sugars. Dextrose equivalent values (Farley and Hixon 1941) of the crude extrudates indicated that about 3-5% of the starch was converted to reducing sugars for the 88% yield products. No evidence for degraded sugars in the products was obtained, except that colors of the crude mixtures ranged from

light yellow (50% conversion) to brown (88% conversion). Unreacted EG, not shown on the chromatograms, was separated by the HPLC column at 16.3 min. There were no significant peaks between those for EG and glycol α -D-glucoside.

When the crude extrudates were mixed with water (2 g/100 ml total), high molecular weight material precipitated, except for the maximum 88% yield product. In this exception, 88% of the starch was converted to the three major glucosides; about 11% was converted to unidentified water-soluble products, and 1% or less was water-insoluble material.

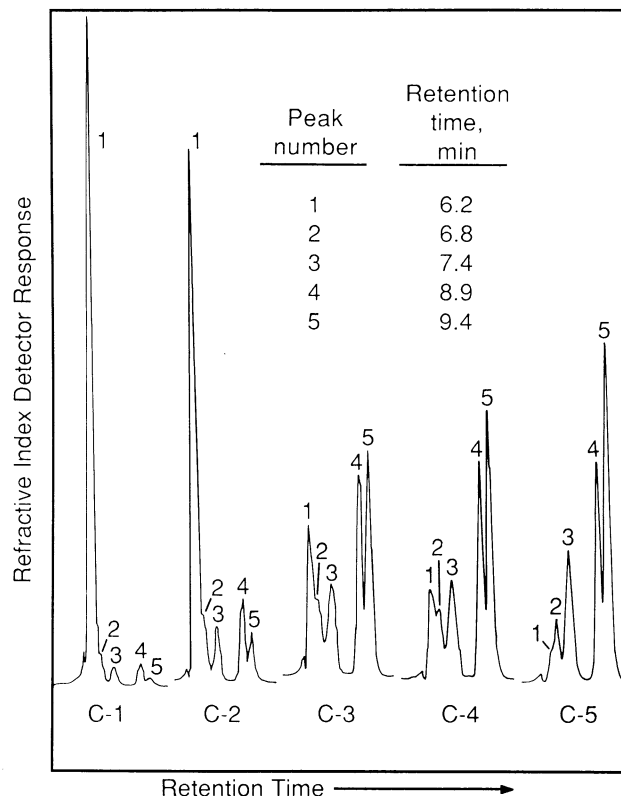


Fig. 3. High-performance liquid chromatograms of starch-derived glycol glucosides (peaks 3, 4, and 5) in extrudates produced by twin-screw extruder processing. Chromatograms C-1 through C-5 were obtained from crude mixtures of glucosides having yields of 5, 20, 50, 70, and 88%, respectively.

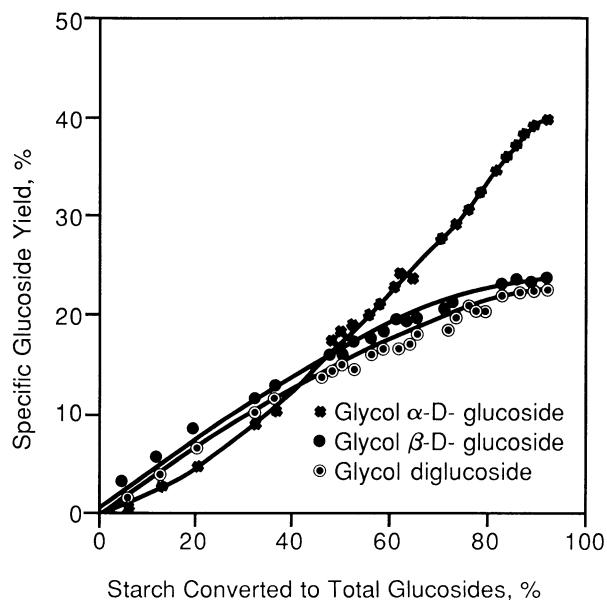


Fig. 4. Percentage distribution of starch-derived glycol glucosides in extrudates produced by twin-screw extruder processing.

TABLE II

Specific Energy Consumed in Twin-Screw Processing^a

Feed Rate/ Throughput (ml/min)	Mechanical Energy (kW × 10 ⁻³)		Yield of Glucosides (%)	Production Rate of Glucosides (kg/hr) ^b	Specific Energy (kW-hr/kg × 10 ⁻³) ^c
	Gross	Net			
100	100	5	87	2.90	1.72
175	117	10	59	2.40	4.17
210	120	10	53	2.31	4.37

^a Processing temperature, 165°C. Extruder screw speed, 100 rpm. Reaction formulation (in Materials and Methods).

^b Production rate of major glucosides only.

^c Extruder power consumption.

