Dow
Liquid Separations

DOWEX
Ion Exchange Resins

The use of DOWEX ion exchange resins and adsorbents in corn sweetener processing

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Corn Sweetener Processing

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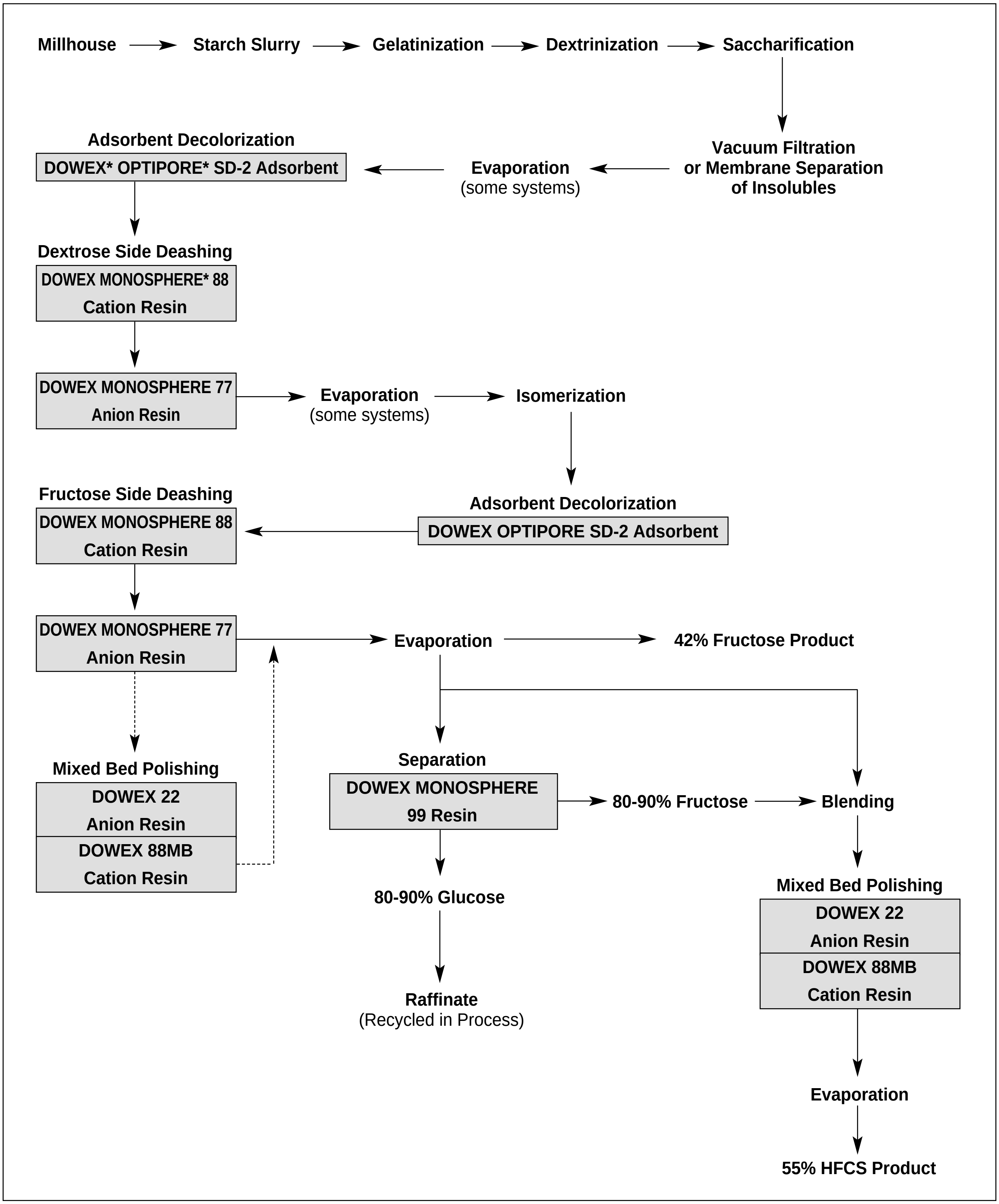


The use of DOWEX Ion Exchange Resins in Corn Sweetener Processing

DOWEX* products are used in four major unit processes

DOWEX resins and adsorbents are used in 4 major unit processes in corn sweetener processing: deashing, chromatographic separation, mixed bed polishing, and color removal.

In deashing and mixed bed polishing, specially designed DOWEX ion exchange resins remove unwanted ions and other contaminants which occur in the syrup stream.

In chromatographic separation, the family of DOWEX MONOSPHERE* 99 separation resins allows the production of enriched fructose by causing glucose and fructose to separate into bands of higher purity as they move down the chromatographic separation column.

