



PROCESS DESIGN FOR SORBITOL PRODUCTION

Engineering

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ABSTRACT

Sorbitol is an important chemical compound which finds wide applications in various fields. In this paper, we have attempted to chart out a sorbitol plant design, complete with economic and process considerations. Different methodologies of production have been discussed and plant optimization has been done.

KEYWORDS

Process Design Sorbitol

Sorbitol - Introduction and Uses

Sorbitol ($C_6H_{14}O_6$) is a polyhydric alcohol with a sweet taste that occurs naturally in fruits and plants and can also be produced from glucose. It is an important organic compound and finds wide application in various different fields such as:

- 1) As a sweetener¹ - Sorbitol is approximately half times as sweet as sucrose and is often used as a sugar substitute. It is used in dietary foods, sugar free chewing gum, cough syrups, etc.
- 2) As a laxative¹ - It is used as a laxative to treat case of constipation. Sorbitol, due to its properties, draws water into large intestine and stimulates bowel movements.
- 3) For medical applications¹ - Sorbitol helps the body in production of Vitamin C. Also, it is used to distinguish pathogenic *Escherichia coli* 0157:H7 with normal *E. coli*.
- 4) Cosmetics¹ - Sorbitol is used in variety of cosmetic products like lotions, shampoos, mouthwash, etc. as a hygroscopic substance and thickener.
- 5) Miscellaneous uses¹ - It is used as Animal or Poultry feed, for production of alkanes in biofuels, foam in construction industry and as soft gels to store liquid medicines.

Target Production

TMR, a leading market intelligence firm based in the U.S., says in its latest report that the annual demand for sorbitol was 1,699.7 ktons in 2011, and will surge to 2,148.9 ktons by the end of 2018.²

We are assuming current global demand as 2,000 ktons/y. We are only considering India as our target consumer since ours is a medium sized plant and initially we want to start from here. Exact sorbitol consumption of India has been surveyed by some companies but it is not available for free. So, from Other Asia/Oceania part in Fig. 1, India and Indonesia are the major consumers of sorbitol in 2016. So, we are assuming that India consumes around 15% (300 ktons/y) of the total world consumption of sorbitol (2,000 ktons/y).

Intended Production: We will be producing 60 ktons/y out of 300ktons/y required for Indian market.

Gulshan Polyols Pvt Ltd, the biggest sorbitol producer in India produced 45 ktons/y of sorbitol at its facility in Gujarat in 2012³ (so our assumption is reasonable). It is marketed mostly in the form of 70% solution.

Various processes for producing Sorbitol

Sorbitol production all over the world has increased drastically from the last 10 to 15 years. This increased demand has led to the development of new technologies for its production.

Process Scheme 1: Hydrogenation of glucose to manufacture sorbitol⁴

Catalyst used has Ni as active metal. Reaction is typically carried out at 393 K and at a hydrogen pressure of 120 bar. SiO_2 , TiO_2 , Al_2O_3 and carbon are used as support materials. Various catalysts are used for hydrogenation of glucose - cobalt, palladium, platinum, rhodium and ruthenium have been used as active metals.

Process Scheme 2: Hydrogenation of starch to produce sorbitol³

This process converts starch to sorbitol. Starch is highly available, and can be obtained by various sources, for eg. from milk, corn, etc. Starch is obtained at low cost, and thus can be used for sorbitol production. Firstly, starch is hydrogenated. Ni is used as a catalyst. The temperature maintained was 120-160 °C, Pressure: 35 to 140 bar, pH: 3-7. The later steps include filtration, ion exchange and concentration.

Process Scheme 3: Hydrogenation of cellulose to produce sorbitol

Cellulose is the most abundant organic polymer on Earth. It can be derived from multiple sources. As it is natural, it is highly sustainable to use in the long run. Cellulose can be hydrogenated to form sorbitol in various ways differing in catalyst and operating conditions.

1. Using magnetic catalyst⁷:

Cellulose converts to sorbitol over the characterized catalyst $Ni_{1.63}Cu_{1.18}Al_{1.85}Fe_{0.79}$ and dilute phosphoric acid. The reaction is done in a high pressure reactor at 215 °C.

