Glycol Glucosides Process Synthesis by Reactive Extrusion with a Static Mixer as Postextruder Reactor[1]

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ABSTRACT

Mixtures of starch (25% amylose), ethylene glycol, and concentrated sulfuric acid were extruded in a Brabender laboratory conical-twin-screw extruder with postextruder reactor modifications. Three reactor models were developed by adding a static mixer and heat exchanger to the die end of the extruder as postextruder reactor modifications. These models affected the residence time and reaction efficiency and, thus, the yield of glucosides. Process variables, including temperature, ethylene glycol–starch mole ratio, and screw speed, were permuted to enhance the yield of glucosides. High-performance liquid chromatography was used to identify the glucosides and evaluate yields. Response surface methodology was used to obtain optimum process conditions of 160°C, 20 rpm screw speed, and mole ratio of 3 with a static mixer and cooler for 91% maximum yield of glucosides.

The recent evolution of extruder design and technology has encouraged researchers to explore the potential of extruders as chemical reactors. The unique capability of extruders to mix, pump, melt, devolatize, and process high-viscosity reaction mixtures has made it feasible to extend their applications to carrying out chemical reactions. Thus, in recent years, the use of extruders as continuous reactors for processes such as polymerization, polymer modifications, and biopolymer processing has gained popularity. Twin-screw extruders are well recognized in the food and plastic industries as versatile and highly efficient continuous mixers for handling complex mixing and compounding requirements (El-Dash 1981, Linko 1981a, Mielecarek 1987, Carr et al 1989). Furthermore, twin-screw extruders are recognized as excellent continuous reactors for carrying out reactive extrusion processes (Eise 1986, Wielgolinski and Nangeroni 1982).

Though there seems to be keen interest in reactive extrusion, much work needs to be done on this process approach with respect to improving reaction efficiency and economics. This is necessary to generate industrial interest and replace existing conventional operations. Incorporation of postextruder devices as integral parts of an extrusion process poses an exciting challenge to tackle the process constraints of reactive extrusion. Static mixers as postextruder reactors are excellent candidates for reaction enhancement (Baker 1991, Grafelman 1993).

Acid-catalyzed transglycosylation of starch with ethylene glycol yields a mixture of glycol diglucoside, glycol β-D-glucoside and glycol α-D-glucoside, which have potential as chemical intermediates for urethane foams, alkyd resins, surfactants, and other materials (Otey et al 1963; Otey et al 1965a,b; Leitheiser et al 1966; Otey et al 1968, 1969; Carr et al 1992, 1993). Figure 1 shows the main reaction products formed in a acid-catalyzed transglycosylation starch and ethylene glycol reaction. The reaction has been studied in batch and extrusion processes. In the batch-reaction process, poor heat transfer and inefficient mixing limited yield of the glucosides to 60%. Moreover, the residence time necessary for the reaction to go to completion was too long. Carr et al (1989) and Carr (1991) studied a twin-screw extrusion process. Though the yield of glycol glucosides obtained was high, this only occurred at inefficient throughput rates, making the process semicontinuous. This was attributed to a short barrel and an inadequate barrel length-to-screw diameter ratio. However, these problems were overcome when the reaction was studied in a corotating, intermeshing, twin-screw extruder with an L/D ratio of 43:1, giving a high yield of 88% of glycol glucosides.

The purpose of this study was to develop a continuous process for the production of glycol glucosides with improved reaction efficiency and to optimize the process variables for maximum yield of glycol glucosides. Acid-catalyzed starch and ethylene glycol transglycosylation via reactive extrusion using a laboratory scale, corotating, intermeshing, conical twin-screw extruder was studied. Reactor models were developed with the extruder and static mixers as postextruder reactors to assess the capability of postextruder modifications to enhance reaction efficiency. Postextruder modifications were successful in obtaining a glucosides yield of 91%.

