

The Preparation of D-glucitol in A Multi-tube Airlift Loop Reactor with Low *H/D* Ratio

W. Jianping*, W. Changlin, and L. Yanxin
School of Chemical Engineering and Technology,
Tianjin University, Tianjin 300072, China

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The preparation of D-glucitol from D-glucose aqueous solution by hydrogenation over Raney Nickel catalysts was carried out in a 0.06 m³ multi-tube airlift loop reactor (MALR) with low *H/D* ratio. Five main affecting factors on reaction time and molar yield to D-glucitol including reaction temperature, reaction pressure, pH, hydrogen gas flowrate and content of active hydrogen were investigated and optimized. Under the optimum operating conditions, the average reaction time and molar yield were 65 min and 98.8 %, respectively. In addition, the comparison of efficiency for the preparation of D-glucitol between the MALR with low *H/D* ratio and stirred tank reactor (STR) under the same operating conditions was conducted.

Keywords:

D-glucose, Hydrogenation, D-glucitol, Multi-tube airlift loop reactor with low *H/D* ratio.

Introduction

D-glucitol is an important material that has been widely used in many fields such as pharmaceutical industry, food industry, tooth-paste, cosmetics, paper industry, chemical industry and so on. Further more, D-glucitol is the main material for the preparation of vitamin C.

There are two methods to synthesize D-glucitol, including catalytic hydrogenation¹ and electro-synthesis.² Of these, the catalytic hydrogenation using STR or fixed bed reactor (FBR) is most widely used in commercial production, where D-glucose in a mass fraction of 50 % aqueous solution or in a mass fraction of 70 % aqueous solution is used as reacting substance and ruthenium,^{3,4} nickel,^{5,6} cobalt⁷ or hydrogen storage alloy^{8–10} are used as catalysts under high reaction temperature and high reaction pressure. Also, at these conditions, reaction materials are easy coked and hereby adversely affecting the reaction efficiency of D-glucose hydrogenation. Nothing is known, however, about the process for the direct hydrogenation of D-glucose to yield D-glucitol in a gas-liquid-solid three-phase flow MALR with low *H/D* ratio, which is suitable for the alteration to STR. Compared with STR, the MALR with low *H/D* ratio, characterized by a well defined flow pattern, better dispersing effects, relatively low power consumption and a higher mass transfer coefficient, are widely used in many chemical reactions.^{11,12} The aims of the present study were both to develop the MALR with low

H/D ratio and to obtain the optimum operating conditions for the preparation of D-glucitol from D-glucose hydrogenation. A comparison of the efficiency between MALR with low *H/D* ratio and STR was carried out to prove that the MALR with low *H/D* ratio could obtain a better result in preparing D-glucitol under the same operating conditions.

Experimental

Principle of synthesis

The product, D-glucitol, was obtained through the catalytic hydrogenation of D-glucose. In this reaction D-glucose was used as starting material, hydrogen gas was used as reductant and Raney Nickel was used as catalyst. The synthetic route was outlined in Fig. 1.