In adsorbent decolorization, DOWEX OPTIPORE* adsorbent replaces or supplements traditional activated carbon systems, adsorbing impurities that contribute to the formation of color and off-flavors.

How ion exchange works

Ion exchange resins used for deashing and mixed bed polishing are **macroporous** polystyrene beads which are functionalized or “charged” to pick up unwanted ions in the syrup stream. The design and manufacture of each specialized DOWEX ion exchange resin is a complex, exacting science which involves controlling bead size, porosity, polymer chain length, crosslinking (molecular links that provide structural integrity), and other properties to give the optimum balance of long life and efficient operation.

Ion exchange resins work by **exchanging** one type of ion for another that has a greater attraction to active sites on the polymer chain. For example, DOWEX 88 strong acid cation resin is initially loaded with positive hydrogen ions. When syrup is pumped through the resin bed, DOWEX 88 resin readily exchanges its hydrogen ions for other, less desirable cations such as calcium, sodium, magnesium, and potassium which occur in the syrup stream.

Because the beads are porous, ion exchange takes place inside the beads, as well as on the surface, as the syrup stream moves through the bed (Figure 1). DOWEX deashing resins are called macroporous beads because of the relatively large pores which allow syrup components to move freely into the bead for efficient ion exchange. The total **exchange capacity** of each specific resin is related to the number of active sites on the polymer. The **operating capacity**, the capacity used to produce syrup of a given quality, of each specific resin is also affected by plant operating conditions and resin design.

When most of the active sites have been exchanged, the resin must be regenerated. For DOWEX 88 strong acid cation resin, **regeneration** involves forcing hydrogen ions back onto the exchange sites by pumping hydrochloric acid (or in some cases sulfuric acid) through the bed. In regenerating DOWEX 66 weak base anion resin, sodium hydroxide, soda ash, or ammonium hydroxide are used to displace acids picked up during syrup service. During the regeneration process, the undesirable ions are forced out of the resin and are rinsed away in the wastewater.

How deashing systems work

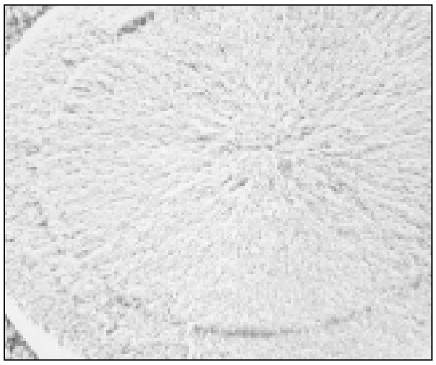
In deashing, a bed of strong acid cation resin is typically followed by a bed of weak base anion resin. This is referred to as a **unit pair**. DOWEX 88 strong acid cation resin and DOWEX 66 weak base anion resin have long been the industry standards for use in this process. They provide the ideal balance of high operating capacity, physical strength, economical regeneration, long life, and low operating costs.

More recently, DOWEX MONOSPHERE 88 and DOWEX MONOSPHERE 77 uniform particle size deashing resins have gained wide acceptance due to their greater ion exchange efficiency, increased syrup service time, and other performance advantages. DOWEX MONOSPHERE resins feature a highly uniform bead size, while standard resins exhibit a range of bead sizes, known as a Gaussian size distribution (Figure 2).

Although DOWEX MONOSPHERE resins offer enhanced performance, they utilize the same proven, optimized chemistry and function in essentially the same way as standard DOWEX 88 and DOWEX 66 resins.

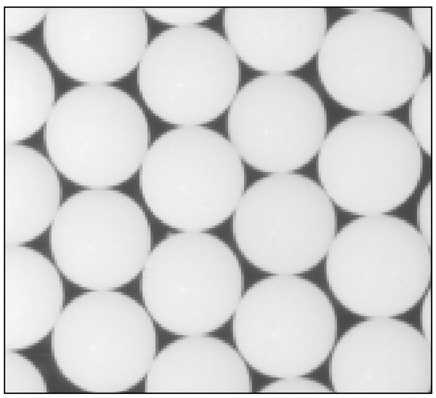
Deashing typically is performed at two stages in the corn sweetener process, first on the **dextrose side** and again later on the **fructose side**.

Figure 1– Cross section of macroporous ion exchange resin

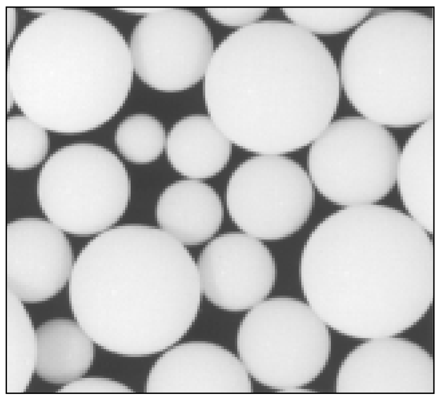


This cross section of a DOWEX macroporous ion exchange bead shows the countless tiny pores through which syrup components diffuse. This structure permits maximum syrup contact with the polymer's functional sites while providing the physical strength required for long life.

