Refining of Starch and Isomerized Sugar

(Extracted from the Diaion Manuals pages 264 to 270)

2. Refining of Starch sugar and Isomerized sugar liquor

(1) Starch sugar

Monosaccharides produced from starch by enzymatic decomposition, acid decomposition, enzymatic transfer and enzymatic linkage, oligo-saccharides, and their reduced materials are generally called as "starch sugar". Raw starch is mainly corn starch, and sweet potato starch, white potato starch and tapioca starch is also used as raw material. Such raw starch is categorized form its stock situation into ground starch, the former, and underground one, the latter.

Starch has the micellar structure of amylopectin, α-amylose, with β-amylose situated in the gaps, and it is in β-type at room temperatures and in α–type with corrupted crystal orientation at high temperatures. Several kinds of sugar are obtained by hydrolysis of starch in α–type with mineral acids or liquefying α-amylase and saccharifying amylase, depending on the decomposition degree. They all have sweetness and thus are called as "starch sugar". The hydrolysis degree is described as DE (Dextrose Equivalent), and those of practical starch sugar are from 15% to over 90%.

$$\text{Dextrose Equivalent (DE)} = \frac{\text{Direct sugar glucose}}{\text{Total solid}} \times 100$$

Glucose, a monosaccharide, is made from starch sugar with the highest DE, and powdered starch syrup or starch syrup is made from one with low DE that is mixture of glucose with dextrin and oligo-saccharides. Table VIII-2-1 summarizes the products from starch sugar.

[Table VIII-2-1] Products from Starch sugar

Produc		Concentration	
Glucose	Crystalline glucose	DE	99.5 ~ 100
	Refined glucose		97 ~ 98
	Liquid glucose		55 ~ 70
Starch syrup	Acid saccharified starch syrup	DE	30 ~ 60
	Enzyme-saccharified starch syrup		40 ~ 50
	Powdered starch syrup		15 ~ 40
	Malt starch syrup		40 ~ 50
Maltose	Crystalline maltose	as maltose	99 ~ 100%
	Powdered maltose		90 ~ 95%
	High maltose syrup		65 ~ 80%
Isomerized sugar	Glucose-fructose liquid sugar	as fructose	50 % below
	Fructose-glucose liquid sugar		50 % over

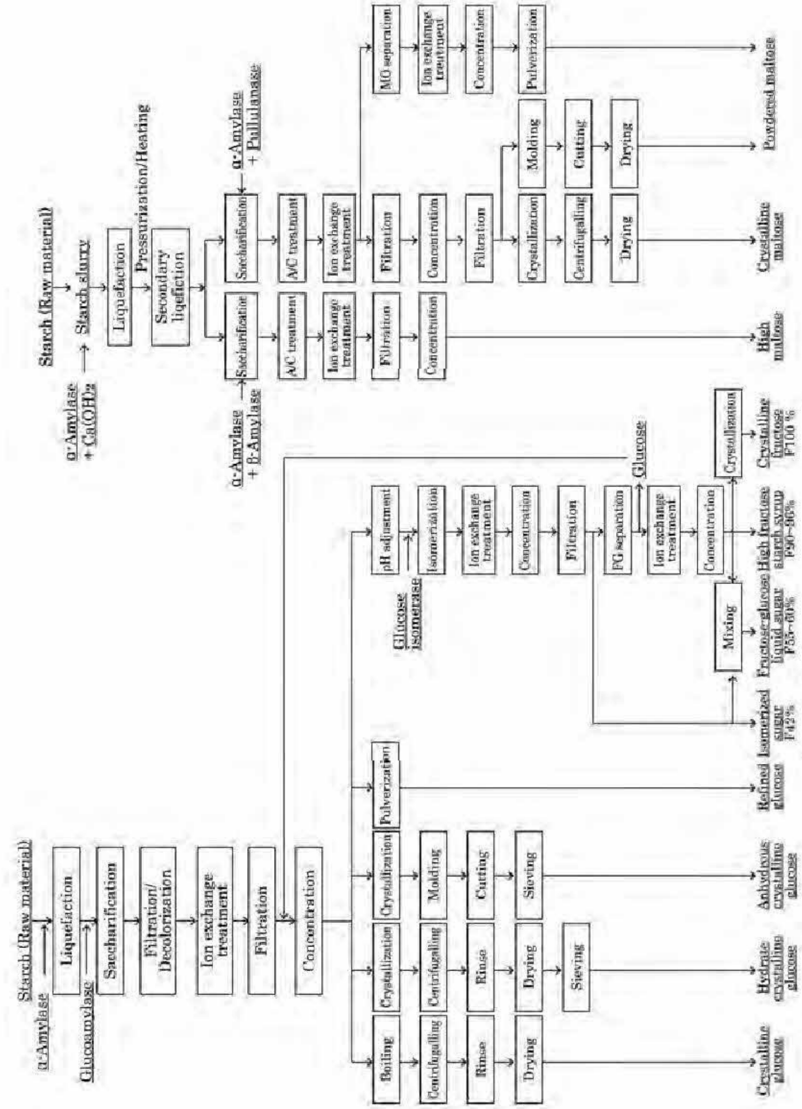
Impurities in starch sugar are primary impurities originated from starch and supplementary agents and secondary ones generated in the manufacturing process. Primary impurities vary in their quality and quantity depending on their resources; ashes, colorants, proteins, fatty acids, fats and tannins are such representatives. Ground starch includes more proteins and fats that are difficult to be removed than underground starch. Enzyme is the main source of impurities from supplementary agents, and affects the product purity, the amounts of ashes and proteins, to an degree not to be ignored. Melanoidin colorants and HMF, or 5-Hydroxymethylfurfural, are typical secondary impurities.

