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Glycerol from the Tubers of Jerusalem Artichoke

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ABSTRACT

The search for alternate sources of chemicals has resulted in a re-evaluation of many carbohydrates for conversion to oxychemicals. Inulin is an example of a carbohydrate receiving an increased amount of attention for use in industrial processes. This polymer is composed almost exclusively of fructofuranose structural units, making it very attractive for conversion into high fructose syrup and ethanol. Inulin can also be oxidized and reduced by a number of methods, and therefore lends itself well as feedstock for the exclusive conversion to glycerol. The advantages of inulin, coupled with a renewable supply, make it a very attractive source for industrial processes.

Index Entries: Glycerol; tubers of Jerusalem artichoke; inulin; periodate oxidation; reductive hydrolysis; periodate regeneration.

INTRODUCTION

This paper presents a simple two-step process for the production of glycerol from inulin. The process involves a periodate oxidation step followed by a reductive hydrolysis step with a 99% recovery of the expensive periodate reagent. Periodate oxidation of the fructofuranose polymer results in scission of the C2–C3 diol bond, yielding a dialdehyde polymer. Reduction followed by hydrolysis (or a one-step reductive hydrolysis) would furnish glycerol as the sole major product (Fig. 1). This is unlike other biomass substrates, which on periodate oxidation-reductive hydrolysis yield a mixture of glycols (ethylene glycol, glycerol, erythritol) that have to be separated to yield the individual oxychemical. Thus, the additional separation step is eliminated in the processing of this biomass

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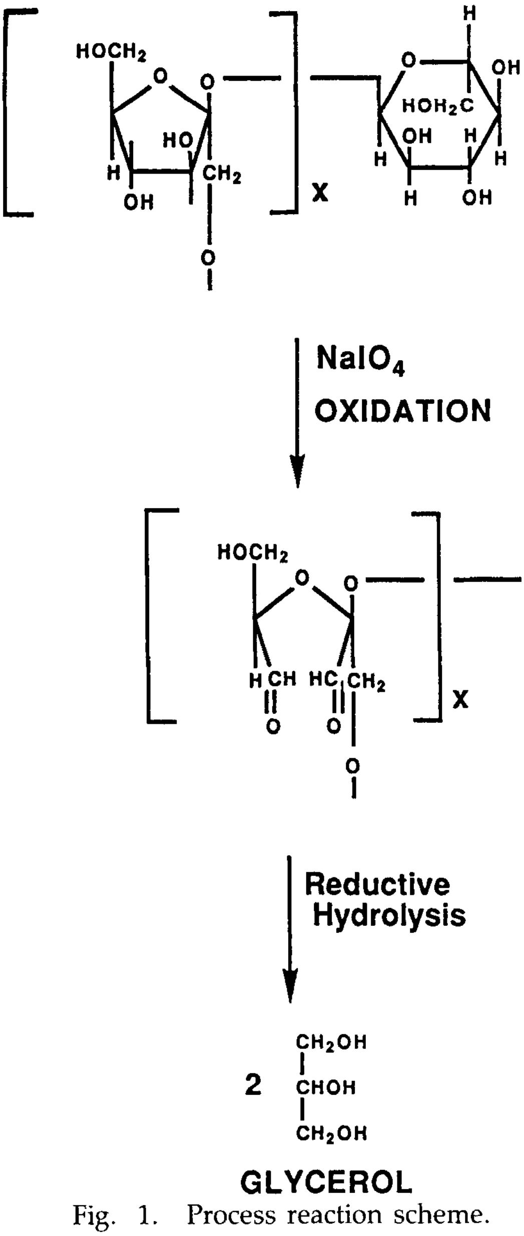

Fig. 1. Process reaction scheme.

substrate. Furthermore, the product formed, glycerol, is the second most widely used oxychemical, has widespread use in many industrial products, and also has a relatively high price per pound.

BACKGROUND LITERATURE

Inulin was first isolated from the tubers of the Jerusalem artichoke by Rose in 1804 (*1*). Of all inulin producing species (i.e., chicory, dahlia, dandelion, Canadian thistle, and so on) the artichoke is probably the highest yielding source (2). Contrary to its name, this plant is neither an artichoke nor is it originally from the Jerusalem area. It is actually closely related to the sunflower plant and is native to North America. The primary interest in the tubers of the Jerusalem artichoke is for the carbohydrate content, which constitutes approximately 80% of the dry matter. The main carbohydrate found in the Jerusalem artichoke is a homologous series of polyfructofuranose units which consist of linear chains of D-fructose molecules linked by β $(2 \rightarrow 1)$ linkages. This chain is terminated by a D-glucose molecule linked to fructose by an α $(1 \rightarrow 2)$ bond as in sucrose (Fig. 2). Carbohydrates of this form are referred to as inulides for degree of polymerization (DP) of 3–30, and inulin for DP > 30.