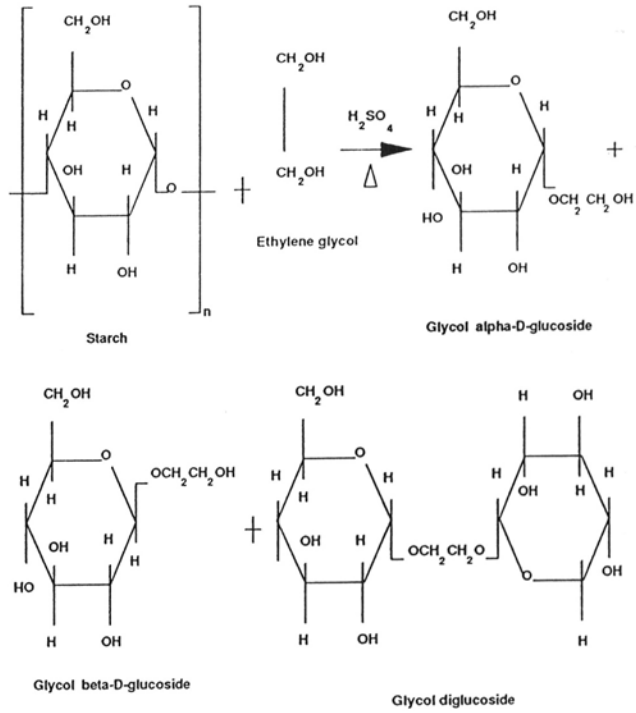

Fig. 1. Major reaction products from starch and ethylene glycol.

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MATERIALS AND METHODS

Chemicals

Materials included 25% amylose corn starch (Amaizo, Hammond, IN), ethylene glycol (99% purity), and concentrated sulfuric acid.

Equipment

A C. W. Brabender model CTSE-V laboratory conical twin-screw extruder was used. The screws had diameters decreasing from 43 to 28 mm along their length of 370 mm. The screws were counter rotating and electrically heated with three band heaters on the barrel. Zones 1, 2, and 3 corresponded to the feed, compression, and metering sections of the extruder screw, respectively. Zone 4 corresponded to the die section of the extruder. Table I describes the extruder screw geometry.

Omega FMX 8462S Kenics static mixers (Omega Engineering, Inc., Stamford, CT) were used for postextruder reactor-modification (Fig. 2). The static mixer was a 1.30 cm i.d. pipe, 24.1 cm long, having six mixing elements. Inside the pipe was a single, removable mixing element, similar in appearance to an auger. The auger or baffle geometry was such that the fluid was split in two and reoriented 180° over the length of one element and then split again. The static mixer was heated with a Thermolyne Brisk heating tape (Fisher Scientific, Pittsburgh, PA) wrapped around it. The heating tape was regulated with a temperature controller connected to thermocouples to achieve and maintain the desired temperature along the static mixer.

A double-tube heat exchanger was designed to control heat transfer to the product extrudate before exiting from the reactor. The tube side of the heat exchanger was packed with a static mixer and the shell side was a 30 cm long galvanized pipe with 5.1 cm i.d. The heat transfer fluid used was a 50:50 blend of ethylene glycol and water pumped through a conventional centrifugal pump. The inlet temperature of the heat transfer fluid was maintained by a heating bath (Tamson, Neslab Instrument Inc., Portsmouth, NH).

TABLE I
Conical Twin-Screw Design

	Section		
Screw Features (mm)	Feeding	Compression	Metering
Screw length	140	70	160
Root diameter	25–19.5	19.5	19.5–14
Flight pitch	10	19.5	12
Flight width	2.6	4.5	3.3
Flight height	7.7	0–8.2	8
Number of flights	12	4	8

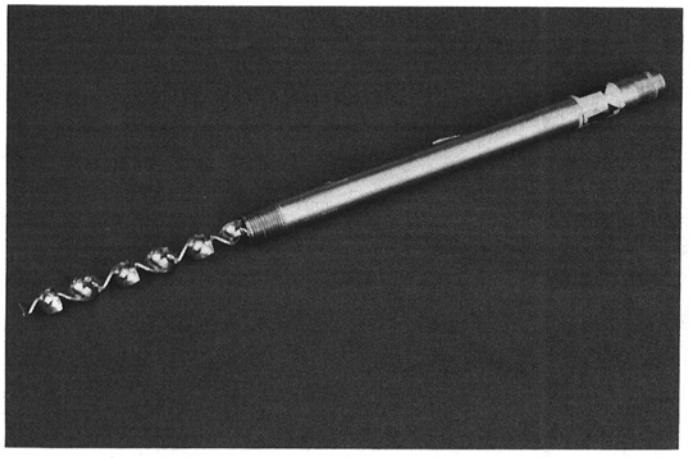

Fig. 2. Static mixer.

Preliminary Investigations

Preliminary investigations were part of the process development. Besides the extruder, several other reactor models were developed. These reactor models had one to three static mixers as postextruder modifications. The temperature maintained in the static mixers was varied from 100 to 130°C according to the process needs. Screw speed, temperatures of the extruder barrel and static mixers, mole ratio of ethylene glycol to anhydrous glucose unit, and acid concentration were studied to enhance glucosides yield. Problems associated with some of the reactor models were plugging of the reactors and formation of degraded products. The first phase of the preliminary studies focused on development of a continuous process for glucosides production. The second phase determined the range of process variables and number of reactor models.