Figure 2 – DOWEX MONOSPHERE resin compared with standard resin



DOWEX MONOSPHERE 77



DOWEX 66

These photomicrographs show the excellent size uniformity of DOWEX MONOSPHERE 77 resin compared with standard DOWEX 66 resin. DOWEX MONOSPHERE resins provide more efficient ion exchange without excessive pressure drop.

Dextrose-side deashing

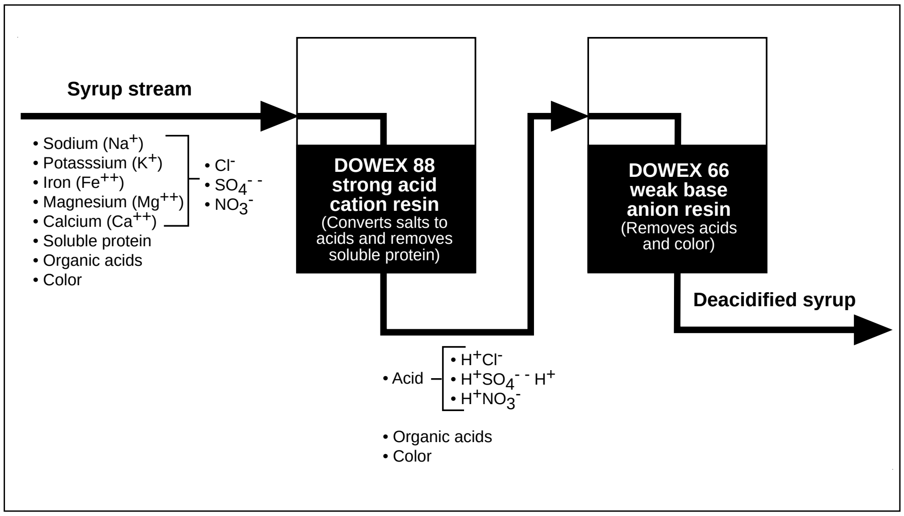
When the syrup stream enters the dextrose-side deashing unit, it carries an ionic load made up of ash (salts and mineral acids), as well as organic compounds which come from the process water, corn starch, and various production additives.

This stream first passes through a bed of DOWEX 88 (or DOWEX MONOSPHERE 88) strong acid cation resin (Figure 3). The main function of the cation resin is to remove **cations** (positively charged ions) such as sodium, potassium, iron, magnesium, and calcium. The cation resin also removes some soluble protein by providing an acidic environment in which amphoteric proteins take on cationic characteristics. During this exchange process, hydrogen cations are released from the exchange sites. The **anions**, e.g., chlorides, sulfates, nitrates, and other negatively charged ions associated with the exchanged cations, are passed on in the syrup stream as free acids.

Consequently, when the syrup leaves the cation bed, the concentration of mineral and organic acids is high. DOWEX 66 or DOWEX MONOSPHERE 77 weak base anion resin in the **free base form** removes these acids, resulting in a syrup which is relatively free of ions (deacidified syrup) as it leaves the unit pair. The weak base anion resin also removes some color from the syrup.

One of the most important functions of dextrose side deashing is the removal of calcium. Even very low levels of calcium will inactivate the isomerization enzyme.

Figure 3 – Dextrose -side deashing with DOWEX resins



In dextrose-side deashing, DOWEX 88 cation resin and DOWEX 66 anion resin work together (in separate beds) to remove salts, proteins, color, acids, and other impurities - resulting in a syrup which is relatively free of ions and color.