The distinction between inulin and inulides is important for several reasons. First, inulin and inulides have different solubilities in aqueous solutions. The inulides are readily soluble in cold water, whereas inulin has very little solubility unless the water is heated. The second reason for distinguishing is that the processes being analyzed make use of the fructose residues in the polymer. Therefore the inulin, with a higher ratio of fructose to glucose units, will produce a greater yield of glycerol per weight of starting material. A final reason for distinguishing between inulin and inulides is that the carbohydrate composition of the artichoke tubers will vary with the season. Therefore the degree of polymerization is a measure of the maturity of the plant.

The use of Jerusalem artichokes as a source of inulin has several advantages. It is well adapted to grow in many geoclimatic regions and has higher tolerance to frost than traditional crops such as wheat or corn (3). As a source of carbohydrates, the artichoke was found to be superior to corn and sugar beets (3), both of which are currently used as carbohydrate sources. An additional advantage is that the pulp remaining after carbohydrate extraction still has high value as fodder for livestock (4). The use of this byproduct will help lower the cost of processing carbohydrates from the tubers.

Extraction of Carbohydrates from the Tubers

The carbohydrates can be extracted by slicing the tubers into water containing 0.1% SO_2 at 70°C, and allowing 15–30 min contact time. This extraction is done in batch, but can also be accomplished through counter current diffusion. Complete extraction could also be accomplished using ground tubers, however, a greater water volume is required. The extract is then filtered to remove small quantities of particulate matter. If this extraction/filtration were performed in untreated water only, the resulting extract would be very difficult to decolorize, requiring a filtration step using 50–80% charcoal (based on the dry weight of tubers). Using sulfur dioxide in the extraction medium results in much less color in the extract. The required amount of charcoal for decolorization is then reduced to 14–20% for the batch extraction and only 5–6% for the countercurrent diffusion.

