

D-SORBITOL PRODUCTION BY CATALYTIC HYDROGENATION OF D-GLUCOSE

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ABSTRACT

Hydrogenation of D-glucose in the presence of Raney nickel as a catalyst is employed for the synthesis of D-sorbitol. The effects of the reaction time in the range of 15-90 min., reaction temperature in the range of 10-60°C, and catalyst to D-glucose ratio in the range of 0.05-0.15 on the yield of D-sorbitol were studied.

High performance liquid chromatography as well as chemical methods were used to analyze the reaction products namely, D-sorbitol and D-mannitol.

The experimental design of Box-Wilson method was adopted to find a useful relationship between the three controllable variables and the D-sorbitol yield. The experimental data collected by this design is successfully fitted to a second order polynomial mathematical model. The analysis of variance (F-test) shows that the catalyst to D-glucose ratio has the greatest effect on the yield of D-sorbitol among other variables.

The optimum operating conditions which lead to maximum D-sorbitol yield are: 67 min. reaction time, 46°C reaction temperature, and 0.145 catalyst to D-glucose ratio. At these conditions the D-sorbitol yield is 87.15%, D-mannitol yield is 6.51%, and D-glucose conversion is 95.93%.

INTRODUCTION

Considerable efforts have been developed to the preparation of D-sorbitol from commercial sources. Both electrolytic reduction and catalytic hydrogenation processes are used. The raw material may be crystalline D-glucose or hydrolyzed cane molasses. The electrolytic reduction process is carried out in alkaline solution, so that D-mannitol and several other isomers are obtained because of the isomerizing effect of the alkaline catholyte. The reduction may require from one to two weeks^[1].

The catalytic hydrogenation of D-glucose or D-glucono-1,4-lactone to D-sorbitol has been widely applied on an industrial scale, and strenuous efforts have been made to achieve quantitative conversions.

Raney nickel catalysts, to which various promoters have been added, are widely used in the hydrogenation. These catalysts, which are prepared from nickel-aluminum alloys, are approximately as effective as platinum catalysts for the catalysis of hydrogenation at low pressures and temperatures. The catalytic hydrogenation process seems to have supplanted the electrolytic process for the manufacture of D-sorbitol^[2].

During the preparation of D-sorbitol from D-glucose by catalytic hydrogenation, D-mannitol is

also formed as a result of isomerization of D-glucose to d-fructose. Both D-sorbitol and D-mannitol can be separated chromatographically on a column of calcium poly(styrenesulfonate), which preferentially retain D-sorbitol^[3,4].

D-sorbitol has pharmaceutical application as well as other important uses such as being the starting material for the synthesis of isosorbide dinitrate. The latter is among the essential drugs as coronary vasodilator^[5]. The present work is concerned with the detailed study of the preparation of D-sorbitol by hydrogenation of D-glucose using Raney nickel as catalyst.

EXPERIMENTAL WORK

Application of Box-Wilson to the Experiments of Sorbitol Preparation

The effect of reaction time, reaction temperature, and catalyst ratio on the yield of D-sorbitol is investigated and analyzed by using the experimental design. Box-Wilson^[6-8] central composite design is used to find a suitable relationship between the three independent variables and the observed response (D-sorbitol yield).

In order to design the experiments, the operating range of the variables is first specified, thus; let X_1 be the reaction time from 15 to 90 min., X_2 be the reaction temperature from 10 to 60°C., and X_3 be catalyst ratio from 0.05 to 0.15.

According to the following equation, the total number of experiments (N) is:

$$N = 2^3 + 2(3) + 1 = 15$$

where 2^3 represents the factorial points, the 2×3 are the axial points, and 1 represents the center point.

The following equations are used to setup the relationship between the coded variables, X_j , where $j=1, 2, 3$, and the corresponding real variables are as shown below, and Table (1) shows the coded and real values of the experiments to be conducted.

$$X_{1 \text{ coded}} = \frac{X_{1 \text{ central}} - 52.5}{37.5} * \sqrt{3} \quad (1)$$

$$X_{2 \text{ coded}} = \frac{X_{2 \text{ central}} - 35.0}{25.0} * \sqrt{3} \quad (2)$$

$$X_{3 \text{ coded}} = \frac{X_{3 \text{ central}} - 0.1}{0.05} * \sqrt{3} \quad (3)$$

Table (1) The coded and real variables of the experiments to be conducted according to Box-Wilson method.