Reactor Models

The three reactor models chosen for further studies were: 1) extruder with a 3 mm dia. and die 15 mm long (Fig. 3); 2) extruder plus static mixer (Fig. 4); and 3) extruder plus static mixer plus heat exchanger (Fig. 5).

Experimental Design and Statistical Analysis

The experimental design used in evaluating glucoside yield was a split plot design with a randomized complete block with regard to three levels of main plot (reaction temperature) treatments, two blocks, and 3^3 levels of completely randomized subplots (screw

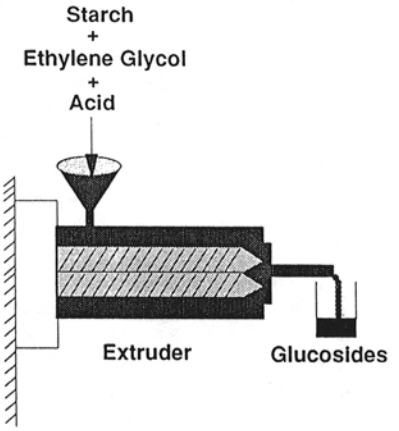

Fig. 3. Reactor model 1 (extruder).

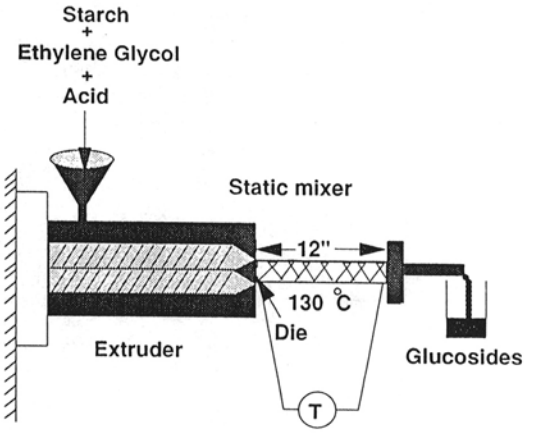

Fig. 4. Reactor model 2 (extruder + static mixer).

speed × mole ratio) treatments within each reaction temperature. Separate statistical analyses were conducted for each model. The treatment design was a 3^3 factorial arrangement treatment. There were two experimental units (Fig. 6): one associated with the main plot was one reaction temperature at each time; and one associated within one reaction temperature was a subplot that was a mole ratio and screw speed combination. Each experiment was replicated twice.

Statistical analyses were conducted using a statistical package (SAS 1989). An analysis of variance (ANOVA) model was fit on the split-plot with reaction temperature as the main plot; the nine screw speed × mole ratio combinations as the subplot to find the two-way and three-way interactions. A 5% significant level was used as the cut-off point to estimate the effect of each treatment on glucoside yield. All significant terms were used to generate a response surface using a Smart computer software package spreadsheet (Smart Ware II, Informix Software Inc., Lenexa, KS).

Acid concentration and sample feed rate were constants. Carr (1989) indicated that a sulfuric acid concentration of 0.75% on dry basis of starch was the optimum value, and this was maintained.

Reaction Process

Three samples, each 1 kg mass and containing mole ratios of ethylene glycol to anhydrous glucose units (AGU) of 3, 4, and 5, and 0.75% sulfuric acid (dry basis of starch) were prepared in a Hobart mixer. The ethylene glycol–AGU mole ratio will be referred to as the ethylene glycol–starch mole ratio hereafter.

The static mixer temperature was maintained at 130°C in reactor models 2 and 3. Temperatures of extruder zones 1, 2, and 4 were set at 80, 130, and 140°C, respectively. Temperature was kept low in zone 1 to allow mixing to occur prior to high temperature contact. Reaction temperatures of 160, 170, and 180°C (zone 3) were studied for all reactor models. After the prescribed barrel temperatures were reached, the extruder was started and the screw speed adjusted. Table II shows specific process conditions. A sample feed rate of 100 ml/min was maintained manually. After maintaining a steady-state condition for 3 min, 50-ml samples of the extrudate were collected for analysis, and barrel and product temperatures, torque, die pressure, and residence time were recorded. To determine the residence time, finely powdered dye (red and blue) was dropped into the extruder feed hooper directly onto the feeding zone of the extruder screw. The times required to see the beginning and end color of the dye from the exit of the reactor were noted. These times were averaged to determine the residence time.

