Sugar alcohols: An overview of manufacturing as a nutritive sweeteners

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Agenda

• Most common sugar alcohols.
• Benefits.
• Applications.
• Manufacturing process.
• Conclusion.
Sugar alcohols

• Know as sugar relatives.
• Naturally occurring in fruits and vegetables.
• Intermediate metabolites for microbial fermentation and in human body.
• Produced commercially by chemicals or microbial enzymes via the reduction (hydrogenation) of both mono-saccharides and di-saccharides.
Most common sugar alcohols

• **Derived from mono-saccharides:**
  - Xylitol → Xylose
  - Sorbitol → Glucose
  - Mannitol → Fructose

• **Derived from di-saccharides:**
  - Isomalt → Sucrose
  - Lactitol → Lactose
  - Maltitol → Maltose
Benefits

• low calorie bulk sweeteners.
• Provide about 2.5 Kcal/g.
• Excellent humectant, texturizing, and anti-crystallizing.
• Doesn't contribute to the formation of dental decay.
• May be useful as an alternative to sugars for people with diabetes.
General applications

- Used in a wide variety of products:
  - Chocolate products.
  - Ice cream.
  - Confectionery.
  - Chewing gums.
  - Backed goods.
Xylitol

- 2.4 kcal /g.
- 100% sweetness as sucrose
- Xylitol metabolism independently of insulin.

[five-carbon polyol]
Xylitol production process

• Can be produced by chemical or microbial process via the reduction of xylose from xylan rich hemi-cellulose hydrolysate.

• Xylan rich hemicellulose such as:
  - Sugar cane baggas.
  - Rice straw.
  - Nut shell.
  - Oat.
Chemical process

- Xylitol are chemically produced from hemi-celluloses via acid hydrolysis.
- The hemi-cellulose hydrolysate composition are xylose, arabinose, mannose, galactose and glucose.
- Catalytic hydrogenation in the presence of raney nickel at 135°C and 40 psi for 2.5 hr.
- Hydrogenation results from hemi-celluloses hydrolysate are: 73% xylitol, 6% arabinitol, 9% mannitol, 5% galactitol, and 6.8% sorbitol.
Chemical process
(Xylitol recovery)

- The xylitol can be separated from other sugar alcohols mixture by crystallization.

- Un-crystallized xylitol can be separated by liquid chromatography method.
**Microbial direct process**

- Several xylose utilizing microorganisms can produce xylitol as intermediate metabolite.
- The microbial pathway of xylose to xylitol is via enzyme xylose reductase in the presence of the co-enzyme NADPH.
- A number of yeast and filamentous fungi posses this enzyme, such as:
  - *Candida guilliermondii*
  - *Candida tropicalis*.
  - *Candida pelliculose*.
  - *Candida boidinni*. 
Factors effecting the microbial production of Xylitol

• Xylose optimum concentration (10%).
• Presence of other sugars (addition of glucose in the fermentation medium increase xylitol yield).
• Culture optimum conditions (inoculums size, PH, temperature, aeration, and agitation).
• Example:
  - Microbial fermentation of rice straw hydrolysate resulted in bioconversion efficiency of 69%.
  - Microorganism used fermentation is Candida guillermondii.
Microbial *indirect* process

- **Isomerization of Xylose to Xylolulse:**
  - Immobilized of Microbial enzyme Xylose isomerase.

- **Converting xylolulse to xylitol:**
  - Microbial fermentation using *Mycobacterium smagematise*. Or
  - Chemical hydrogenation using catalyst (raney nickel) at $120^\circ$C.

- **Xylitol recovery:**
  - Xylitol concentration to 84% solids.
  - Crystallization of Xylitol.
Sorbitol

- 2.6 kcal/g.
- 40-70% sweetness of sucrose
- Produced on large scale for over fifty years.
- Total consumption in US., Europe, and Japan 700,000 MT/year.

[six-carbon polyol]
Production process

• Can be produced by chemical, enzymatic, or microbial process.
• Raw materials (substrate) for sorbitol production are glucose or fructose.

1-Chemical process:
- Catalytic hydrogenation of glucose or fructose
Production process (Cont.)

2- **Enzymatic process**: (Immobilized system)

- **Glucose dehydrogenase**
  - **Glucose** → **Sorbitol**
    - *Bacillus subtilis*

- **Sorbitol dehydrogenase**
  - **Fructose** → **Sorbitol**
    - *Bacillus megaterium*

**Disadvantage**

- These two enzymes require costly co-factors.
Production process (cont.)