Run No.	Coded Variables			Real variables		
	X_1	X_2	X_3	X_1	X_2	X_3
1	-1	-1	-1	31	21	0.0711
2	1	-1	-1	74	21	0.0711
3	-1	1	-1	31	49	0.0711
4	1	1	-1	74	49	0.0711
5	-1	-1	1	31	21	0.1289
6	1	-1	1	74	21	0.1289
7	-1	1	1	31	49	0.1289
8	1	1	1	74	49	0.1289
9	-1.732	0	0	15	35	0.1
10	1.732	0	0	90	35	0.1
11	0	-1.732	0	52.5	10	0.1
12	0	1.732	0	52.5	10	0.1
13	0	0	-1.732	52.2	35	0.05
14	0	0	1.732	54.2	35	0.15
15	0	0	0	52.5	35	0.1

Feedstock

The feedstock for the reaction consists of the following: (1) A high purity dextrose (99%) manufactured by Hopkin and Williams Searle Company was used for the preparation of D-sorbitol. The molecular weight of D-glucose is 180.16 g/gmol. (2) Hydrogen with high purity (99.9%) from Al-Mansour Factory was used for dextrose hydrogenation. (3) High active Raney nickel catalyst manufactured by Aldrich Company was used for the hydrogenation of D-glucose to D-sorbitol. It is finely divided powder with pore size of 50 μ m and surface area of 90 m²/g. It was stored as 50% slurry in water.

The Procedure

Fig. (1) shows a schematic diagram of laboratory experimental unit for hydrogenation of D-glucose.

20 wt% D-glucose solution is prepared by dissolving 40 g D-glucose in 160 ml distilled water. This solution is brought to pH value of 9 by addition of 0.01 g calcium hydroxide per 40 g D-glucose and mixed with 2.8 g Raney nickel to form the reaction slurry. The resultant slurry is charged through the dropping funnel into the reaction flask. When the required temperature is reached, hydrogen gas is fed continuously at a flow rate of 1.86 liter/min through the reaction slurry by means of the perforated glass bulb tube to keep the slurry in considerable agitation during the reaction time. At the end of duration time, the solution is cooled and the catalyst is allowed to settle at the bottom of the reaction flask. The supernatant solution is filtered and analyzed by high performance liquid chromatography method for its D-sorbitol, D-mannitol, and D-glucose content.

Methods of Analysis^[10]

The determination of product composition is done quantitatively with a Shimadzu Lc-6A HPLC system. The operating conditions are: Column type – Shim Pack CLC-ODS, dimensions – 6 mm ID x 150 mm L, Mobile phase – a mixed solvent containing 10 mg sodium phosphate (6 parts) and acetonitrile (4 parts) at pH of 2.6, Flow rate – 1.5 ml/min, Column temperature – 40°C, Detector type – SPD-6A at 263 nm (spectrophotometric detector).

RESULTS AND DISCUSSION

Postulating the Mathematical Model

The experimental design of Box-Wilson method is adopted to find a useful relationship between the controllable variables and the observed response, i.e., the effect of reaction time, reaction temperature, and catalyst to D-glucose ratio on the observed D-sorbitol yield. Table (1) represents the experimental design approach. These experimental data are used to find a suitable model to represent the effect of the three variables on D-sorbitol yield within the variables ranges. The following second order model is the most suitable one:

$$y = -1.168413 + 2.040103 \times 10^{-2} X_1 + 2.377045 \times 10^{-2} X_2 + 11.45814 X_3 - 1.531997 \times 10^{-4} X_1^2 - 2.574208 \times 10^{-4} X_2^2 - 39.58045 X_3^2 \quad (4)$$

Determination of the Optimum Operating Conditions^[11]

The problem of finding the levels giving the best response can be solved by differentiating the ratio fitted expression for each independent variable and equating the derivative to zero.

According to this method, differentiating both sides of equation (4) for each independent variable and equating the derivative to zero, and solving these linear equations, the values of X_1 , X_2 , and X_3 corresponding to a maximum D-sorbitol yield on the fitted curve would be found. So, the reaction time (X_1) is equal to 67 min, reaction temperature (X_2) equal to 46°C, and the catalyst ratio (X_3) equal to 0.145.

At this optimum operating conditions, the optimum D-sorbitol yield according to equation (4) is 88.87% and the experimental D-sorbitol yield at the same conditions is 87.15%. also at this operating conditions, the experimental D-mannitol yield is 6.51% and the D-glucose conversion is 95.93%.