Fructose side deashing

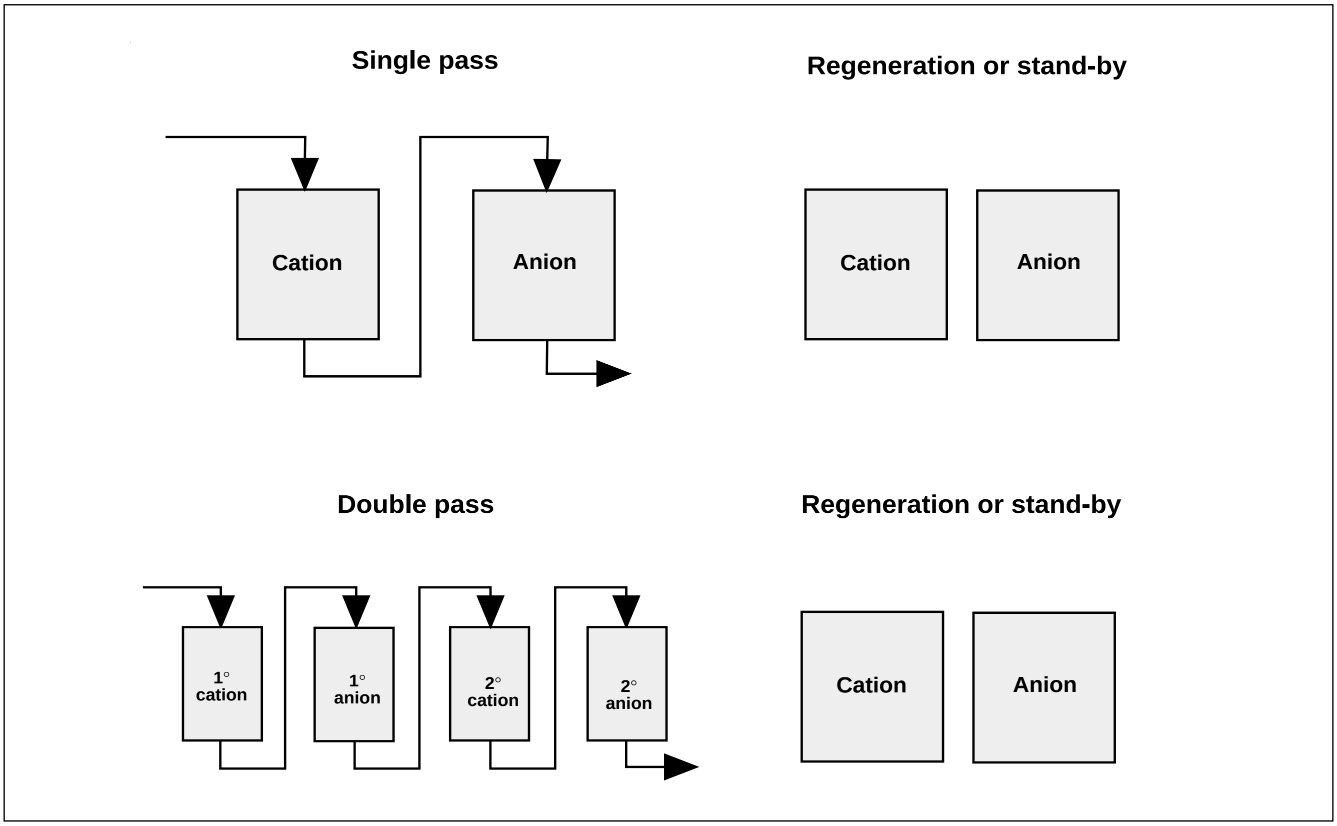
On the fructose side (after isomerization), deashing units perform the same basic function that they did on the dextrose-side. Impurities picked up during isomerization and pH adjustment need to be removed, but overall, there's a lower non-sugar load than on the dextrose side. As a result, the units typically run longer between regenerations. Since fructose is forty times more reactive than glucose, quality requirements are more stringent at this point in the process. Therefore, fructose side deashing units are often monitored more closely than those on the dextrose side.

Single pass vs. double pass systems

While systems vary considerably in their specific configurations, deashing systems generally consist of two or more unit pairs. In the simplest configuration, one unit pair is in service while the other is in the process of being regenerated or in is "standby". When the on-line unit approaches exhaustion, the regenerated unit is switched from standby to syrup service. This configuration is called a **single pass** system. **Double pass** systems have two unit pairs in series at any given time. In double-pass systems, the most recently regenerated pair is in the **secondary** position; the oldest unit pair in service is in the **primary** position.

Double pass systems produce a cleaner syrup than single pass systems because the effluent from the first pair is further deashed by the second. Running double pass also gives the plant a further insurance against upsets because of the larger on-line volume.

Figure 4 – Single pass vs. double pass systems



Because the syrup is treated by two pairs, a double pass system produces a much cleaner syrup. When breakthrough occurs, the secondary pair is moved to the primary position, the primary pair is regenerated, and the fresh pair moves to the secondary position.