Glucosides Yield Analysis

A high-performance liquid chromatography (HPLC) system (model M-6000 A pump, WISP 710 automatic injector, R401 differential refractometer from Water Associates, Milford, MA and Aminex HPX-87H column from Bio-Rad Laboratories, Richmond, CA) was used to identify the glucosides and determine the yields. The procedure was similar to that used by Carr (1991). Due to unavailability of pure glycol glucosides, the results were compared with Carr's data. "Glucoside yield" refers to the total percentage of product formed to the three major glucosides. The chromatogram of the extrudate sample contained six peaks emerging at retention times between 5 and 16 min. The peak with a retention time of 15–16 min was identified as unreacted ethylene glycol. Carr et al (1989) and Carr (1991) indicated that peaks 1 and 2, with retention times between 5 and 7 min, could not be identified. Carr et al (1989) further indicate that peak 1 probably contained low molecular weight starch products that were gradually converted to glycol glucosides or other water-soluble products as the extent of reaction increased. Peaks 3, 4, and 5 were identified as glycol diglucoside, glycol β-D-glucoside, and glycol α-D-glucoside, respectively. Glucosides yield was defined as the area under peaks 3, 4, and 5 divided by the area under the first five peaks (excluding the unreacted ethylene glycol peak).

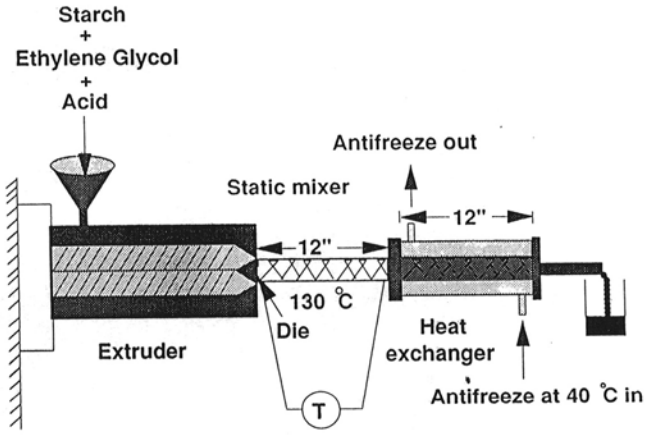

Fig. 5. Reactor model 3 (extruder + static mixer + heat exchanger).

RESULTS AND DISCUSSIONS

Glycol Glucosides Yield

HPLC showed that the crude extrudate samples of glycol glucosides contained glycol α-D-glucoside, glycol β-D-glucoside, glycol diglucoside, unidentified converted starch, and unreacted ethylene glycol. In this discussion, glucosides yield refers to the total percentage of the three glucosides formed.

TABLE II
Process Conditions

Temperature of extruder zone 1	80°C
Temperature of extruder zone 2	130°C
Temperature of extruder zone 3	160, 170, 180°C
Temperature of extruder die	140°C
Static mixer temperature (reactor model 2 and 3)	130°C
Inlet temperature of antifreeze in heat exchanger (reactor model 3)	40°C
Screw speed	20, 30, 40 rpm
Mole ratio (ethylene glycol/AGU[a])	3, 4, 5
Acid concentration (sulfuric acid)	0.75%, dry starch basis

[a] Anhydrous glucose units.

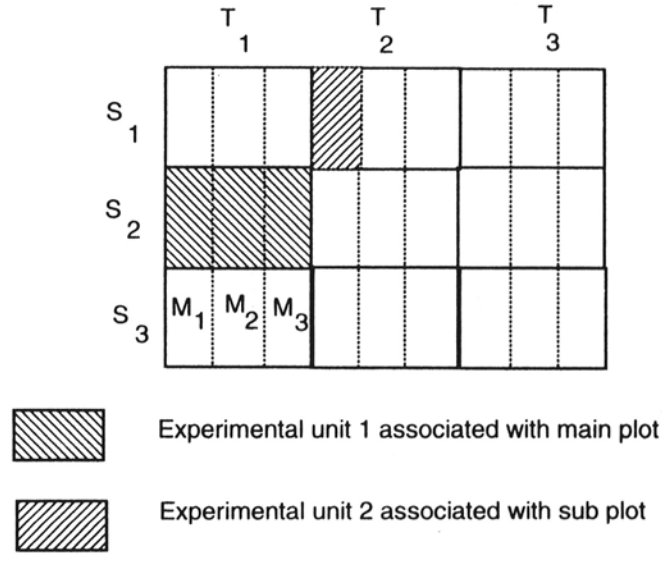

Fig. 6. Diagram showing experimental units.