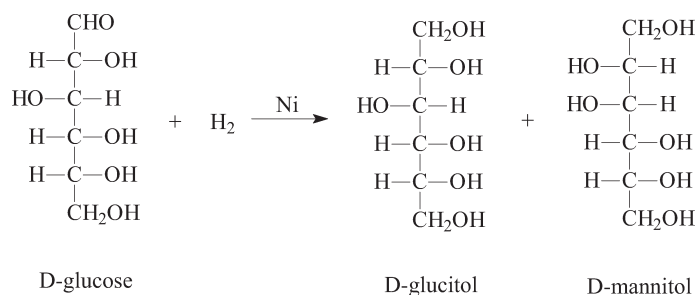
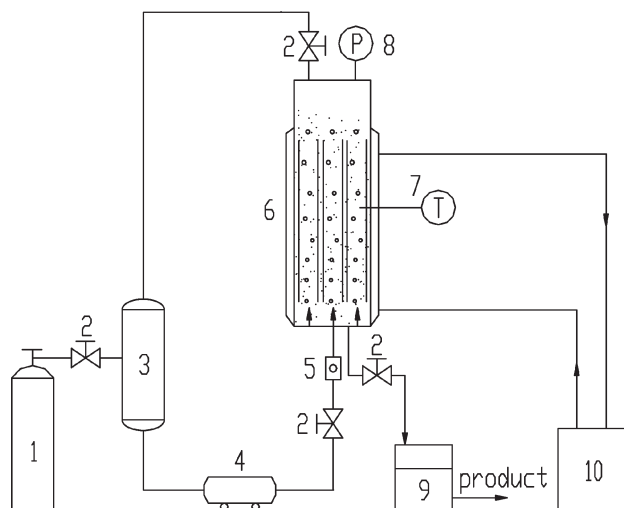


Fig. 1 – Structural formula and synthetic route of D-glucitol

Experimental setup

The flow chart and equipment drawing of the experimental setup used to prepare D-glucitol are schematically shown in Fig. 2 and Fig. 3, respec-

*Corresponding author. Tel: +86-22-27401664, Fax: +86-22-23501622, E-mail: jpwen@tju.edu.cn



1 – Stock tank of H₂; 2 – Stopvalve; 3 – Buffer tank; 4 – Air compressor; 5 – Gas flowmeter; 6 – MALR; 7 – Temperature detector; 8 – Pressure detector; 9 – Decompressed filtration unit; 10 – Temperature controller system

Fig. 2 – Flow chart of the experiment

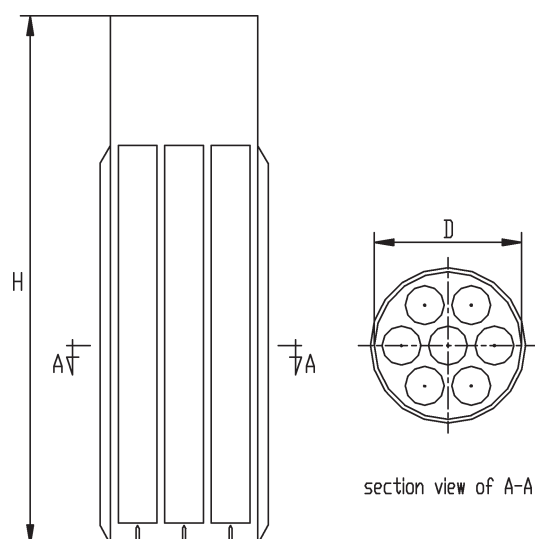


Fig. 3 – Equipment drawing of MALR

tively. Seven 0.6 m high draft tubes of 0.08 m inside diameter were centrosymmetrical and uniformly fixed inside the main 0.9 m high reactor tube of 0.3 m inside diameter. Correspondingly H/D was 3.0 and the work volume of the reactor was 0.06 m³. The space between the draft-tube and the bottom of the reactor was 0.021 m. Seven concentric jet nozzles of 0.004 m inside diameter were located in the bottom part of the riser, respectively. Hydrogen gas in the storage tank flew through buffer tank and was jet into the reactor by air compressor's pressurization. The jetting of hydrogen gas made the reaction material upflow through the seven draft-tubes and downflow through the gap between the draft-tubes and the reactor. The hydrogen gas flowrate was controlled by calibrated rotameter.

The extra hydrogen gas was reintroduced into buffer tank for recycling. The reaction temperature was adjusted by the temperature controller system.

Materials

Glucose with specific rotation 53.20 was prepared into mass fraction of 50 % aqueous solution, in which the concentration of chloride ion was controlled at less than 0.3 mg·m⁻³. Hydrogen gas was obtained through methanol splitting decomposition and its purity is above 99 %. FNL20 Nickel-aluminum-molybdenum alloy powder (Grain diameter: 0.1–0.35 mm, Nickel mass fraction, $w > 80\%$) with different content of active hydrogen was purchased from Jinzhou Catalyst Factory and used as catalyst.