Chromatographic separation

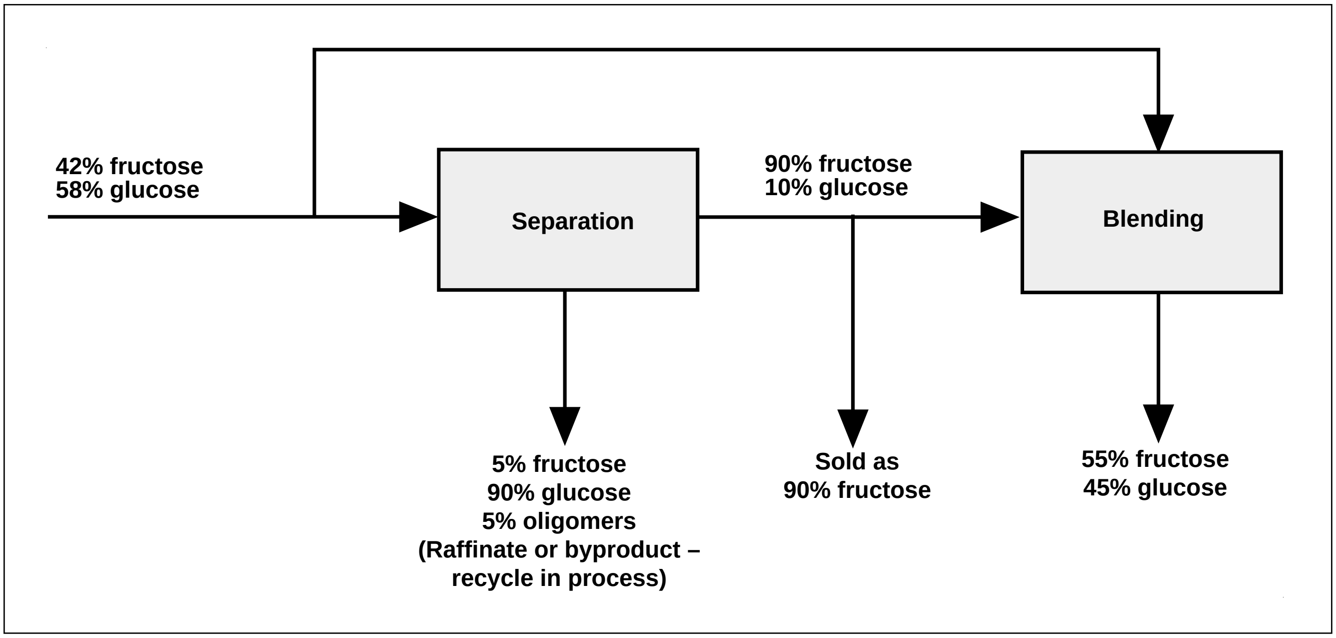
When the syrup stream reaches the chromatographic separation unit process, fructose concentration is approximately 42-45% of dissolved solids. This fructose level is as high as practical using current isomerization enzymes. Using chromatographic separation, fructose concentration can be increased to over 90%. The family of DOWEX MONOSPHERE 99 uniform particle size resins is used in this process.

Unlike the macroporous structure of DOWEX resins used in deashing, DOWEX MONOSPHERE 99 separation resins are **gel** beads which have a smooth, uniform surface (Figure 6). While macroporous resins are opaque, gel resins are translucent. Chromatographic separation resins are functionalized and they pick up a large amount of water. The sugars to be separated can dissolve into the water of the beads and interact with the calcium ion, which is the mechanism of separation of fructose from glucose.

DOWEX MONOSPHERE 99 resins for glucose/fructose separation are used in the calcium form, but similar resins for other separations are also available in the potassium and sodium forms. Fructose, glucose, and water form weak complexes with the calcium ion, with the glucose, fructose, or water functioning as a ligand associated with the calcium. The complex that calcium ions form with fructose is stronger than the complex formed with glucose; this difference is the basis for chromatographic separation of fructose from glucose[2]. This mechanism of separation is called **ligand exchange chromatography**.

[2]Chromatographic separation resins don’t “exchange” ions as do the resins used in deashing and mixed bed polishing. They function by adsorbing and “slowing” fructose as it moves down the column. The syrup doesn’t exchange ions in the process.

Figure 5 – HFCS Enrichment



Larger molecules such as the DP3s, DP4s, and higher oligosaccharides are not able to physically fit into some of the very small openings between polymer chains found in the gel resins. The mechanism of separating large molecules from small molecules by preventing some of the large molecules from getting inside the stationary packing is called size exclusion chromatography. Size exclusion chromatography is also taking place simultaneously with ligand exchange chromatography in the purification of fructose. The polysaccharides in the syrup stay outside the resin beads and are constantly moving down the column. As a result, they exit first. This mechanism is not usually used in purifying fructose, but chromatographic separation resins in the sodium or potassium form can be used for removing undesired oligosaccharides (higher molecular weight sugars) from dextrose to produce a high-purity (>99%) dextrose.