2. From waste cellulosic materials⁸:

Waste materials including cotton, paper, containing cellulose can be converted into sorbitol. Catalyst used for the process was 0.4% Ru/CNT (carbon nanotubes), including hydrogen and water (which acts as a solvent). The raw material and the catalyst were crushed using a ball-miller, resulting in 50% yield of sorbitol. The reaction was carried out at 205 °C, and 50 bar.

3. Hydrolytic hydrogenation of cellulose⁹:

The catalyst used here is Ru/C in aq. sulphuric solution. Sulphuric acid solubilizes the insoluble components of cellulose. This cellulose is first converted into glucose and subsequently, glucose is hydrogenated to form sorbitol.

Process Scheme 4: Production of sorbitol by the use of different sources for hydrogen¹⁰

In each of these processes, dextrose/glucose is hydrogenated over a catalyst, and then the product is concentrated and filtered. The source of hydrogen added is different leading to various methods:

1. Using ammonia syn gas: Ammonia synthesis gas under certain conditions, can act as a source of hydrogen analogous to pure H_2 . The underlying principle of hydrogenation of dextrose is the same as that of glucose here. The difference lies in the source of hydrogen. 2-4% Ni is used as catalyst. Syn gas, highly compressed and expanded to 202 bar, flows through Sorbitol plant from the ammonia plant.

3. Using hydrogen production from electrolytic cells: Used by Merck, this process involves hydrogenation of 50% aq. solution of dextrose at 71 bar and 150 °C, using Raney catalyst. The hydrogen used comes from electrolytic cells.

3. Using copper alloy: VEB Deutsche uses copper-nickel catalyst to produce sorbitol in a fixed bed at 135 °C, 202 bar.

Process Scheme 5: Production of sorbitol by different biotechnological methods:

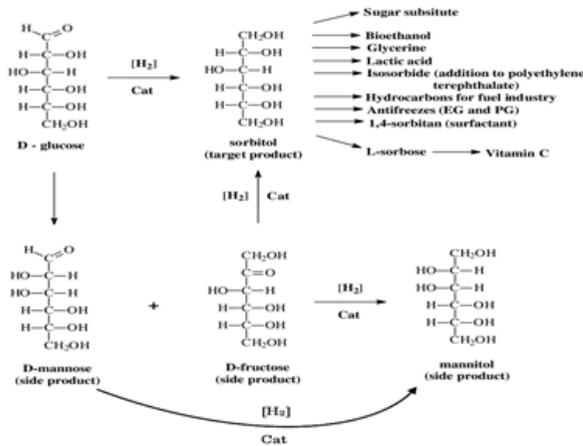
Biomolecules are used for direct conversion of biomass to sorbitol. This is highly natural and is potentially the future of sorbitol production as biotechnological advances are on the rise. The disadvantage is that there are various by-products produced and a large change in the existing infrastructure and machinery would be required by the companies to adopt this technology. Biomass includes glucose, fructose, dextrose, xylose etc. The different technologies used could be:

1. Zymomonas Mobilis:

It is a bacterium which produces a one-step reaction to produce sorbitol.

2. Lactobacillus Plantarum 12:

This lactic acid bacteria is found in fermented food products abundantly. pH control is found to be important for such reactions.



Process Verdict

We go ahead with the process of converting Glucose to Sorbitol, and then purification followed by concentration. The EP for this process is positive as Sorbitol is costlier than glucose (Rs. 30 - Rs. 35 = Rs. 5). The catalyst used for the reaction is Nickel.SiO2 is used as support material, since it produces least amount of by-product and is less prone to poisoning and deactivation of the catalyst.⁶ As the activity of the catalyst is high, the cost of Ni used to convert 1 Kg of glucose to sorbitol is low. In liquid phase batch type hydrogenation of glucose, mannitol, fructose and glycol were identified as the main side products.

Fig 6: Side Reactions of hydrogenation of glucose

Ref: No. 17 The conditions used for high yield, have been reported as 373K and 80 bar hydrogen pressure. This process is sustainable in the long run as all the materials used are environment-friendly and are present abundantly. The safety also won't be an issue as none of the materials used are corrosive, carcinogenic or deadly. We have already considered ease of startup during the selection of our process. Similar method is also used industrially (by Air Liquide), thus it can seamlessly integrated into existing market technologies.