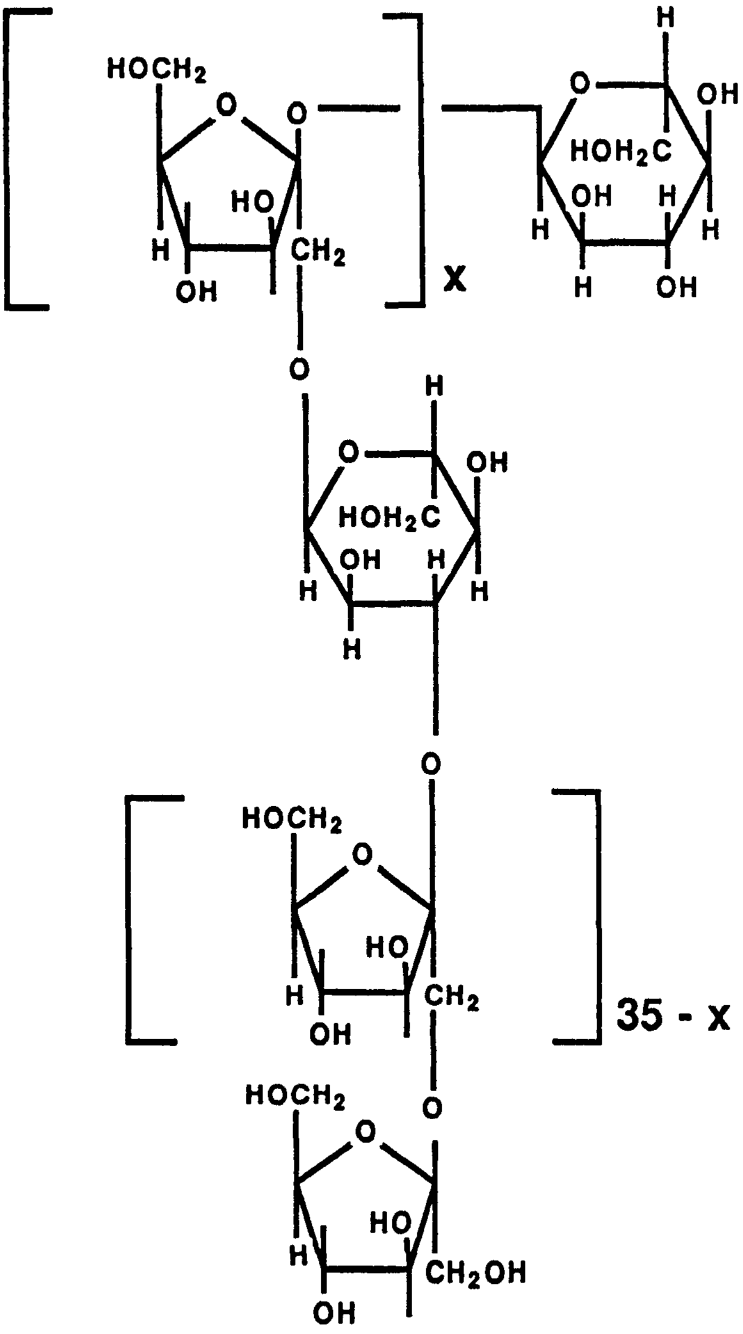

Fig. 2. Structure of inulin.

EXPERIMENTAL

The experimental process involved the following steps: (a) periodate oxidation, (b) reduction, (c) hydrolysis. This procedure can be further simplified by combining steps b and c into one reductive-hydrolysis step.

Periodate Oxidation

Oxidation of the inulin was performed using a 1.5:1 ratio of periodate to theoretical fructose units. Despite the increased possibility of over oxidation by the periodate, this ratio resulted in a higher overall yield than when a 1:1 ratio was employed. The inulin solution was prepared by adding 2.5 g inulin (15.4 mmol theoretical fructose units) to 50 mL of water and then slowly heating the water to 45°C to dissolve the inulin. The periodate solution was prepared by dissolving 4.95 g $NaIO_4$ (23.1 mmol) in 50 mL water. The periodate solution was then added dropwise to the inulin solution with constant mixing. The reaction was performed in darkness (to avoid decomposition of the periodate in light) for 24 h. The resulting reaction mixture was clear and colorless, indicating that either the oxidized product was soluble in water at room temperature (unlike inulin), or the inulin had been partially hydrolyzed, yielding inulides and oxidized inulides.

Carbonyl Content of the Dialdehyde

The progression of the reaction was determined by analyzing the carbonyl concentration of the dialdehyde intermediates after oxidation. This was done using the method of Rankin and Mehltretter (5). A 1 mL sample of the reaction mixture was reduced in a closed system using 4 mL sodium borohydride solution in sodium hydroxide (500 mg $NaBH_4$/50 mL 0.1*M* NaOH). After two hours the unreacted borohydride was decomposed by adding 5 mL 2*N* sulfuric acid. The volume of hydrogen evolved was measured using a 100 mL gas buret and subtracted from the volume of gas evolved by a blank to determine the hydrogen consumed by the dialdehyde sample.

Analysis of Periodate Consumption

The concentration of periodate and iodate in the reaction mixture were determined spectrophotometrically using the method of Khym (6). A sample of reaction mixture was diluted to a known volume and passed through an acetate based anion exchange resin column. The column was washed with water, which was discarded, and then with 0.95 M NH_4Cl. This filtrate was collected and the absorbance measured to determine the concentration of iodate ions. The column was then washed with a solution of 1*M* glycerol and 1*M* NH_4Cl. The absorbance of this filtrate was then measured to determine the concentration of unreacted periodate ions. The sum of the iodate and periodate concentrations was calculated and compared with the original concentration of periodate. This served as a check that no side reactions involving periodate occurred.

Reduction and Hydrolysis of Reaction Mixture

The reaction mixture was reduced by adding 2 mol of sodium borohydride for every mole of oxidized fructose residue (15.4 mmol

$NaBH_4$ for 50 mL of reaction mixture). This addition was performed slowly (over a span of 5 min) due to the immediate exothermic reaction. The resulting solution was then mixed for 20 h at room temperature, after which sodium borohydride was again added (a 1:1 ratio, or 7.7 mmol for 50 mL of reaction mixture) and the solution was mixed for a further 2 h. The solution was then acidified with sulfuric acid to pH 1.0 and refluxed for 1 h at 100°C.