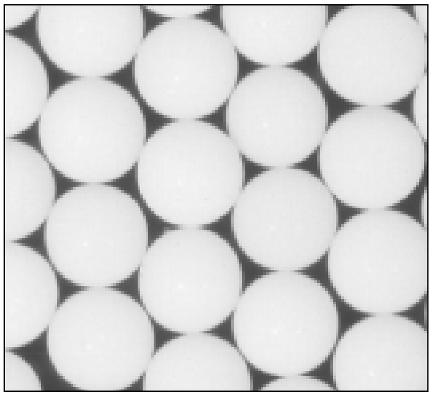
In service, 42% fructose syrup is added to a column or set of columns containing the resin (Figure 5). As the syrup stream moves down the column, on average, fructose moves more slowly than glucose. This results in separated bands of higher purity of each component within the column. Complex computer controls track these bands as they move down the column and cause streams of purified fructose (also called **extract** or **product**) and glucose plus oligosaccharides (also called **raffinate** or **by-product**) to be withdrawn through a series of outlets. At the same time, elution water and additional feed stock are being introduced to the column at various points as required in this continuous process.[3] Recycle is also used to advance the band profiles. At predetermined intervals the valves for incoming and exiting streams move downstream to keep pace with the established component profile in the separator.

Raffinate is typically sent back in the process to be re-isomerized. For HFCS 55 production, the highly purity (80-90%) fructose is blended with 42-45% fructose.

Two of the most critical factors in separation efficiency are the size and the size uniformity of the separation beads. Beads with a wide size distribution result in wide, less distinct bands of separation, higher pressure drop, and decreased operating efficiency. Operation with resins of a broader particle size distribution requires the use of additional elution water. The evaporation of elution water is by far the largest cost of operating a chromatographic separation process. By offering the most uniform bead size in the industry, DOWEX MONOSPHERE 99 separation resins help processors obtain faster, sharper, more economical separations.

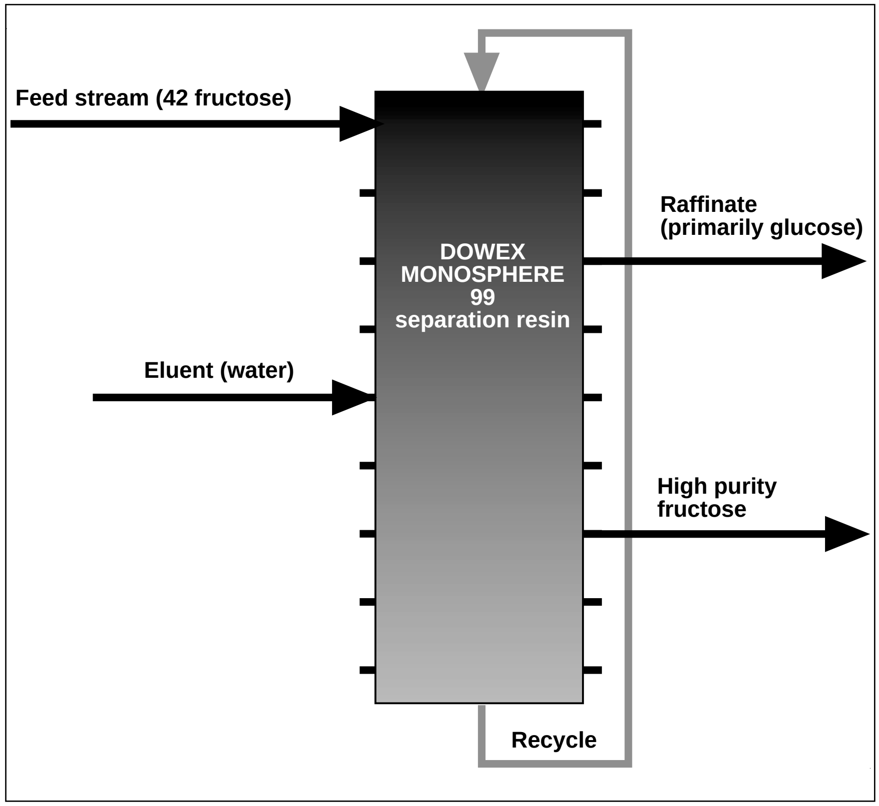
[3]This sophisticated process, called a "pseudo-moving bed" system, is described in greater detail in a separate brochure, *"Chromatographic Separation of Fructose and Glucose with DOWEX MONOSPHERE Resins",* Form No. 177-01566/171-400-E.

Figure 6 – DOWEX MONOSPHERE 99 gel resin



Unlike the macroporous resins used in deashing and mixed-bed polishing, DOWEX 99 separation resins are gel-type resins with a smooth, non-porous structure. Gel resins perform chromatographic separation by selective affinity for syrup stream components rather than by exchanging ions.