Process Parameters

Effect of Pressure¹⁴: At low hydrogen pressure, the rate of the reaction is lower, as the concentration of dissolved hydrogen is low. Higher hydrogen pressure implies better yield of sorbitol. At high hydrogen pressure, the adsorption and desorption of hydrogen on the metal surface is higher, which increases the glucose conversion and reduces reaction time to form the product.

Effect of temperature¹⁴: On increasing temperature, glucose hydrogenation reaction is favoured, thus sorbitol yield is increased. With an increase in temperature from 353K to 383K, the activity of the catalyst increased by a factor of 3. Also, the yield increased with rise in temperature. But, the selectivity of sorbitol reduced at very high temperature, due to side product formation. So, the optimum temperature is taken as 373K.

Effect of feed concentration¹⁵: At low glucose concentration, saturated adsorption is reached very fast, due to strong adsorption of glucose molecules during hydrogenation. On increasing feed concentration, conversion of glucose decreases due to weak adsorption at high glucose concentration. The sorbitol selectivity also decreases with increase in concentration. Therefore, low glucose concentration is used for higher conversion and selectivity.

Type of reactor: Industrially, a batch reactor is used for this process. However, batch processes have the following disadvantages:¹⁶

1. New catalyst must be made in situ for every batch of feed
2. Large storage tanks required as capacity relative to reaction volume is very small
3. Steam consumption and power and labor requirements are relatively high
4. Ni catalyst is found to produce higher yield and selectivity in continuous than in batch reactor.⁶

Since, our production rate is high, and the need for sorbitol is throughout the year, therefore for now, we will go ahead with continuous reactor.

Reaction rate constants: All reactions are first order. For Glucose to Fructose isomerisation, rate constant data is not available.²⁰ We are assuming that our industry is based in India, and we are currently trying to cater to the Indian consumers.

Flow Chart

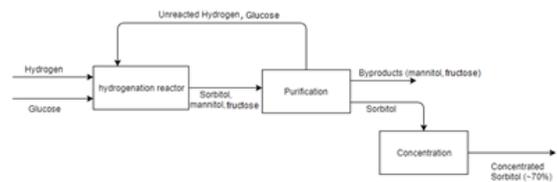


Fig 9: Flow Chart for Sorbitol Production

Mass Balance

Assumption: We are taking 330 plant operation days in a year (rest are for maintenance)

Selectivity = Desired product produced/ Reactant consumed in reactor
 Sorbitol production rate = 60ktons /yr = 60 ktons /yr × 1 yr /330 days × 1 day /24 hr × 1000tons /1ktons × 1kmol /182.17 kg = 41.58 kmol/hr
 Let selectivity of sorbitol from glucose be S 1

So, reactant consumed in reactor = Desired product produced/ selectivity = 41.58/S 1 kmol/hr

Conversion of glucose to sorbitol is X 1
 Feed of glucose entering reactor = reactant consumed in reactor/ conversion = 41.58/S 1 X 1 kmol/hr

Recycle of glucose = glucose entering reactor*(1 - conversion) = 41.58 (1-X 1) /S 1 X 1

Selectivity of glucose to sorbitol is 0.8, glucose isomerizing into fructose has been taken as S 2 and that to mannose is S 3 .

Sorbitol formed directly from glucose = reactant consumed in reactor* selectivity = (41.58/S 1) *S 1 kmol/hr = 41.58 kmol/hr

Fructose formed from glucose = reactant consumed in reactor* selectivity = (41.58/S 1) *S 2 kmol/hr

Mannose formed from glucose = reactant consumed in reactor* selectivity = (41.58/S 1) *S 3 kmol/hr

Conversion of fructose is taken as 0.82 into sorbitol and mannitol. Selectivity of fructose to sorbitol is

S 4 and of fructose to mannitol is S 5 .
 So sorbitol produced from fructose = fructose that converted* selectivity = 41.58 *S 2 /S 1 *(0.82 *S 4) kmol/hr