An alternative way to reduce and hydrolyze the oxidized inulin is by using reductive hydrolysis. This method reduces and hydrolyzes the oxidized inulin in one step. This not only simplifies the process, but also decreases the amount of time needed for reduction. The method involves reacting the oxidized inulin solution with hydrogen at a pressure of 700 psia and a temperature of 30°C. The catalyst used in this system is 5% ruthenium on carbon, and dilute phosphoric acid (5%) is used as the reaction medium. The catalyst to substrate ratio is 1:500 (based on the weight of the metal). The time for reductive hydrolysis was 6 h. This is somewhat less than the time for reductive hydrolysis of other cellulosic materials (usually about 8 h), which results from the relative ease of hydrolyzing the oxidized inulin (*7*). The use of reductive hydrolysis results in a substantial improvement over the separate reduction and hydrolysis, which takes over 23 h.

The product solution was analyzed by high performance liquid chromatography (HPLC) using a Waters Associates APL-GPC 201 with a 401 differential refractometer and a WISP 710B autosampler. The chromatography column contained AG50WX-4 cation exchange resin (20–30 μm dry mesh size, 4% cross linkage). Sulfuric acid was used as the solvent at a flow rate of 0.5 mL/min.

Recovery and Regeneration of Periodate

Periodate is expensive and, therefore, represents an important cost factor in the conversion process. Thus, the commercial success of the proposed process for the production of oxychemicals from biomass residues is in part based on the recovery and reuse of the iodine. It is known (*8*) that under the reaction conditions of the periodate oxidations all of the iodine exists either as unconsumed periodate or as its reduction product (iodate) and can be recovered in 99.9% molar yield. The reoxidation of the iodate to periodate can be carried out electrolytically. This process is currently being used in a commercial plant for producing dialdehyde starch (*9,10*). Another approach to reoxidation of the iodate is to use sodium hypochlorite as described by Hearon et al. (*8*). The procedure is essentially an electrolytic reoxidation using salt as a carrier effecting a 99.7% recovery of periodate. This technique with slight modification can be adopted for the recovery and regeneration of periodate. One of the major advantages of using this system is that a commercial process has already been developed for brine electrolysis. In addition, efficient commercial brine electrolytic cells of different capacitites with an extended electrode lifetime can be purchased at very reasonable prices.

Another promising scheme for the regeneration of periodate is the oxidation of iodate using molecular oxygen. Jernigan and Sheffield (*11*) have demonstrated that sodium periodate can be obtained in quantitative yields by reaction of sodium iodate for 5 h at a temperature of 300°C, an oxygen partial pressure of 500 psia, and a sodium hydroxide to sodium iodate molar ratio of ten to one.

Thus, with a 99% recovery of periodate and the use of electrolytic cells, the use cost of a periodate reagent is no longer a serious economic constraint.

RESULTS AND DISCUSSION

The results for this process are very promising, as they indicate that glycerol can be produced from inulin, which is a major component of the tubers of the Jerusalem artichoke. The method presented resulted in a 70% yield of glycerol from inulin (Table 1), based on theoretical yield of two molecules of glycerol for each fructose unit. Oxidation followed by a one-step reductive hydrolysis gave glycerol yields in the range of only 16–19% for elevated temperatures, and a range of 24–30% at lower temperatures (Tables 2 and 3). Note that at lower temperatures (30–60°C), similar yields resulted from several different operating conditions. Figure 3 shows the HPCL analysis for the lower temperature runs. HPLC trace *a* represents the standard, theoretical yield of glycerol. Traces *b*, *c*, and *d* resulted from reduction at 30°C and 700 psia followed by one, two, and four hours of acid hydrolysis at 100°C, respectively. During the hydrolysis the amount of lower molecular weight molecules increased, but it did not result in more glycerol produced. Trace *e* resulted from reductive hydrolysis at 30°C and 700 psia. Here the lower hydrolysis temperature did not appear to affect the glycerol yield. Traces *f* and *g* resulted from reduction at 60°C and 700 psia followed by acid hydrolysis at 100°C for 1 and 2 h, respectively. The elevated temperature during reduction did not appear to greatly affect the overall glycerol yield. All of these reductions were performed for 6 h. Each sample chromatograph shows a large acid peak, which slightly increased the retention times for all of the com-

Table 1
Oxidation Followed by $NaBH_4$ Reduction and Acid Hydrolysis

Ratio of $NaIO_4$:fructose units	Time of oxidation, h	Glycerol yield, %	Theoretical concentration, mol/L
1.0:1	24	59	0.154
1.5:1	24	69	0.154

Table 2
Oxidation Followed by One-step Reductive Hydrolysis of Inulin

Ratio of $NaIO_4$: fructose units	Time of reductive hydrolysis, h	Temp., °C	Pressure, psia	Yield,[a] %
1.5:1	5	110	700	16.3
1.5:1	11	150	700	19.0
1.5:1	6	30	700	29.4

[a] Based on theoretical yield of 0.154 mol/L glycerol.