Figure 7 – Chromatographic separation with a pseudo-moving bed system



This simplified diagram represents the pseudo-moving bed system commonly used in corn sweetener production. The column, filled with resin beads, has multiple inlets and outlets. Feed stock (42% fructose), eluent (water), and recycled syrup from the column are continuously added at various inlets as dictated by a sophisticated computer control system. At the same time, high purity fructose (90+%) and enriched glucose (raffinate) are withdrawn from the zones of high purity that form as the syrup moves down the column.

Mixed bed polishing

Mixed bed polishing is used near the end of the 55 HFCS process to **polish** the final product and ensure that it meets purity and storage stability requirements. Mixed bed polishers remove color, color precursors, silica, weak organic acids, and other substances which can destabilize syrups. Mixed bed polishers are capable of deashing syrups to very low levels (below 0.5 micro mhos/cm or 0.2 ppm as NaCl) of impurities.

Two DOWEX resins designed specifically for mixed beds are used: DOWEX 88MB strong acid cation resin and DOWEX 22 strong base anion resin. They are contained in the same bed and are intimately mixed during service (Figure 8).

The resin composition of mixed bed polishers is typically 60% by volume DOWEX 22 strong base anion resin to 40% DOWEX 88MB strong acid cation resin. This provides a good balance between cationic and anionic sites in the bed, since the cation beads have more functional sites than the anion beads.

DOWEX 22 strong base anion resin is used in mixed bed polishers because it does a better job of picking up salts, silica, color bodies, and color precursors than a weak base anion resin. DOWEX 88 MB is similar to the standard DOWEX 88 strong acid cation resin but has been specially designed to distinctly separate from the anion resin during the regeneration procedure. This helps prevent cross-contamination during regeneration.

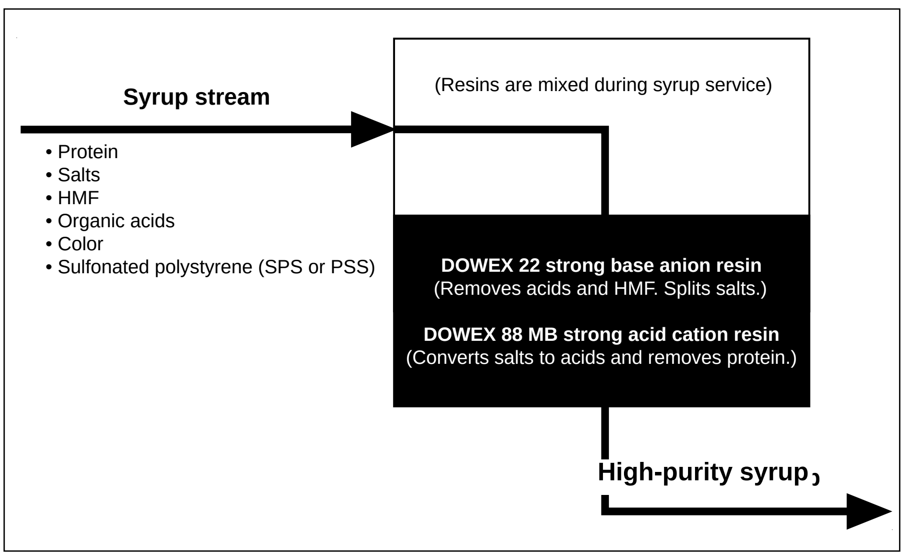
The major reason that separate cation and anion beds aren't used at this point in the process is that fructose is sensitive to degradation in extreme pH conditions. If this syrup were passed through a separate bed of strong acid cation resin, the highly acidic conditions that result as the cation resin picks up salts could cause formation of by-products such as 5-hydroxymethyl-2-furfural (HMF). The highly basic conditions that result from the strong base anion resin could cause the formation of base-catalyzed reaction products such as psicose and mannose.

In the mixed bed, the function of the cation resin remains the same as in deashing, except that now the anion resin beads are right next to the cation beads. The localized high pH of the syrup surrounding the strong base anion bead is counteracted by the close proximity of the localized low pH of the syrup surrounding the strong acid cation bead. So the cation and anion resins work together in a mixed bed to minimize the residence time at unfavorable pH conditions.

DOWEX 22 strong base anion resins are used instead of weak base anion resins because, in addition to picking up acids produced by the cation, the strong base anion also picks up weak acids which might not be picked up by the weak base anion resin. It's said to have a "salt-splitting capacity"[4]. Proper operation of the mixed bed polisher depends on the strong base capacity of DOWEX 22 resin.

Another reason DOWEX 22 strong base resins are used in mixed bed polishing is that they do a better job of picking up components like silica and the color precursor HMF which can degrade final syrup quality.

Figure 8 – Mixed bed polishing with DOWEX resins



Mixed bed polishing is used near the end of the 55% corn sweetener process to remove remaining impurities. A strong acid cation resin and a strong base anion resin are intimately mixed during syrup service. Mixed beds remove organic acids, HMF, and other impurities which can destabilize syrups.