Effect of Reaction Time

Fig. (2) shows the effect of reaction time on the yield of D-sorbitol at different reaction temperatures and at the optimum catalyst ratio. It is clear that the yield increased with increasing

reaction time from 15 to 67 min. Beyond such reaction time, the yield of D-sorbitol decreased due to its isomerization to D-mannitol in the presence of Raney nickel catalyst as explained by Wright and Hartmann^[12] and also by Pigman and Hortorn^[2].

Fig. (3) shows the effect of reaction time on the yield of D-sorbitol at different catalyst ratios and at the optimum reaction temperature. This figure together with Fig. (2) show that there is no interaction between reaction time and temperature and also between reaction time and catalyst ratio.

Effect of Reaction Temperature

The effect of reaction temperature on the yield of D-sorbitol is shown in Fig. (4) and Fig. (5). These figures indicate that at lower temperature, longer reaction time and larger amounts of catalyst are necessary to obtain comparable values of D-sorbitol yield. At 45°C and 0.145 catalyst ratio, 67.5% D-sorbitol yield is achieved in 30 min, while at 17°C and 0.145 catalyst ratio, 67 min is needed to achieve the same yield, as shown in Fig. (4).

Fig. (5) shows that at 35°C and 67 min, 69% D-sorbitol yield is obtained using 0.08 catalyst ratio, while at 19°C and 67 min it is necessary to use 0.145 catalyst ratio in order to reach the same yield.

Figs. (4) and (5) also show that the use of high temperatures (above 46°C) reduces D-sorbitol yield, because at high temperatures, Raney nickel loses its hydrothermal stability causing at the same time the formation of colloidal nickel as explained by Phillips^[13].

Effect of Catalyst Ratio

Figs. (6) and (7) show the effect of catalyst ratio on the yield of D-sorbitol at different reaction times and temperatures respectively.

In Fig. (6), D-sorbitol yield increased with the increase of the catalyst ratio. For example, increasing the catalyst ratio from 0.05 to 0.13 at 46°C and 67 min causes an increase in the yield of D-sorbitol from 53% to 87.5%. This figure also shows that the time required to reach 67.5% yield can be reduced from 67 to 30 min by increasing catalyst ratio from 0.07 to 0.13.

Fig. (7) shows that there is no interaction between the catalyst ratio and the reaction temperature.

CONCLUSIONS

1. The three variables of reaction time, reaction temperature, and catalyst ratio affect the D-sorbitol yield in the order of: catalyst ratio > reaction time > reaction temperature.
2. A quantitative relationship between D-sorbitol yield and the three variables, is well represented by a second-order polynomial model.
3. The optimum operating conditions are 67 min reaction time, 46° C reaction temperature, and 0.145 catalyst ratio. At these conditions the yield of D-sorbitol is 87.15%, the yield of D-mannitol is 6.51%, and the conversion of D-glucose is 95.93%.
4. Beyond 67 min reaction time, the D-sorbitol yield is decreased.
5. Increasing the reaction temperature above 46°C leads to decrease in D-sorbitol yield.
6. D-sorbitol yield and D-glucose conversion increased by increasing the catalyst ratio from 0.05 to 0.15. While D-mannitol yield decreased as the catalyst ratio is increased.