Carr et al (1991) studies indicated that glucosides yield was a function of screw speed, ethylene glycol–starch mole ratio, and temperature. Besides these process variables, Carr et al (1989) reported complex interrelationships of these variables with viscosity, barrel fill, shear stress, heat transferred, and residence time.

In our study, glucosides yield response was a result of, not only the aforementioned complex interrelationships, but also the complex rheology of ethylene glycol–starch mole ratios. Though the glucosides yield improved as the reactor model was modified with the addition of postreactors to the extruder, categorical explanations cannot be made on the basis of any one process variable. This is because a combination of a particular screw speed, mole ratio, and temperature was responsible for a particular yield of glucosides.

The reactor models had an impact on the yield of the glucosides. The yield was directly proportional to the length of the reactor which, in turn, was a function of the postextruder reactor modifications. Results obtained from the three reactor models clearly indicated that the glucosides yield was enhanced by the addition of postextruder reactor modifications. The yield increased from a minimum of 23% for reactor model 1 to a maximum of 91% for reactor model 3. This process approach enabled a smaller extruder to accomplish acid-catalyzed ethylene glycol–starch reactive extrusion, due to the postextruder reactor modifications.

The statistical analyses on the effects of reaction temperature, screw speed, and mole ratio on glucosides yield for all reactor models showed different significant two-way interactions.

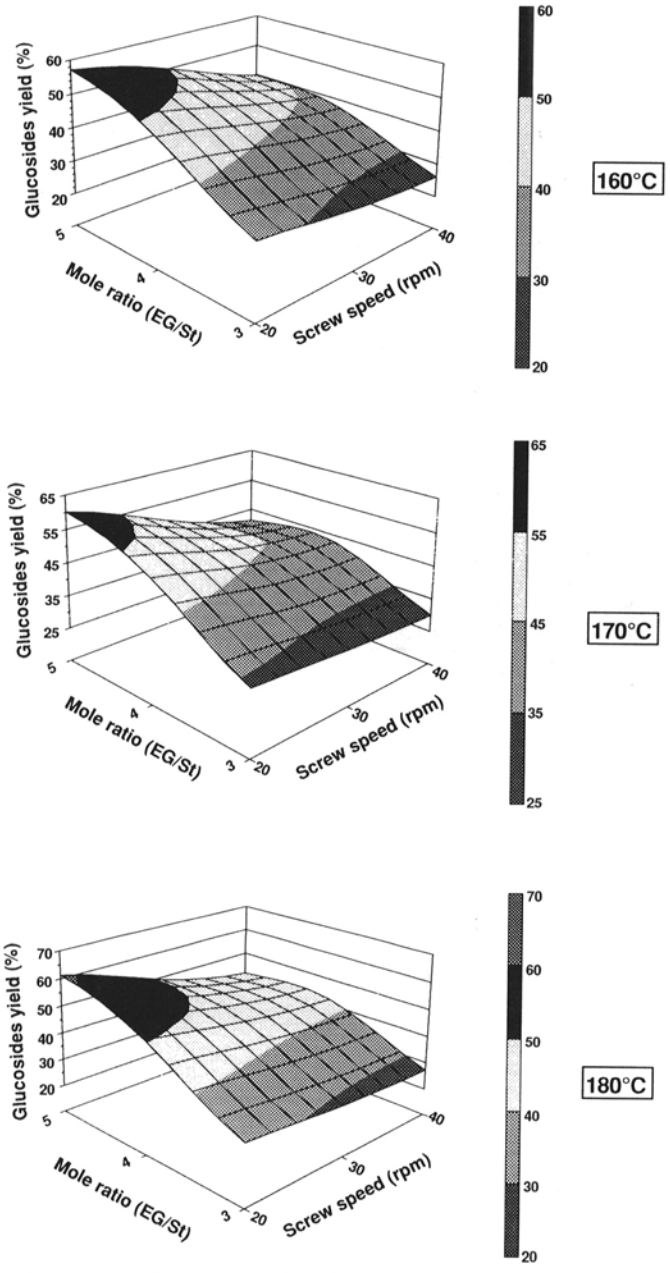

Fig. 7. Effects of screw speed and mole ratio on glucosides yield averages at different reaction temperatures for reactor model 1.

Effect of Reactor Model 1 on Glucosides Yield

In reactor model 1, the extruder was used as a continuous reactor for carrying out the ethylene glycol–starch transglycosylation reaction. The yield of glucosides varied between 23% (40 rpm, 160°C, mole ratio 3) and 66% (20 rpm, 180°C, mole ratio 5). As was expected, the residence time decreased with increases in mole ratio and screw speed. The maximum residence time was 68 sec at 20 rpm and mole ratio 3, and the minimum was 35 sec at 40 rpm and mole ratio 5.