Distribution of Glycol Glucosides in Crude Reaction Mixtures

The percentage of starch converted to each specific glucoside discussed above is shown in Figure 4. The ratio of the glycol β -D-glucoside to the glycol diglucoside (β /di) in the extrudates was fairly constant for various extents of reaction (yields), whereas the ratio of the α -D-glucoside to the other two glucosides (α/β and α /di) were highly related to extents of reaction. The ratio of α to β to di (glucosides) was 1.0:0.57:0.58 for the 88% yield. Regardless of extruder processing conditions previously discussed, all points were plotted and found to fit the curves reasonably well. This could be a distinct advantage for industrial production of uniform product mixtures without need for exacting process control measures.

Mole Ratio of Reactants

A reaction parameter that importantly affected the ratio of glucosides in the crude mixture is the EG/AGU mole ratio. This parameter was examined only in small batch experiments (7.2 g dry starch basis) due to equipment limitations. When the EG/AGU mole ratio was varied from 1.3 to 4.0 with temperature and acidic conditions held constant, the ratios of α , β , and di (glucoside) varied considerably (Figs. 5 and 6 for 60 and 88% yields). As the mole ratio was increased the α/β ratio decreased moderately, the α - β -di ratio was 1.0:0.59:1.26 at the 60% yield and 1.0:0.45:1.11 at the projected 88% yield. The α - β -di ratio for the 4.0 EG/AGU mole ratio was essentially the same in batch experiments as those obtained in the extrusion work. In essence, higher proportions of the α -D-glucoside and lower proportions of diglucoside were obtained as the EG/AGU mole ratio was increased. The significance of these data in the preparation of urethane foams has not been studied.

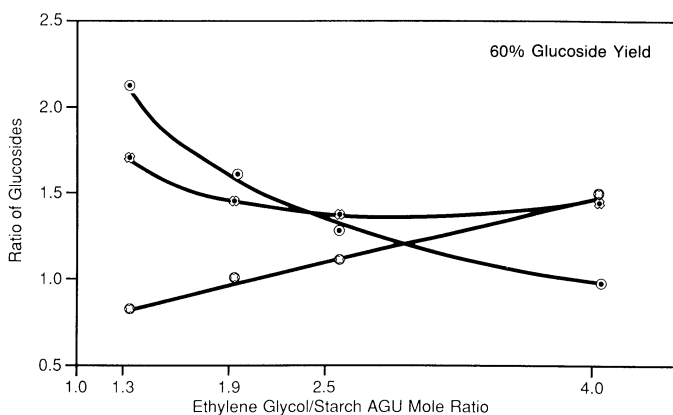


Fig. 5. Ratios of starch-derived glycol glucosides in extrudates for 60% yield, produced by twin-screw extruder processing at various ethylene glycol/starch anhydroglucose unit (AGU) mole ratios.

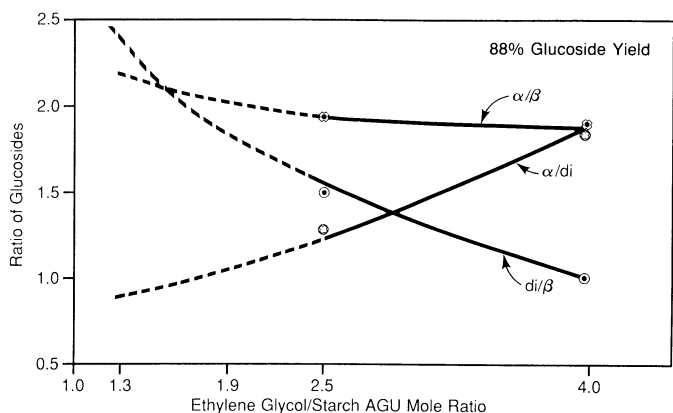


Fig. 6. Ratios of starch-derived glycol glucosides in extrudates for 88% yield, produced at various ethylene glycol/starch anhydroglucose unit (AGU) mole ratios.

The dotted lines in Figure 6 are extrapolations of the solid lines. These extrapolations may not be justified, because yields substantially greater than 60% were not obtained with the 1.3 EG/AGU mole ratio under several batch reaction conditions examined. Data examined, including some not presented, suggest that rate and extent as well as ratio of the glucoside constituents are functions of the concentration equilibrium between reactants and products.

Of considerable importance, a minimum of about 20 min was required to achieve an 88% yield in the small batch work compared to about 1 min for extruder reactions when using the 4.0 EG/AGU mole ratio. Although this extruder is suitable for carrying out this starch transglycosylation reaction continuously and rapidly, glucoside production rates were less than desirable for the size of the equipment. This is believed to be due primarily to the barrel length/diameter ratio ($L/D = 9$), which is substantially greater in most modern twin-screw extruders. A greater L/D ratio enhances mixing and heat transfer characteristics and increases the residence time for a given screw configuration and speed.

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