Synthesis process

The preparation of D-glucitol was performed as follows: in the MALR, 0.05 m³ solutions of D-glucose (mass fraction of $w = 50\%$) and 1.0 kg nickel catalysts was added and mixed thoroughly feeding hydrogen gas by continuously. The reaction pressure and the reaction temperature were then increased to the required pressure and temperature. The concentration of D-glucose was detected by high performance liquid chromatography (HPLC). The hydrogenating reaction stopped when the concentration of D-glucose decreased to less than 0.5 %. Then the reaction pressure was reduced to the ordinary pressure and the reaction temperature was cooled to room temperature. Later, the reaction mixture was filtered under reduced pressure in order to get rid of the solid catalysts. The solution of D-glucitol product was obtained. The concentration of D-glucitol and D-mannitol were detected by HPLC.

Detecting method

Active hydrogen (atomic symbol "H") is single atom bonding on the surface of catalyst. The content of active hydrogen is determined by the specific surface area of catalyst and is measured by ¹H-NMR. The specific rotation of glucose and pH of the reaction mixture were detected by polarimeter (WXG-4, China) and acidimeter (PHS-3C, China), respectively. The quantity of D-glucitol and D-mannitol were detected by HPLC (Waters 510, USA) with a UR detector (Waters 486). The detecting conditions of HPLC were listed in Table 1.

The detected results of HPLC showed that the retention time, average recovery, standard deviation, variation coefficient, and linear correlation were 15.5 min, 100.2 %, 1.24 %, 1.23 %, 0.9999, respectively. The major byproduct was D-mannitol and its retention time was 14.5 min.

Table 1 – Detecting conditions of HPLC

Column temperature	Analytical column	Mobile phase $V_{\text{acetonitrile}}/V_{\text{water}}$	Detectic wavelength	Flow rate	Injection volume
90 °C	YWG-C ₁₈ , 10 μm 30 × 0.4 cm	60/40	240 nm	0.5 cm ³ min ⁻¹	20 μL

Results and discussion

Effect of T_R

The effect of T_R on reaction time and molar yield is shown in Fig. 4. The reaction time decreased gradually with T_R but the molar yield of D-glucitol was insensitive to T_R when T_R was less than 140 °C and decreased evidently when T_R is greater than 140 °C. This result may be explained by the increase in reaction temperature increasing the reaction rate and hereby shortening the reaction time; on the other hand, the further increase in the reaction temperature caused the reaction material coking and resulting in an increase in the molar yield of byproduct. So the optimum reaction temperature was selected as 140 °C.

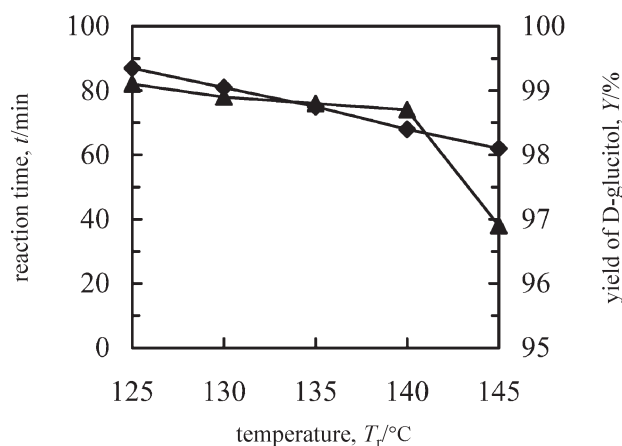


Fig. 4 – Effect of reaction temperature on reaction time and yield of D-glucitol. Reaction time (◆) and yield (▲) ($p_R = 6$ MPa; Active hydrogen, $v = 290$ cm³ · g⁻¹; pH 4; $Q_g = 75 \times 10^3$ cm³ · min⁻¹)

Effect of p_R

Fig. 5 shows the effect of p_R on the reaction time and molar yield of D-glucitol. The reaction time decreased with the increase in the reaction pressure but the molar yield of D-glucitol increased. An increase in the reaction pressure would enhance the solubility of hydrogen gas in the solution and thus increase the reaction rate. The optimum p_R for the shortest reaction time and the highest molar yield of D-glucitol was selected as 7 MPa.