Statistical analysis showed a significant interaction between mole ratio and screw speed ($Pr>F = 0.0002$). There was no interaction of temperature with the other factors, but the main effect of reaction temperature was significant on glucosides yield ($Pr>F = 0.0412$)

Figure 7 shows the combined effects of screw speeds and mole ratios on the glucosides yield at 160, 170, and 180°C. The response surfaces in Figure 7 show the glucosides yield decreased with increases in screw speed for all mole ratios. The yields, averaged over all temperatures and mole ratios, were 49, 40, and 36% for screw speeds of 20, 30, and 40 rpm, respectively. The residence times, averaged over all mole ratios and temperatures, were 62, 56, and 48 sec for 20, 30, and 40 rpm, respectively. As the screw speed was increased, the residence time and glucosides yield decreased.

Since there was no interaction of temperature with either screw speed or mole ratio, the glucosides yields were averaged over mole ratios and screw speeds at each temperature. The yield of glucosides increased from 40% at 160°C to 43% at 170°C and then decreased to 42% at 180°C. The increase in temperature from 160 to 170°C enhanced the reaction efficiency, since more molecules were able to reach the activation energy (minimum energy required by the molecules to react) at a faster rate. At 180°C, the reduction in glucosides yield corresponded with a degradation reaction as evidenced by the dark color and stickiness of the extrudates.

Effect of Reactor Model 2 on Glucosides Yield

A static mixer, maintained at 130°C, was added to the extruder as a postextruder reactor modification. The yield of glucosides varied between 41% (40 rpm, mole ratio 5) and 72% (20 rpm, mole ratio 3). As was expected, the residence time decreased with increases in mole ratio and screw speed. The maximum residence time was 134 sec at 20 rpm and mole ratio 3; and the minimum was 65 sec at 40 rpm and mole ratio 5. The static mixer increased residence time by increasing the length of the reactor and offering resistance to the flow of the process fluid, allowing the reaction to approach completion. The glucosides yields obtained were somewhat higher than those for reactor model 1.

Statistical analysis showed a significant interaction between mole ratio and screw speed ($Pr>F = 0.0092$), but there was no significant effect ($Pr>F = 0.1117$) of reaction temperature on glucosides yield. The yields averaged over the reaction temperatures for all screw speeds and mole ratios were 61, 59, and 60% at 160, 170, and 180°C, respectively. The increase in residence time, evidently resulting from the greater length of this model over model 1, was sufficient to nullify the temperature effect.

Figure 8 shows the combined effects of screw speeds and mole ratios on the glucosides yield averaged over all reaction temperatures. As screw speed was increased from 20 to 30 rpm, there was no marked change in the glucoside yield, but there was a slight decrease in yield when the screw speed was further increased to 40 rpm. Furthermore, the response surface in Figure 8 shows the glucosides yields were not affected much when the mole ratio was increased from 3 to 4. However, the glucosides yields decreased when the mole ratio was further increased to 5.

With the addition of the static mixer, the length of reactor model 2 was greater than that of reactor model 1. Thus, the residence time was increased. Furthermore, the presence of the static mixer increased mixing and product homogeneity.

Effect of Reactor Model 3 on Glucosides Yield

Reactor model 3 increased the yield over reactor model 2. A heat exchanger was incorporated as an additional downstream unit. The heat exchanger was employed to reduce the temperature of the viscous reaction products to suppress the formation of ethylene glycol vapors. The addition of the heat exchanger further increased the residence time, thus bringing completion of the reaction. It also was instrumental in achieving a homogeneous product.

Reactor model 3 was the longest reactor, as it had a static mixer and a heat exchanger attached to the extruder as postextruder reactor modifications. The yields of glucosides were higher than for models 1 and 2 and varied from 60% (40 rpm, 160°C, mole ratio 5) to 91% (20 rpm, 160°C, mole ratio 3). The residence times were higher than those for reactor models 1 and 2 because of increased length and the resistance offered by the downstream units. The maximum residence time was 193 sec at 20 rpm and mole ratio 3; the minimum was 159 sec at 40 rpm and mole ratio 5. This was expected, as the changes in flow characteristics of the process fluid with the increase in the mole ratio and the increase in screw speed reduced the residence time.

Statistical analysis showed a significant interaction between mole ratio and reaction temperature ($Pr>F = 0.0417$). There was no interaction of screw speed with any other factor considered but the main effect of screw speed was significant on glucosides yield ($Pr>F = 0.0001$).

