PREPARATION OF D-SORBITOL FROM ENZYMIC HYDROLYZATES OF STARCH

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As is known crystalline glucose is used in the manufacture of D-sorbitol. However, a more economic method is the direct hydrogenation of polysaccharides of vegetable origin or their hydrolyzates [1-7]. Such routes reduce the cost of sorbitol manufacture and exclude the series of operations of the preparation of crystalline glucose. Starting from the concept of manufacturing glucose by enzymic hydrolysis of starch we have investigated the possibility of substituting enzymic hydrolyzates for crystalline glucose in the manufacture of D-sorbitol.

The process of hydrogenating enzymic hydrolyzates of starch of various degrees of purity over Raney nickel was studied. Samples were prepared in the All-Union Scientific-Research Institute for Starch Products by the method of Ladur and Borodina [8, 9]. Ion exchange purification of hydrolyzates was carried out by the method of Sudorov [10]. The characteristics of the samples studied are given in Table 1.

The kinetics of hydrogenating enzymic hydrolyzates of starch and crystalline glucose at constant pressure and temperature have been studied (for an outline drawing of the equipment built in the Special Construction Department of the Institute of Organic Chemistry of the Academy of Sciences of the USSR, see Fig. 1). The extent of hydrogenation was assessed by the absorption of hydrogen and the amount of reducing substances (RS). The RS were determined by the method of Bertrand with a precision of  $\pm 4.5$  rel. %. The results of experiments are given in Table 2 and Fig. 2. It was established that all samples were effectively completely hydrogenated under the conditions indicated. However, the rate of hydrogenation depended on the amount of proteinaceous and ash contaminants in the hydrolyzates. The semilogarithmic dependence of log  $(v_{\infty} - v)$  on t shown in Fig. 3 indicates that the change of volume of hydrogen att  $\rightarrow \infty$  converted to normal conditions). From the angle of slope of the linear dependence of log  $(v_{\infty} - v)$  on t the constant k (k = 2.3 tan  $\alpha$ ) may be calculated and then the initial rate of the process  $w_0$  from the formula  $w_0 = kv_{\infty}$ .

According to the obtained data the initial rates of hydrogenation (Table 2) of crystalline glucose and hydrolyzates I, IV, and V were related by the ratio 1:0.6:0.2:0.3. The reduction of the hydrogenation rate of hydrolyzates compared with the hydrogenation rate of crystalline glucose led to an increase of 5- to 10-fold in the content of RS and a reduction in the quality of solutions. The content of RS in sorbitol used in the manufacture of ascorbic acid is limited to 0.1% calculated on absolutely dry substance.

Different regimens were studied for the hydrogenation of hydrolyzate III in a Vishnevskii hydrogenator provided with a turbulent drive [11] with the aim of obtaining sorbitol solutions of the necessary quality. An outline of the equipment is shown in Fig. 4. We showed that on hydrogenating crystalline glucose in a Vishnevskii hydrogenator (ratio of Raney nickel to glucose was 2.5%, 60 atm, 150°C, pH 7.8) it was possible to obtain high quality sorbitol solutions containing about 0.02% RS in a short time (1.5-2 h). Curtailing the time for glucose hydrogenation and improvement of the sorbitol quality due to reduction of side reactions made it expedient to use autoclaves of the Vishnevskii type in practice for preparing pure sorbitol.

Hydrogenation of 50% solutions of hydrolyzate III with an increased content of proteinaceous and ash contaminants in a Vishnevskii hydrogenator was effected by us at various pressures, temperatures, and amounts of catalyst. Results are given in Table 3.