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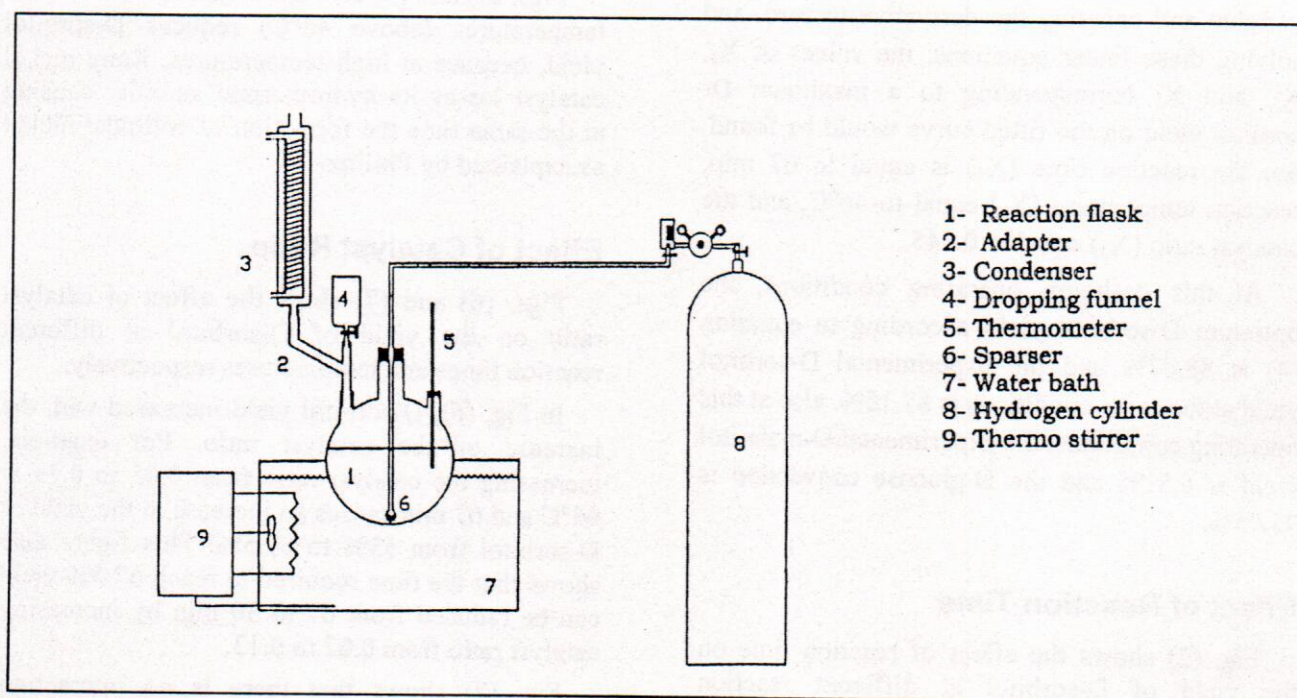