In acid saccharification, glucose generates bitter ingredients by the reverse reaction, and increases colored byproducts in severe conditions. In enzymatic saccharification, on the other side, inorganic salts from additives and proteins that enzyme carries increase during fermentation, although with little colored impurities.

(2) Isomerized sugar

Glucose made by saccharification of starch is difficult to be a substitute of sucrose, because its sweetness is only 0.5 ~0.6 times as high as sucrose. Fructose, isomerized sugar, however, has sweetness that is 1.7 times as high in cool conditions and 1.0 times in hot conditions as sucrose.

Glucose isomerizes by isomerase, enzyme to isomerize, at economical conditions at the best yield of 40 ~45%. New natural sweetner, the mixture of glucose and fructose, launched on the market in 1965, is called as "isomerized sugar"; the agricultural standard name is "liquid sugar of glucose and fructose". The demand for isomerized sugar has rapidly expanded mainly because it has almost the same sweetness as sucrose. Isomerized sugar with highly concentrated fructose at 55% is sweeter than sucrose. Table VIII-2-2 shows the compositions of the relevant products..



[Fig.VIII-2-1] Products from Starch sugar

Chromatographical separation of glucose and fructose in isomerized sugar liquor is explained at Clause 3 "Separation of sugar".

[Table VIII-2-2] Specifications of Isomerized sugar

JAS name	Glucose-fructose liquid sugar	Fructose-glucose liquid sugar	High-fructose Starch sugar
Fructose content	< 50%	≧50%, < 90%	≧90%
Reducing sugar other than glucose and fructose	Fructose content < 40% : ≦ 15% Fructose content 40~50% : ≦ 8%	≦6%	≦6%

(3) Refining of Starch sugar

Though there are many kinds of starch sugar and impurities in sugar liquor as already explained at the preceding clause, the refining process is almost the same. The manufacturing process of starch sugar is also illustrated in Fig.VIII-2-1. It is essential to remove the impurities as much as possible in the preparation steps, e.g. filtration and A/C treatment. Since starch sugars include impurities that cannot be removed by demineralization and decolorization with IERs and decrease IERs' efficiency drastically when adsorbed in IERs.

(i) Filtration

Precipitates generated by neutralization and others are removed from solutions by filter presses, pressurized leaf filters or micro filters. Filter aids, e.g. kieselguhr, are used to increase the filtration efficiency.

(ii) A/C treatment

Non-electrolytic and polymeric organic impurities are removed with powder or granulated A/C from plants and coals. Absorbing towers filled with granulated A/C can remove colorants, proteins, fatty acids, organic acids, hydroxymethylfurfural, HMF, and colloidal particles. However, colorants cannot be removed perfectly with A/C only, and thus they should be treated with A/C and IERs.

(iii) IERs treatment

IER treatments are categorized as follows and the actual process is selected from the points of raw liquor, impurities and required product quality.

a) SACER tower + WBAER tower: Two-bed and two-tower system (2B2T)
b) SACER and SBAER: Mixed-bed system (MB)
c) Combination of a) and b) systems (2B2T + MB)
d) Tandem repeat system of a) systems: (4B4T)

Underground starch can be treated by b) MB method only, since it holds limited impurities. Ground starch, on the contrary, is treated mainly by c) 2B2T + MB method, because it includes many kinds of impurities and proteins or fatty acids that can be removed perfectly in the preparation steps.

Majority of impurities are removed at the first 2B2T system and the latter 2B2T system plays a role as a polisher. The first 2B2T consists of DIAION® SK1B and WA30, and the former SK1B, a SACER, is difficult to be regenerated, and in cocurrent regeneration the Na ions in un-regenerated portions tend to leak. Thus, countercurrent regeneration is applied: high purity, quick increase of purity and high regeneration efficiency are realized by the perfect regeneration into H-form of the bottom IERs.

By countercurrent regeneration, the electric conductivity of liquid sugar with high dextyrose equivalent is 0.1 ~0.2 mS/m, 0.5 ~1 million Ωcm in electrical resistivity, at 25 °C. The life of IERs is 300 ~400 cycles, because they are gradually contaminated by the remaining impurities and deteriorated.