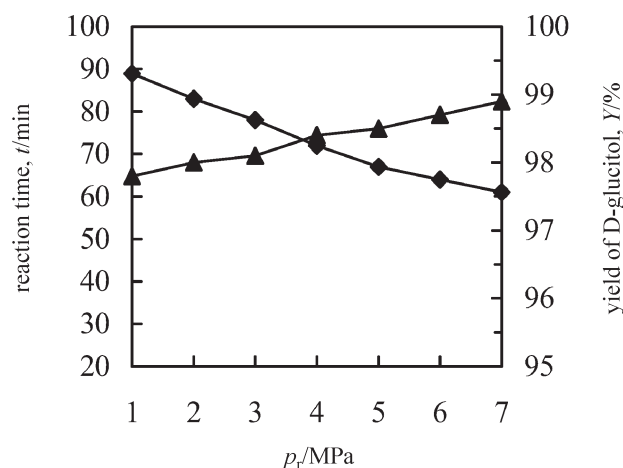


Fig. 5 – Effect of reaction pressure on reaction time and yield of D-glucitol. Reaction time (◆) and yield (▲) ($T_R = 130$ °C; Active hydrogen, $v = 290$ cm³ · g⁻¹; pH 4; $Q_g = 75 \times 10^3$ cm³ · min⁻¹)

Effect of active hydrogen

As observed from Fig. 6, the increase of active hydrogen contained in unit mass of nickel catalysts can accelerate of hydrogenating D-glucose but not alter the reaction equilibrium. The optimum content of active hydrogen was selected as specific volume, $v = 310$ cm³ · g⁻¹.

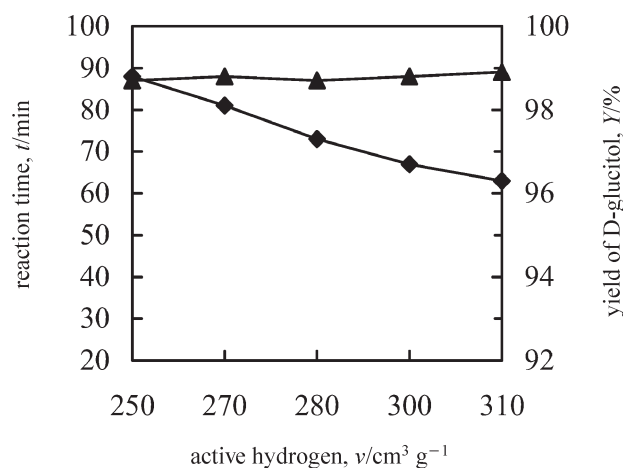


Fig. 6 – Effect of active hydrogen on reaction time and yield of D-glucitol. Reaction time (◆) and yield (▲) ($T_R = 130$ °C; $p_R = 6$ MPa; pH 4; $Q_g = 75 \times 10^3$ cm³ · min⁻¹)

Effect of pH

The typical results of the reaction time and molar yield of D-glucitol as a function of pH are illustrated in Fig. 7. The reaction time decreased with increase in pH but molar yield of D-mannitol increased more remarkably. This may be attributed to the fact that the increase in pH can increase the amount of negative charge in the active regions of catalysts and enhance the ability of catalysts' donating electrons, resulting in increased reaction rate. But the increase in pH can also bring about isomeric change of D-glucose into D-mannitol. The optimum pH of the reaction solution was selected as 4.2 for molar yield of D-mannitol less than 1.0 %.