Table 3
Oxidation Followed by Catalyzed Reduction and Acid Hydrolysis

Ratio of $NaIO_4$: fructose units	Time reduction, h	Temp., °C	Pressure, psia	Time of hydrolysis, h	Yield, %
1.5:1	6	30	700	1	27.5
1.5:1	6	30	700	2	24.3
1.5:1	6	30	700	4	27.3
1.5:1	6	60	700	1	27.8
1.5:1	6	60	700	2	30.4

pounds. The fact that the various reduction and hydrolysis conditions and times resulted in very similar yields indicates that the oxidation step is the determining factor for the yields. This could be caused by the formation of a hemiacetal structure upon initial oxidation, thereby prohibiting further oxidation. The reaction conditions need to be optimized, especially the operating temperatures, to enhance the glycerol yields. The yields are based on the structure of inulin developed by Hirst et al. (*12*), which contains 36 fructose units and two glucose units. Any differences in the degree of polymerization or in the fructose to glucose ratio from this model will result in the calculated yield being inaccurate. Even with this uncertainty the results still indicate that this process could have industrial applications.

CONCLUSION

This process is promising as a commercial method for producing glycerol, however, research needs to be continued on several factors before the process can be used. Reductive hydrolysis procedure has to be optimized to enhance yields, since this would substantially decrease the cost of the process at an industrial level. Further study should be done on the effect of concentration and reaction time on the overall yields. Although sodium metaperiodate has limited solubility in water (max of about 0.6 *M*) (*13*), there is still room to increase the concentration, thereby resulting in higher yields. The intermediate from the oxidation of

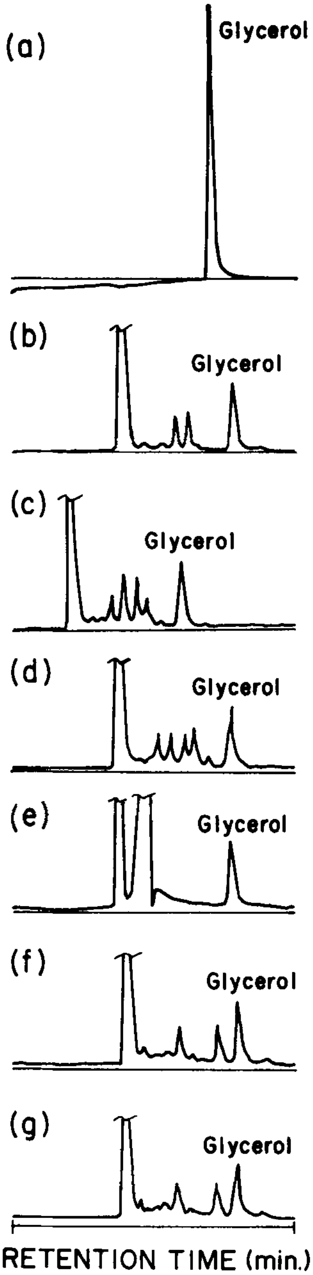

Fig. 3. HPLC analysis of the reaction mixture: (a) glycerol standard; (b) reduction at 30°C followed by 1 h acid hydrolysis; (c) reduction at 30°C followed by 2 h acid hydrolysis; (d) reduction at 30°C followed by 4 h acid hydrolysis; (e) reductive hydrolysis at 30°C; (f) reduction at 60°C followed by 1 h acid hydrolysis; (g) reduction at 60°C followed by 2 h acid hydrolysis.

inulin should be determined, since that would indicate the reasons for the reduced yields. Also, the process should be tried using Jerusalem artichoke juice as was used in the production of high fructose syrup and ethanol. An industrial process would be much more likely to use the juice with extracted carbohydrates than use the solid inulin, as was done in this experimental process. Finally, an economic analysis should be done to determine the cost and feasibility of the process. The analysis would need to include such variables as the effect of the (assumed) widespread cultivation of Jerusalem artichokes on raw material costs, and the effect that the utilization of byproducts (especially for animal feed) will have on the process costs.

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