Figure 9 shows the combined effects of reaction temperatures and mole ratios on the glucosides yield for screw speeds of 20, 30, and 40 rpm. Reactor model 3 had a maximum yield of 91% at 20 rpm, 160°C, and mole ratio 3; and a minimum yield of 60% at 160°C, 40 rpm, and mole ratio 5. The temperature response can be explained by the fact that, as the temperature increased, the reaction efficiency increased; more molecules reached their activation energy faster. But, when the temperature was increased from 170 to 180°C, some degradation occurred.

Optimization of Glucosides Yield

Response surface methodology, based on least significant differences, was used to determine optimum process conditions for maximum glucosides yield. Reactor model 3 gave maximum yield of glucosides. There was a significant interaction between mole ratio and reaction temperature. A combination of 20 rpm screw speed, an ethylene glycol–starch mole ratio of 3, and a reaction temperature of 160°C was optimum for maximum yield. The maximum yield obtained was 91%.

The above procedure for determining the optimum process conditions was further strengthened when these conditions were viewed on the basis of engineering optimization, which is based on cost and energy. Reaction temperature of 160°C used minimum thermal energy in the selected range of process conditions. Furthermore, a mole ratio of 3 was the lowest concentration of ethylene glycol, thereby reducing the raw material costs and reducing the level of unreacted ethylene glycol that ultimately would have to be separated.

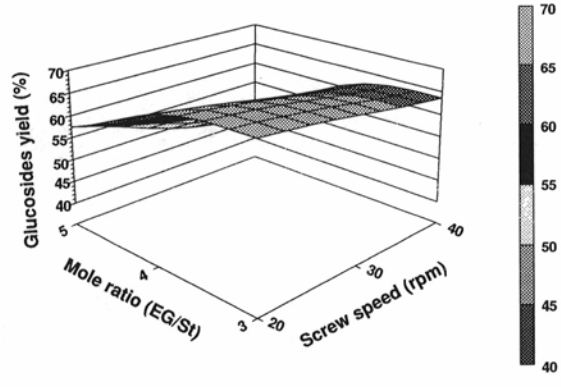

Fig. 8. Effects of screw speed and mole ratio on glucosides yield averaged at all reaction temperatures for reactor model 2.