Fig. (1) Laboratory experimental unit

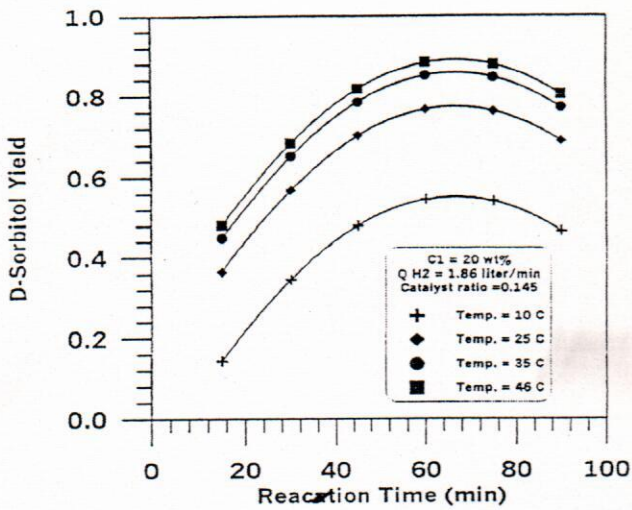


Fig. (2) D-sorbitol yield vs. reaction time at different temperatures

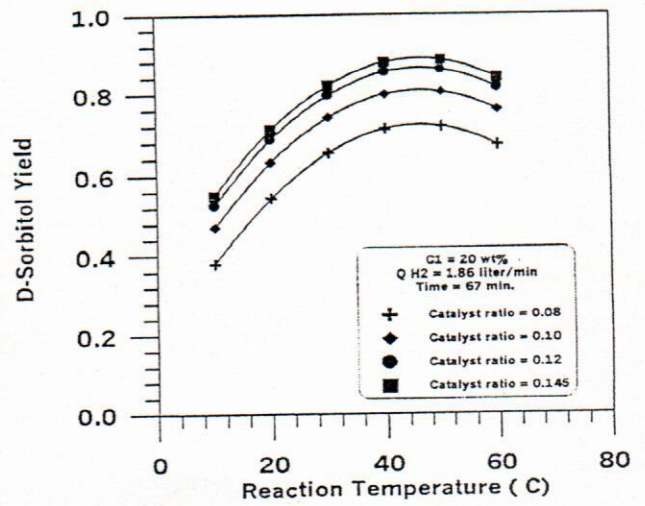


Fig. (5) D-sorbitol yield vs. reaction temperature at different catalyst ratios

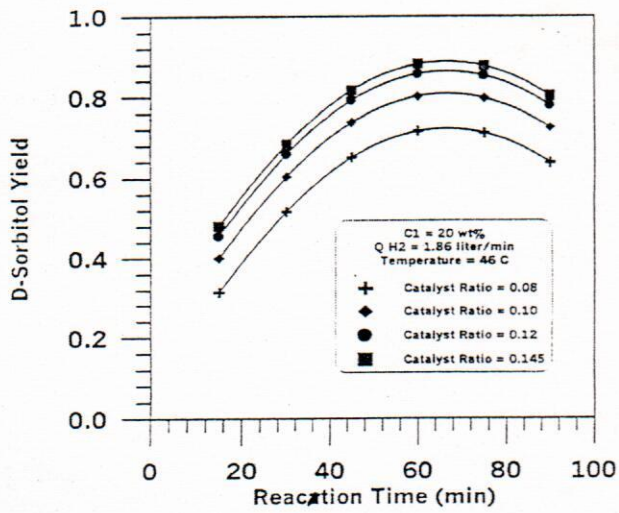


Fig. (3) D-sorbitol yield vs. reaction time at different catalyst ratios

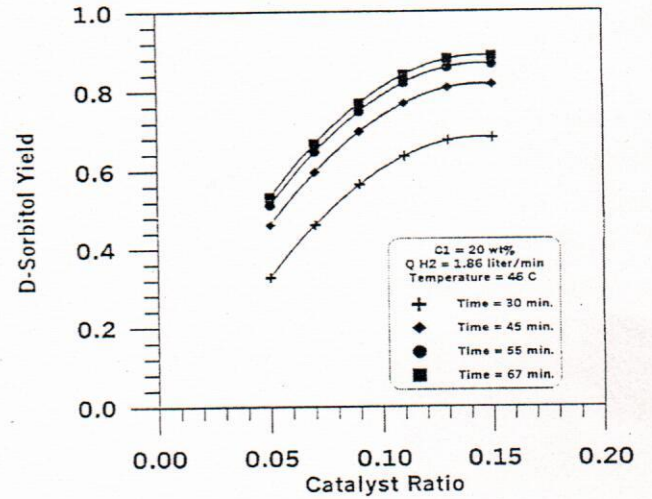


Fig. (6) D-sorbitol yield vs. catalyst ratio at different times

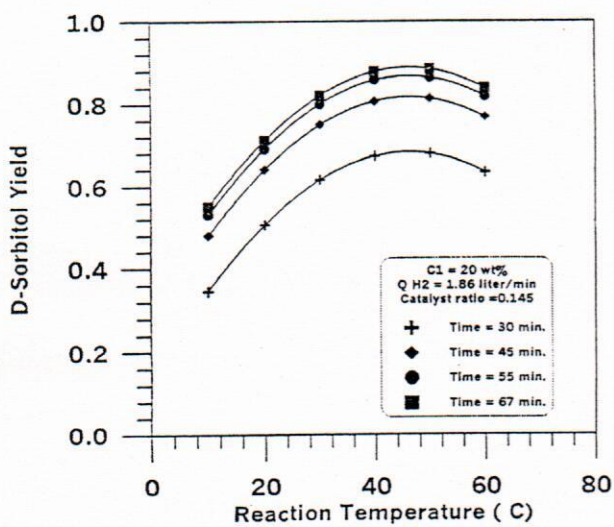


Fig. (4) D-sorbitol yield vs. reaction temperature at different times

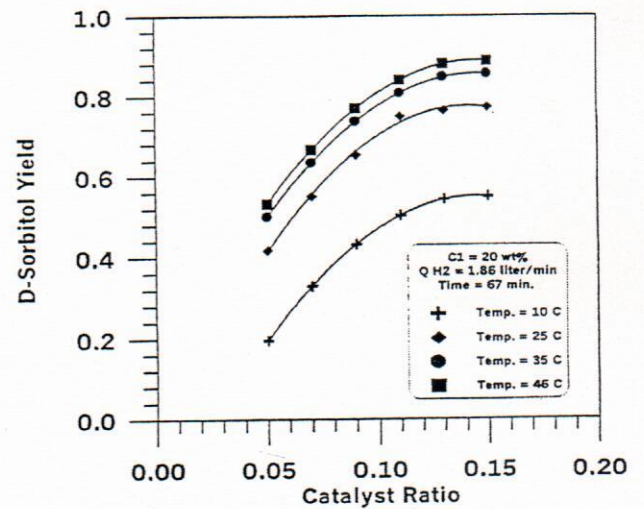


Fig. (7) D-sorbitol yield vs. catalyst ratio at different temperatures