Mannitol produced from fructose = fructose that converted* selectivity = 41.58 *S 2 /S 1 *(0.82 *S 5) kmol/hr

Mannitol produced from mannose = (41.58/S 1) *S 3 kmol/hr (assuming all mannose goes to mannitol on hydrogenation)

Fructose left unconverted = Fructose formed *(1-conversion) = (41.58/S 1) *S 2 *(1-0.82) kmol/hr

H 2 required for glucose to sorbitol = number of moles of glucose that

converted directly to sorbitol
= 41.58 kmol/hr

H₂ required for fructose to sorbitol = number of moles of fructose that converted to sorbitol
= $41.58 \times 2 / S_1 \times (0.82 \times S_4)$ kmol/hr

H₂ required for fructose to mannitol = number of moles of fructose that converted to mannitol
= $41.58 \times 2 / S_1 \times (0.82 \times S_5)$ kmol/hr

Total H₂ required = $[41.58 + 41.58 \times 2 / S_1 \times (0.82 \times S_4) + 41.58 \times 2 / S_1 \times (0.82 \times S_5)]$ kmol/hr

We are taking excess of H₂ as hydrogen will favour more of sorbitol production from glucose as well as from fructose.

We will take 1.5 times of required H₂, which is $1.5 \times [41.58 + 41.58 \times 2 / S_1 \times (0.82 \times S_4) + 41.58 \times 2 / S_1 \times (0.82 \times S_5)]$ kmol/hr

Recycle H₂ = $0.5 \times [41.58 + 41.58 \times 2 / S_1 \times (0.82 \times S_4) + 41.58 \times 2 / S_1 \times (0.82 \times S_5)]$ kmol/hr

We will take 7.5 wt% glucose as feed, so mass of water entering = 92.5 wt% of feed

Glucose entering reactor = $41.58 / S_1 \times 1 \text{ kmol/hr} \times 182.172 \text{ kg/kmol}$
So water entering reactor = $41.58 / S_1 \times 1 \text{ kmol/hr} \times 182.172 \text{ kg/kmol} \times 92.5 / 7.5 \times 1 \text{ kmol/18 kg}$

= $5190.08 / S_1 \times 1 \text{ kmol/hr}$
Sorbitol produced is 70 wt%.
Sorbitol exiting reactor = $41.58 \text{ kmol/hr} = 41.58 \text{ kmol/hr} \times 182.172 \text{ kg/kmol} = 7,754.71 \text{ kg/hr}$

So water exiting reactor with sorbitol = $7,754.71 \times 30 / 70 \text{ kg/hr} = 3,246.3 \text{ kg/hr} \times 1 \text{ kmol/18 kg} = 180.35 \text{ kmol/hr}$

Since mass balance has to be there, water goes out with other side products.

Water exiting reactor = water entering reactor (since it is not undergoing a chemical reaction)

= $5190.08 / S_1 \times 1 \text{ kmol/hr}$
Selectivity Selection:²² Glucose goes to sorbitol, fructose and mannose as parallel reactions. The order of these reactions is equal to 1, so selectivity can't be chosen based on the order of these reactions. So we choose selectivity of glucose converting to sorbitol as 0.8 because sorbitol is our primary product. High selectivity ensures that desired product is formed as much as possible. This value is also backed by literature.

Fructose goes to sorbitol and mannitol in parallel which are also first order reactions. Selectivity of fructose to sorbitol is again chosen at a high value as sorbitol is our desired product and literature also gives a high value.

Mannose just forms mannitol so selectivity is 1 there. Equilibrium constants of the reactions are so high that they are nearly irreversible reactions so we don't have any equilibrium conversion.

Energy Balance

Energy Balance = $Q - H_{in} + H_{out} = 0$ (steadystate)
 $H_{in} = \sum F_{i0} H_{i0} = \sum F_i H_i$

We will not be calculating heat of reaction by using change in bond energies from reactants to products. It is a method used for only gaseous substances.