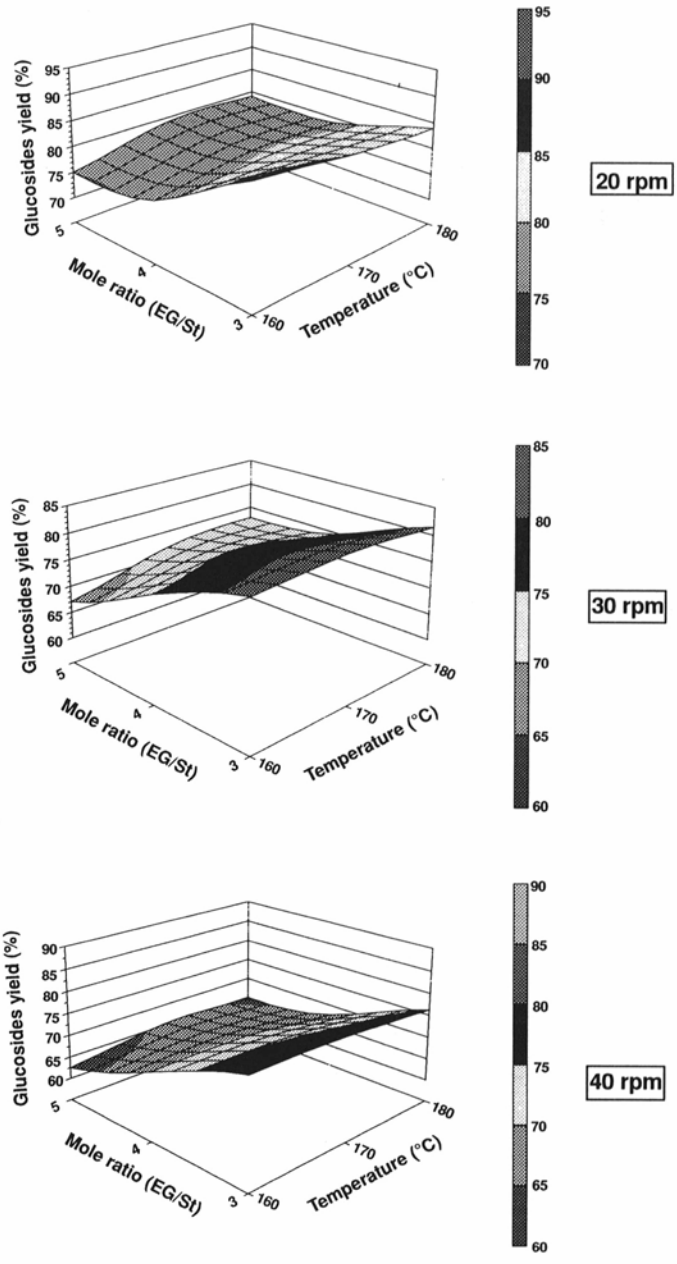

Fig. 9. Effects of temperature and mole ratio on glucosides yield averages at different screw speeds for reactor model 3.

CONCLUSIONS

Continuous transglycosylation of starch with ethylene glycol was accomplished with an extruder with a short barrel length and postextruder reactor modifications.

Glucosides yields were a function of screw speed, reaction temperature, and ethylene glycol–starch mole ratio.

Maximum glucosides yield of 91% corresponded to optimum process conditions of 20 rpm, 160°C, and a mole ratio of 3 for reactor model 3.

LITERATURE CITED

BAKER, R. J. 1991. Motionless mixers stir up new use. Chem. Eng. Prog. 6:32-38.

CARR, M. E., and CUNNINGHAM, L. R. 1989. Glycol glucosides from starch by continuous twin-screw extruder processing. Cereal Chem. 66:238-243.

CARR, M. E. 1991. Starch-derived glycol and glycerol glucosides prepared by reactive extrusion processing. J. Appl. Polym. Sci. 42:45-53.

CARR, M. E. 1992. Rigid polyurethane foam prepared from extruded starch—Derived glycol glucosides as chemical intermediates. Starch/Staerke 44:183.

EISE, K. 1986. Continuous reactive processing with twin-screw extruders. Plast. Compounding 9:44.

EL-DASH, A. A. 1981. Application and control of thermoplastic extrusion of cereal for food and industrial uses. Pages 165-216 in: Cereals: A Renewable Resource. Y. Pomeranz and L. Munck, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.

GRAFELMAN, D. D. 1993. Liquefaction of starch by a single-screw extruder and post-extrusion reactor. MS thesis. University of Nebraska: Lincoln, NE.

LEITHEISER, R. H., IMPOLA, C. N., REID, R. J., and OTEY, F. H. 1966. Starch-derived glycosides polyethers for urethane foam. Process scale ups, performance in foams and cost estimates. Ind. Eng. Chem. Res. Dev. 5:276.

LINKO, P., COLONNA, P., and MERCIER, C. 1981a. High-temperature, short-time extrusion cooking. Pages 145-235 in: Advances in Cereal Science and Technology, Vol. 4. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.

MIELECAREK, D. F. 1987. Twin-screw compounding. Chem. Eng. Prog. 83:59.

OTEY, F. H., ZAGOREN, B. L., BENNETT, F. L., and MEHLTRETTER, C. L. 1963. Preparation and properties of glycol-glucosides polyethers for rigid urethane foams. Ind. Eng. Chem. Prod. Res. Dev. 4:224.

OTEY, F. H., ZAGOREN, B. L., and MEHLTRETTER, C. L. 1965a. Rigid urethane foams from glycosides polyethers. Ind. Eng. Chem. Prod. Res. Dev. 2:256.

OTEY, F. H., BENNET, F. L. ZAGOREN, B. L., and MEHLTRETTER, C. L. 1965b. Separation of isomeric glycosides produced by transglycosylation of starch with ethylene glycol. Ind. Eng. Chem. Prod. Res. Dev. 4:228.

OTEY, F. H., MEHLTRETTER, C. L., and RIST, C. E. 1968. Starch-derived polyol glucosides. Cereal Sci. Today 13:199.

OTEY, F. H., WESTHOFF, R. P., KWOLEK, W. F., and MEHLTRETTER, C. L. 1969. Urethane plastics based on starch and starch-derived glycosides. Ind. Eng. Chem. Prod. Res. Dev. 8:267.

SAS. 1989. Statistical package, version 6.0. SAS Institute: Cary, NC.

WIELGOLINSKI, L., and NANGERONI, J. 1982. Twin screw extruders—A versatile tool for reactions and ploymerizations. Pages 303-314 in: Proc. Int. Conf. React. Process. Polym., 2nd. J. T. Lindt, ed. University of Pittsburgh School of Engineering: Pittsburgh, PA.

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