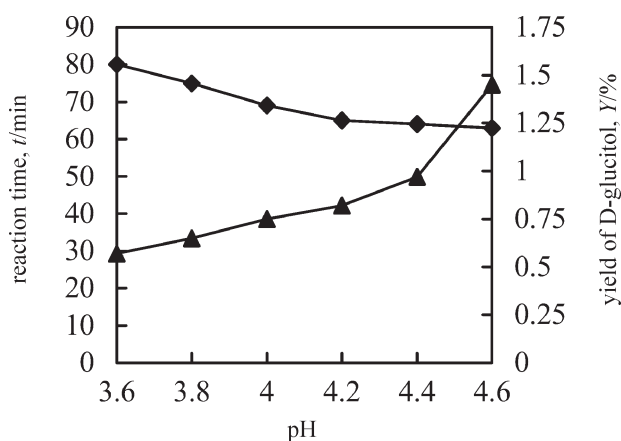


Fig. 7 – Effect of pH on reaction time and yield of D-mannitol. Reaction time (◆) and yield (▲) ($T_R = 130\text{ }^\circ\text{C}$; $p_R = 6\text{ MPa}$; Active hydrogen, $v = 290\text{ cm}^3 \cdot \text{g}^{-1}$; $Q_g = 75 \times 10^3\text{ cm}^3 \cdot \text{min}^{-1}$)

Effect of Q_g

As seen from Fig. 8, the reaction time decreased with increasing the hydrogen gas flowrates. This was mainly attributed to the fact that the increasing gas flowrates brings about the uniform distribution of nickel catalysts as the solid phase, the increase of the gas holdup and the decrease of the bubble diameter. These variations increased the gas-solid and liquid-solid interfacial area and the overall gas-liquid and liquid-solid volumetric mass transfer coefficient, thus changed the hydrogen gas kinetic regime and produced an increase in the reaction rate with fixed selectivity. However, when Q_g is greater than $65 \times 10^3\text{ cm}^3 \cdot \text{min}^{-1}$, both the reaction time and molar yield of D-glucitol are insensitive to the further increasing in the Q_g , and leading to excessive power consumption. The optimum hydrogen gas flowrate was selected as $65 \times 10^3\text{ cm}^3 \cdot \text{min}^{-1}$.

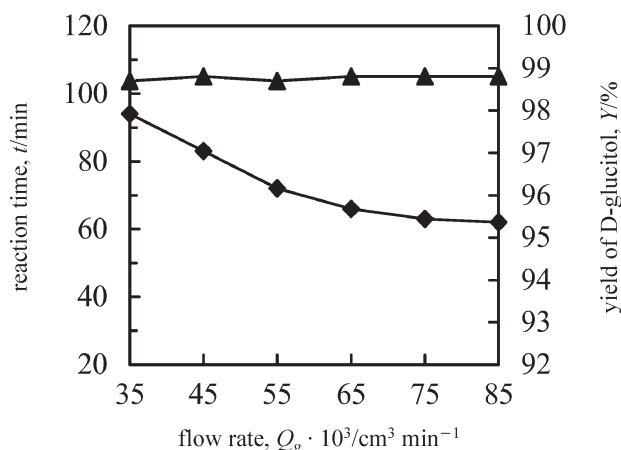


Fig. 8 – Effect of gas flowrate on reaction time and yield of D-glucitol. Reaction time (◆) and yield (▲) ($T_R = 130\text{ }^\circ\text{C}$; $p_R = 6\text{ MPa}$; Active hydrogen, $v = 290\text{ cm}^3 \cdot \text{g}^{-1}$; pH 4)

Stability observation under the optimum operating conditions

The experiment was carried out at $T_R = 140\text{ }^\circ\text{C}$, $p_R = 7\text{ MPa}$, active hydrogen $v = 310\text{ cm}^3 \cdot \text{g}^{-1}$, pH 4.2, $Q_g = 65 \times 10^3\text{ cm}^3 \cdot \text{min}^{-1}$. As it can be seen from Fig. 9, under the above optimum operating conditions, the average reaction time and the average yield of D-glucitol were 65 min and 98.8 % for ten times, respectively.