Various cares are required in sugar liquor refining, differently from pure water manufacturing, to prevent the contamination of enzymes and proteins and the pollution and the blocking in IERs from organisms.

The fractions in chromatographic separations to obtain high fructose starch syrup are treated by mixed-bed systems, since impurities concentrations are low and syrup viscosity is also low.

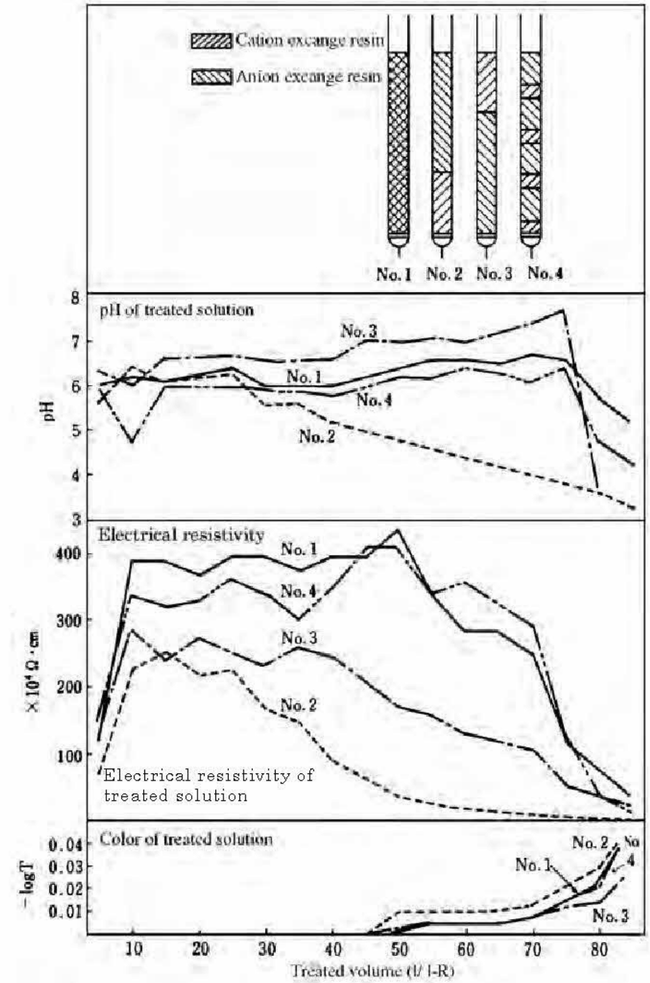
The selection of IERs is very important in sugar liquor refining. DIAION® SK1B, with standard crosslinkage in CERs, is applied with no problem, WBAERs or Type II SBAERs are used as AER since glucose is apt to deteriorate derived from their instability in alkaline conditions. The reason is that glucose decomposes to become organic acids or colored compounds and partly is isomerized to form fructose. Fructose is also unstable in alkaline conditions to become brown in color, to be isomerized or to be oligomerized by the reverse reaction, and finally causes decreases of purities and yields. Highly crosslinked SBAERs of Type II are easily contaminated by organic compounds, and decrease rapidly their own demineralization and decolorization functions. The life is sometimes shortened by half in the extremely situations.

Please note the slow diffusion rate of ions within liquid and resin phases due to the low viscosity compared to water. Porous type IERs, e.g. DIAION® PA406 and PA408, are suitable. We provide with two grades of WBAERs, DIAION® WA10 with good resistivity and DIAION® WA30. WA10 declines its function due to the partly hydrolysis during operation, and thus WA30 is usually applied in this field.

(iv) Notices in operation

The compositions and properties of raw liquor affect the refining methods seriously. Powdered starch syrup and relevant sugar products

with low saccharification but with high dextrin content should be carefully treated, because it is difficult to be demineralized.



[Fig.VIII-2-2] Effects by mixing in Mixed bed of toward treatments of sugar liquor

Colloidal polymeric organic compounds in sugar liquor tend to be adsorbed by porous resins, and thus resin layers are apt to become in blocks. Aeration is effective to prevent this blocking. In the resins that are used to treat sugar liquor, bacteria is easy to breed and deteriorates IERs' performance of decolorization and demineralization. Care should be taken to avoid such breeding of bacteria.

Since sugar liquor is unstable in alkaline conditions as already explained, not only the pH of feed liquor should be controlled to keep the inner and the treated liquor weakly acidic but the IERs grade and the operation conditions are carefully fixed. In mixed-bed systems, insufficient mixing of CERs and AERs brings local alkaline parts and thus worsen the quality of the treated liquor, as shown in Fig.VIII-2-2.

The most proper refining method and operation conditions are selected based on the physical and chemical properties of sugar liquor; e.g. maltose syrup and oligo-saccharides.