3- Fermentation process:

- Several mutants of the Genus *Zymomonas* bacteria are known to produce sorbitol instead of ethanol.
- These mutants convert fructose to sorbitol and glucose to gluconic acid.
- Conversion efficiency of fructose to sorbitol can be improved in the presence of glucose in fermentation media.
Fermentation process (cont.)

- *Zymomonas mutants* produce the enzyme glucose/fructose trans-hydrogenase as intracellular enzyme.
- This enzyme transfers hydrogen atom from glucose to fructose through the co-enzyme NADP.
- The gluconic acid produced from glucose can be converted to ethanol via 6-phospho-gluconate pathway.
Erythritol

- Human diet for thousands of years.
- Naturally exists in pears, melon, grapes, wine, soy sauce, cheeses and mushrooms.
- Currently used as a bulk sweetener to reduced calories in foods and beverages.

\[
\text{Erythritol} \\
\begin{array}{c}
\text{CH}_2\text{OH} \\
\text{H-C-OH} \\
\text{H-C-OH} \\
\text{CH}_2\text{OH}
\end{array}
\]

[4 carbon polyol]
Production process

• It can be produced by fermentation using wild osmophillic yeasts such as: *Trichosporon, Pichia, Candida, Torulopsis*, and *Trichosporonoides*.

• All these wild microorganisms can not be applied for production on large scale because it produce glycerol and ribitol as by-products.

• Microorganisms used commercially are mutants of *Aureobasidium sp. Moniliella pollinis* and *Torula corallina*.

• These industrial mutants do not produce these two by-products of glycerol and ribitol.
Optimum fermentation conditions

• These mutants under the following conditions are capable to produce up to 20% erythritol yield and over 49% conversion rate of glucose to erythritol:
  
  - Controlling glucose concentration in fed-batch process (30-40%).
  
  - Addition of Cu$^{2+}$ (3.2-12.9 mM) in fermentation media to improve catabolic repression of fumarate from glucose and CO$_2$ (*fumarate inhibits the enzyme erythrose reductase*).
  
  - Adding in the fermentation media inisitol & phytic acid (growth factors) and Mn $^{2+}$ (enzymes activator).
It was found that erythritol is biosynthesized from Fructose-6 phosphate as follow:

\[
\begin{align*}
\text{Fructose-6-P} & \xrightarrow{\text{Transketolase}} \text{Erythrose-4-P} + \text{acetyl- P} + \text{H}_2\text{O} \\
\text{Erythrose-4-P} & \xrightarrow{\text{ADP}} \text{Erythrose} + \text{ATP} \\
\text{Erythrose} & \xrightarrow{\text{Erythrose reductase}} \text{Erythritol} + \text{NADP} \\
\text{Erythrose} & \xrightarrow{\text{NADPH}} \text{Erythrose} + \text{ATP} \\
\end{align*}
\]
Erythritol Applications

• It is Generally Recognized as Safe (GRAS).
• It has a caloric value of 0.2 calories/ gram.
• Used as sugar substitutes.
• Its general applications are as flavor enhancer, formulation aid, humectants, nutritive sweetener, stabilizer and thickener.
• Its applications in foods are:
  - Cakes, cookies and bakery fillings.
  - Hard & soft candies and chewing gum.
  - Dairy drinks, frozen dairy desserts and yogurt.
  - Puddings.
  - Reduced and low-calorie carbonated & non-carbonated beverages.
Isomalt

- It belongs to the group of disaccharide alcohols.
- It is a mixture of gluco-sorbitol and gluco-mannitol.
- Internationally approved for foods and pharmaceutical applications.
Manufacturing process

• It is manufactured from sucrose in a two steps process.

1- **Enzymatic rearrangement process:**

Sucrose $\xrightarrow{1,2 \rightarrow 1,6 \text{ convertase}}$ Isomaltulose

Protaminobacter rubrum

Palatinos

2- **Hydrogenation process:**

Isomaltulose $\xrightarrow{100^0\text{C} / 4 \text{ bar hydrogen}}$

Raney nickel

1,6 glucopyranosyl-D-sorbitol (GPS)

1,1 glucopyranosyl-D-mannitol (GPM)
**Isomalt Applications**

- Isomalt is low caloric sweetener (2 Kcal./g) with unique, excellent tasting sugar-free bulk sweetener.
- Food products with Isomalt have the same appearance and texture as those made with sugar.
- It is being used in USA for several years in products such as hard candies, toffees, chewing gum, chocolates, backed goods, nutritional supplements, cough drops and throat lozenges.
- Currently used in a wide variety of products in Europe and in more than 70 countries.
Lactitol

- It is sugar alcohol derived from di-saccharide lactose.
- It is low calorie sweetener with about 40% the sweetness of sugar (sucrose).
- Used as bulk sweetener for low calorie foods.
- It is also used medically as a laxative.
Chemical process