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	% of dry substance							
Name	reducing sub- stances	glucose	iso- maltose	oligo- sugar	fat	ash	pro- tein	mois- ture
Crystalline glucose Hydrolyzate (glucoamylase) of corn starch purified by ion ex- change resin:	99,8	-				_	_	4
I II III Unpurified starch hydrolyzate (glucoamylase) IV	96,6 98 98,6 96,3	95 94 95,3 94,4	2,5 2,5 2,5 2,7	2 2 1,8 2,5	 0,13	0,003 0,01 0,05 0,16	0,003 0,1 0,1	10 20 10
Unpurified starch hydrolyzate (glucoendomycopsin) V	97,5	95,45	2,4	1,7		0,2	0,21	10

## TABLE 1. Characteristics of Raw Material Samples



Fig. 1. Outline drawing of equipment for hydrogenating glucose with automatic gas metering at high pressure. 1) U-shaped tube; 2) thermostatted reactor; 3) large volume receiver; 4) hollow float; 5) ferromagnetic core; 6) transformer controller; 7) screw; 8) reversing motor; 9) amplifier; 10) electronic recorder; 11) slide wire; 12) sliding contact; 13) stabilized power supply; 14) open valve; 15) open valve; 16) closed valve; 17) hydrogen cylinder; 18) standard manometer.



Fig. 2. Curves of hydrogen absorption with time. 1) Crystalline glucose; 2) hydrolyzate I, 3) hydrolyzate IV; 4) hydrolyzate V.



Fig. 3. Dependence of log  $(v_{\infty} - v)$  on t. 1) Crystalline glucose; 2) hydrolyzate III; 3) hydrolyzate V; 4) hydrolyzate IV.

Fig. 4. Outline drawing of glucose hydrogenation in a high pressure sealed reactor with electromagnetic drive. 1) Nitrogen cylinder; 2) sealed high pressure reactor; 3) electromagnetic drive; 4) standard manometer; 5) automatic potentiometer; 6) pressure regulating panel; 7) sampler; 8) thermostat.

TABLE 2. Hydrogenation of 25% Aqueous Solutions of Samples at 80 atm, 110  $^\circ\text{C},$  pH 8.0\*

Sample	∞₀ (ml • min <sup>-1</sup> )	% RS after 4 h based on dry substance		
Crystalline glucose	6,5	0,16		
Hydrolyzate I	3,9	0,5		
Hydrolyzate IV	1,2	1,4		
Hydrolyzate V	1,7	1,1		

\*The amount of Raney nickel was 2% the weight of the glucose.

TABLE 3. Hydrogenation of Hydrolyzate III in a Vishnevskii Hydrogenator

Hydrogenation procedure			% RS in 50% solutions after				
pressure, atm	temper- ature, •C	pH	% catalyst	1 1/2 h	2 h	3 h	4 h
60 60 60 110 100 110	150 150 150 110 150 150 150 150	7,8 7,8 9,0 7,8 7,8 7,8 7,8 7,8	5 2,5 2,5 5 5 5 2,5	1,9  0,12 0,15 		0,1 0,09    	0,06 0,08 0,13 2,1 0,03 0,05 —

As is seen from Table 3, a change of pressure from 60 to 110 atm did not affect the reaction rate when conducting the reaction at 150°C. Residual RS were 0.05% after 4 h in experiments at 60 and 110 atm. Reduction of temperature to 110°C slowed the reaction as a result of which an increase of RS content was observed in the sorbitol solutions.

The most effective factor determining the hydrogenation rate and the RS content was the amount of catalyst. At a ratio of Raney nickel to starting glucose of 2.5% the content of RS after hydrogenation was 0.08%. An increase in the amount of nickel to 5% led to acceleration of the hydrogenation and a reduction of RS contnet.

The optimal region for hydrogenation of hydrolyzates is considered to be: 60 atm, 150°C, pH 8.0, ratio of Raney nickel to glucose 5%, time 4 h. The yield of sorbitol calculated on the hydrolyzate was determined by gas—liquid chromatography [12] and amounted to 95%.

Hydrolyzates may also be hydrogenated in horizontal autoclaves with number of revolutions 100-200 rpm at 80-100 atm under the same conditions with an increase in the time of hydrogenation.

Laboratory workup of the process of hydrogenating enzymic hydrolyzates has been carried out and checked in the Ioshkar-Olinsk Vitamin Work\* in AVD-180 horizontal autoclaves with a working volume of 120 liter. Solutions of sorbitol were obtained with an RS content of 0.04 and 0.062%. The yield of sorbitol was 95% by gas-liquid chromatography. Sorbitol solutions were examined in the process of microbiological oxidation of sorbitol to sorbose.

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