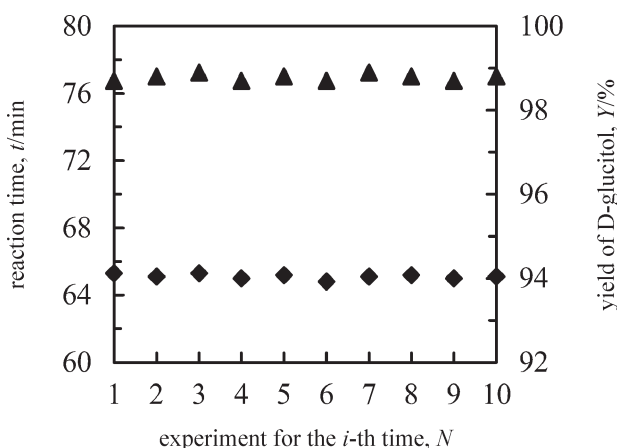


Fig. 9 – Stability of reaction time and yield under the optimum operating conditions. Reaction time (◆) and molar yield (▲) ($T_R = 140\text{ }^\circ\text{C}$; $p_R = 7\text{ MPa}$; Active hydrogen, $v = 310\text{ cm}^3 \cdot \text{g}^{-1}$; pH 4.2; $Q_g = 65 \times 10^3\text{ cm}^3 \cdot \text{min}^{-1}$)

Comparison of efficiency between MALR with low H/D ratio and STR

As can be calculated from table 2, the reaction time has decreased 16.7 %, molar yield of D-glucitol has increased 0.82 %, molar yield of D-mannitol has decreased 37.1 % in the MALR with low H/D ratio relatively to these in the STR under the same operating conditions, such as $T_R = 140\text{ }^\circ\text{C}$, p_R

Table 2 – Comparison of economical efficiency of MALR with low H/D ratio to that of STR

Reactor	Reaction time, t/min	yield of D-glucitol, $Y/\%$	yield of D-mannitol, $Y/\%$
MALR	65	98.8	0.83
STR	78	98.0	1.32

= 7 MPa, active hydrogen $v = 310 \text{ cm}^3 \cdot \text{g}^{-1}$, pH 4.2, $Q_g = 65 \times 10^3 \text{ cm}^3 \cdot \text{min}^{-1}$. It may be due to the higher liquid-solid and gas-liquid mass transfer coefficients in the MALR with low H/D ratio.

Conclusions

A new process for the production of D-glucitol by direct hydrogenation of D-glucose over Raney Nickel catalysts in MALR with low H/D ratio has been considered. The optimum operating conditions are listed as follows: T_R is 140 °C, p_R is 7 MPa, active hydrogen is $v = 310 \text{ cm}^3 \cdot \text{g}^{-1}$, pH is 4.2, Q_g is $65 \times 10^3 \text{ cm}^3 \cdot \text{min}^{-1}$. Under the optimum operating conditions, the average reaction time and the average molar yield of D-glucitol are 65 min and 98.8 %, respectively. The MALR with low H/D ratio has a better reaction time and molar yield of D-glucitol compared to the STR under the same operating conditions.

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Nomenclature

- D – diameter of the MALR, m
 H – height of the MALR, m
 p_R – reaction pressure, MPa
 Q_g – hydrogen gas flowrate, $\text{cm}^3 \cdot \text{min}^{-1}$
 T_R – reaction temperature, °C
 v_{H_2} – specific volume, $\text{cm}^3 \cdot \text{g}^{-1}$
 Y_m – molar yield, dimensionless
 w – mass fraction, %

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