H_f^0 of reactants and products have been found which is defined at 25° C.²¹
Heat of formation at 373K = Standard heat of formation (at 298K) + Latent heat from 298K to 373K

Hence, Heat of formation of a substance at temperature other than 298K = $H_f^0 + C_p \Delta T \times \text{molar flow rate}$

Distillation Sequencing for products

The product stream exiting the reactor (i.e. stream 3) contains the following compounds- Glucose, Fructose, Sorbitol and Mannitol. The boiling point of Glucose and Fructose are very close and hence they are considered as a single stream. Similarly, Sorbitol and Mannitol are considered as a single stream. So basically, we are left with only two components to separate (glucose, fructose as blend 1, and sorbitol and mannitol as blend 2). These two blend streams can be separated by a distillation column. Marginal Vapour Load calculations are not needed, as the split is obvious as we have only two components.

Glucose and Fructose are isomers, and have very close boiling points. They cannot be further separated by distillation column. The best way to separate glucose and fructose industrially is by liquid liquid extraction (as per literature)²² by using butanol as the solvent. Glucose is separated, and the mixture of butanol and fructose is left. Since their difference in boiling points is significant. They can be separated by a distillation column.

Similarly, sorbitol and mannitol also have close boiling points, and cannot be separated by a distillation column. To separate these two, we are using ion exchange chromatography, which is used industrially to separate them.

These two options, LLE and ion exchange chromatography will surely add up to the cost, but it has to be done, in order to achieve separation.

Once the two streams are separated out, Glucose and Fructose are separated using Liquid-Liquid Extraction with Butanol whereas Sorbitol and Mannitol are separated using Ion-Exchange Chromatography. Further Butanol and Fructose are separated using a distillation column.

Mass Balance Table

The process consists of 7 streams- 4 cold streams and 3 hot streams. ΔT_{min} is assumed to be 10° C for our problem. All the hot streams are shifted down by 5° C and cold stream, up by 5° C. Cascading of the streams has been done for process heat integration in the figure below

Stream No.	Glucose	Fructose	Mannitol	Sorbitol	Hydrogen
1	0	0	0	0	52.79
2	55.12	0	0	0	0
3	9.92	1.464	2.171	41.58	0
4	0	0	2.171	41.58	0
5	0	0	0	41.58	0
6	9.92	1.464	0	0	0
7	0	1.464	0	0	0

Cascading

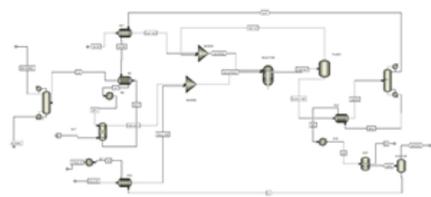
$T_{pinch} = 293^\circ\text{C}$
 T_{pinch} for hot streams = $293 + 5 = 298^\circ\text{C}$
 T_{pinch} for cold streams = $293 - 5 = 288^\circ\text{C}$
 $Q_{Hmin} = 0 \text{ kJ/mol}$
 $Q_{Cmin} = 114.17 \text{ kJ/mol}$
 $Q_{rec} = \sum Q_{hotstream} - Q_{cmin}$
 $= 148.69 - 114.17$
 $= 34.52 \text{ kJ/mol}$

The heat integration above turns out to be a threshold problem where no hot utility is required and the pinch point comes out to be at the highest operation temperature. The Grand composite curve of the process is also developed.

MER Design

The MER analysis yields 4 heat exchangers along with 3 cold utilities. No stream splitting was required and there wasn't any violation in the Cp inequality criteria. The Non-MER diagram was also made. After this, the economic analysis of the process was carried out.

Conclusions and Recommendations



Sorbitol is an important industrial chemical that finds its use in various industries. In this report, we reviewed various techniques for production of sorbitol and narrowed down to the optimum technique of production of sorbitol from Glucose. The process parameters were determined along with the distillation sequencing, Heat Exchanger Network Design and the Economic Analysis of the process. The calculated values were also matched with simulations done using Aspen Plus software.

The cost of production can be brought down if the location of the plant is such that there is easy access to Glucose and hydrogen to use as raw material. Also the by-products formed can be sold to appropriate industries. Also, the IRR of the process comes out to be 18.78% which suggests that this method of production of Sorbitol will be profitable and can be used industrially.

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