[4]DOWEX 66 and DOWEX MONOSPHERE 77 weak base anion resins also have a degree of salt splitting capacity, but it is a minor component of their total capacity.

Adsorbent decolorization

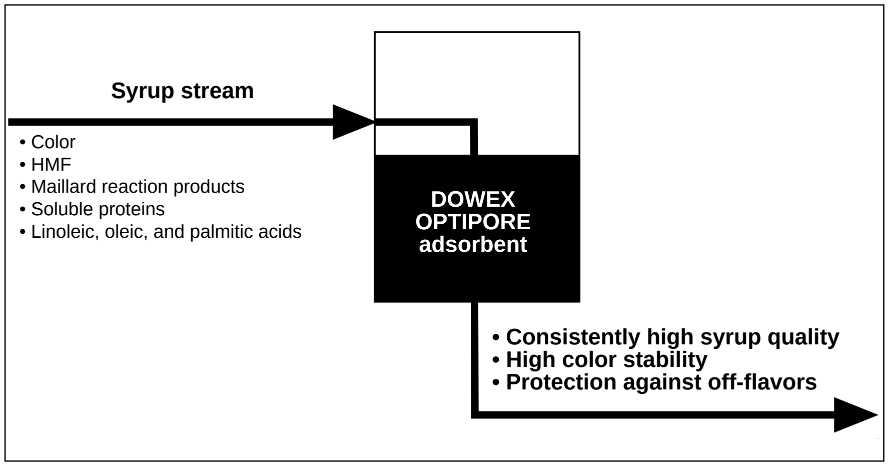
Decolorization units are typically used in the corn sweetener process just before deashing units. Their main purpose is to remove syrup stream components which contribute to color and off-flavors (Figure 9). DOWEX OPTIPORE* adsorbent was developed to replace or supplement traditional activated carbon systems in this process. DOWEX OPTIPORE adsorbent is able to consistently remove 75% of color from even highly colored syrups. Due to a tremendous reserve capacity, DOWEX OPTIPORE adsorbent is also able to correct for color spikes in the syrup stream such as can be caused by a process upset or shutdown.

DOWEX OPTIPORE adsorbent also removes unwanted flavors and aromas as well as a variety of impurities such as HMF, which acts as an indicator of future color development.

How to get more information on DOWEX products and Dow support services

To learn more about DOWEX products, Dow technical support services, request additional literature, or to get help resolving a particular problem, simply call us toll-free at 1-800-447-4369. You'll talk with someone who understands your needs and can provide the prompt, personal service you deserve.

Figure 9 – Color removal with DOWEX OPTIPORE adsorbent



DOWEX OPTIPORE adsorbent offers a clean, effective alternative to traditional carbon systems for color removal. Advantages include: More consistent syrup quality, improved color stability, better protection against off-flavors, simple regeneration, and modest equipment requirements.

Dow Liquid Separations Offices.
For more information call Dow Liquid Separations:

Dow Europe
Dow Customer Information Group
Liquid Separations
Prins Boudewijnlaan 41
B-2650 Edegem
Belgium
Tel. +32 3 450 2240
Tel. +800 3 694 6367 †
Fax +32 3 450 2815
E-mail: dowcig@dow.com

Dow Pacific
Dow Chemical Japan Ltd.
Liquid Separations
Tennoz Central Tower
2-24 Higashi Shinagawa 2-chome
Shinagawa-ku, Tokyo 140-8617
Japan
Tel. +81 3 5460 2100
Fax +81 3 5460 6246

Dow Pacific
Dow Chemical Australia Ltd.
Liquid Separations
Level 5
20 Rodborough Road
French's Forest, NSW 2086
Australia
Tel. 61-2-9776-3226
Fax 61-2-9776-3299

Dow Latin America
Dow Quimica S.A.
Liquid Separations
Rua Alexandre Dumas, 1671
Sao Paulo – SP – Brazil
CEP 04717-903
Tel. 55-11-5188 9277
Fax 55-11-5188 9919

Dow North America
The Dow Chemical Company
Liquid Separations
Customer Information Group
P.O. Box 1206
Midland, MI 48641-1206
USA
Tel. 1-800-447-4369
Fax (989) 832-1465

Internet
http://www.dowex.com

† Toll-free telephone number for the following countries: Austria, Belgium, Denmark, Finland, France, Germany, Hungary, Ireland, Italy, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and the United Kingdom

Warning: Oxidizing agents such as nitric acid attack organic ion exchange resins under certain conditions. This could lead to anything from slight resin degradation to a violent exothermic reaction (explosion). Before using strong oxidizing agents, consult sources knowledgeable in handling such materials.

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