4-O-α-D-Galactopyranosyl-D-glucito
Maltitol

- It is a sugar alcohol derived from di-saccharide maltose.
- Has 75-90% the sweetness of sugar (sucrose).
- Produced by hydrogenation of maltose obtained from starch.
- Used for sugarless hard candies, chewing gum, chocolate, baked goods and ice cream.
- It is recognized as GRAS in USA.
Sugar alcohols as food additives

<table>
<thead>
<tr>
<th>Name</th>
<th>Sweetness relative to sucrose</th>
<th>Food energy (kcal/g)</th>
<th>Sweetness per food energy, relative to sucrose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabinol</td>
<td>0.7</td>
<td>0.2</td>
<td>14</td>
</tr>
<tr>
<td>Erythritol</td>
<td>0.812</td>
<td>0.213</td>
<td>15</td>
</tr>
<tr>
<td>Glycerol</td>
<td>0.6</td>
<td>4.3</td>
<td>0.56</td>
</tr>
<tr>
<td>HSH</td>
<td>0.4–0.9</td>
<td>3.0</td>
<td>0.52–1.2</td>
</tr>
<tr>
<td>Isomalt</td>
<td>0.5</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Lactitol</td>
<td>0.4</td>
<td>2.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Maltitol</td>
<td>0.9</td>
<td>2.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Mannitol</td>
<td>0.5</td>
<td>1.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>0.6</td>
<td>2.6</td>
<td>0.92</td>
</tr>
<tr>
<td>Xylitol</td>
<td>1.0</td>
<td>2.4</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*Compare with: Sucrose*

|                | 1.0 | 4.0 | 1.0 |

## Sugar alcohols applications

<table>
<thead>
<tr>
<th>Type</th>
<th>Calories per gram</th>
<th>Approximate Sweetness (sucrose = 100%)</th>
<th>Typical Food Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbitol</td>
<td>2.6</td>
<td>50 - 70%</td>
<td>Sugar-free candies, chewing gums, frozen desserts and baked goods</td>
</tr>
<tr>
<td>Xylitol</td>
<td>2.4</td>
<td>100%</td>
<td>Chewing gum, gum drops and hard candy, pharmaceuticals and oral health products, such as throat lozenges, cough syrups, children’s chewable multivitamins, toothpastes and mouthwashes; used in foods for special dietary purposes</td>
</tr>
<tr>
<td>Maltitol</td>
<td>2.1</td>
<td>75%</td>
<td>Hard candies, chewing gum, chocolates, baked goods and ice cream</td>
</tr>
<tr>
<td>Isomalt</td>
<td>2.0</td>
<td>45 - 65%</td>
<td>Candies, toffee, lollipops, fudge, wafers, cough drops, throat lozenges</td>
</tr>
<tr>
<td>Lactitol</td>
<td>2.0</td>
<td>30 - 40%</td>
<td>Chocolate, some baked goods (cookies and cakes), hard and soft candy and frozen dairy desserts</td>
</tr>
<tr>
<td>Mannitol</td>
<td>1.6</td>
<td>50 - 70%</td>
<td>Dusting powder for chewing gum, ingredient in chocolate-flavored coating agents for ice cream and confections</td>
</tr>
<tr>
<td>Erythritol</td>
<td>0 - 0.2*</td>
<td>60 - 80%</td>
<td>Bulk sweetener in low calorie foods</td>
</tr>
<tr>
<td>Hydrogenated Starch Hydrolysates (HSH)</td>
<td>3</td>
<td>25 - 50%</td>
<td>Bulk sweetener in low calorie foods, provide sweetness, texture and bulk to a variety of sugarless products</td>
</tr>
</tbody>
</table>

* FDA accepts 0.2 kcal/s, but some other countries, such as Japan and the European Union, use 60 kcal/s.
Global sugar alcohols Market

• Sugar alcohols industry grow from ~ $1.9 billion in 2011 to ~$ 2.0 billion in 2012.

• The market is expected to grow at CAGR (compound annual growth rate) of 7.9 % and reach value ~ $ 3.0 billion by 2017.

• The biggest consumer market for sugar alcohols are in Europe.

• Due to the future demand, there are needs to increase sugar alcohols production capacity.

• The major manufacturing bases in the world are China and India.
Summary

• There are a worldwide need for healthy food products that are lower in calories.
• The USA consumption of sugar alcohols estimated about 376,640 tons per year.
• Sorbitol consumption in USA is about 54% of total sugar alcohols.
• Other sugar alcohols consumption in USA are sharing the 46%.
• Other sugar alcohols are showing market share increase.