



Dow Water Solutions

DOWEX™ MONOSPHERE™
Ion Exchange Resins

Chromatographic Separation of
Fructose and Glucose with
DOWEX MONOSPHERE Ion Exchange Resins

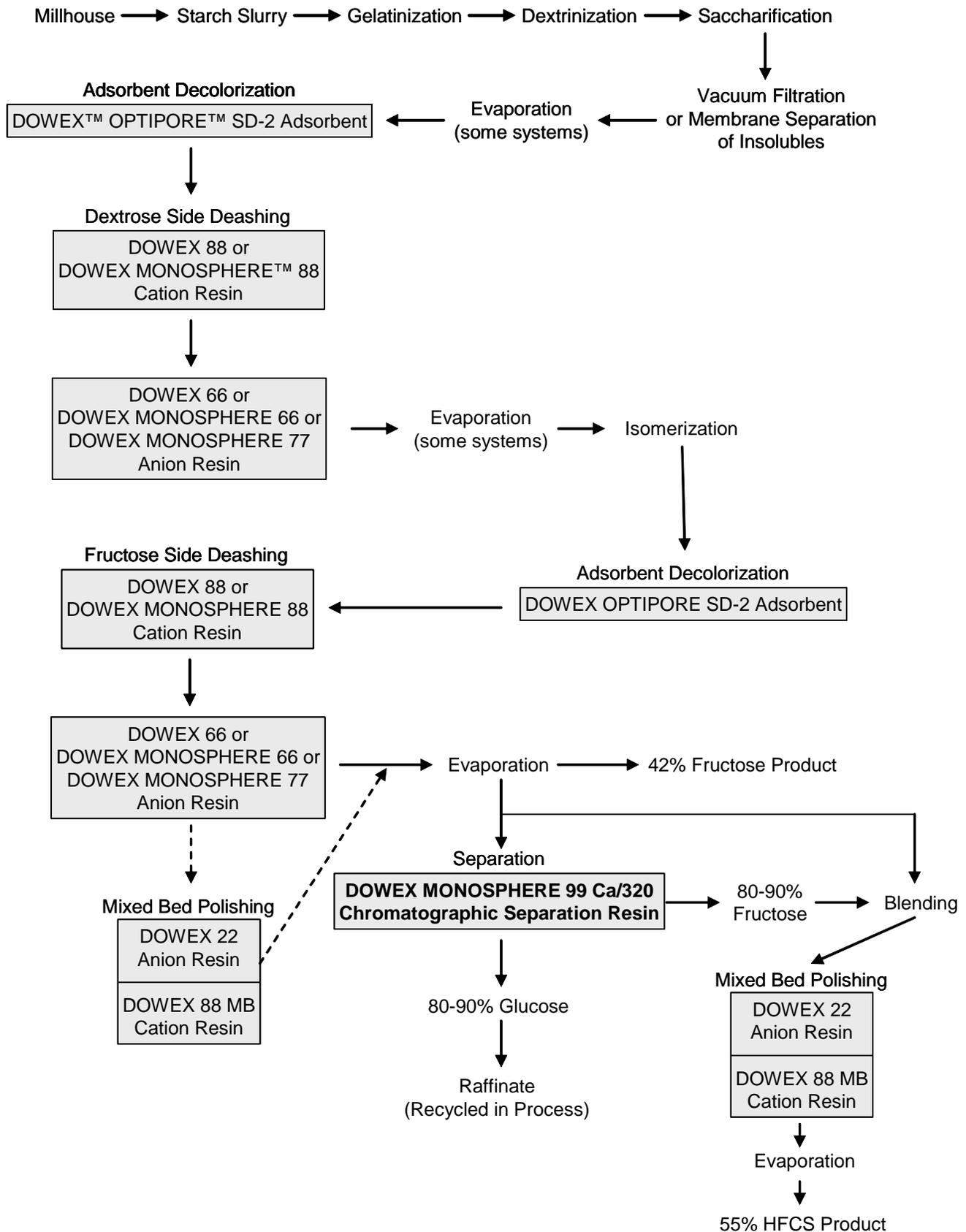
Technical Manual

Chromatographic separation of fructose and glucose with DOWEX™ MONOSPHERE™ resins

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Corn Sweetener Processing

The use of DOWEX™ ion exchange resins in corn sweetener processing



Introduction

The Need for Chromatographic Separation

With current enzyme isomerization technology, the conversion of glucose to fructose is economically limited to 42-46% fructose on a dry weight basis. To make a 55% fructose high fructose corn syrup (HFCS), 42% syrup is separated into a high-purity fructose stream and a high-purity glucose stream. Blending the high fructose cut with additional 42% syrup results in a 55% HFCS product suitable as a sweetener for soft drink bottlers. Using chromatographic separation, fructose concentration can easily be increased to over 90%. The family of DOWEX™ MONOSPHERE™ 99 uniform particle size resins is used in this process.

Dow Resin Products for Chromatographic Separation

DOWEX MONOSPHERE 99 Ca separation resins have established themselves as the standard in the industry for efficient, economical fructose enrichment. There are three standard particle sizes, the selection of which depends on the pressure drop constraints of the particular separator. The nominal sizes (volume median diameter) are 310, 320 and 350 microns.

These products are extremely consistent lot-to-lot and are produced to the tightest specifications in the industry. The particle size distributions are extremely narrow (Table 1). The lack of large beads minimizes the smearing of component profiles. The lack of small beads minimizes the operating pressure drop.

For properties, specifications, price or availability, contact your Dow sales representative.

Fundamentals of Chromatographic Separation

The Chromatographic Mechanism

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 1). While macroporous resins are opaque, gel resins are translucent. Chromatographic separation resins are functionalized and the beads contain a significant amount of water. While going through the column sections, the sugars to be separated dissolve in the water contained within the beads. Inside the bead, the dissolved sugars interact with the calcium ions held by the resin. Fructose, glucose and water form weak ligand complexes with the calcium ion. A stronger interaction in the fructose/calcium ion complex than in the glucose/calcium ion complex is the basis of the mechanism of separation of fructose from glucose¹. This mechanism of separation is called ligand exchange chromatography.

DOWEX MONOSPHERE 99 resins for glucose/fructose separation are used in the calcium form. Similar resins for other separations are available in other ionic forms.

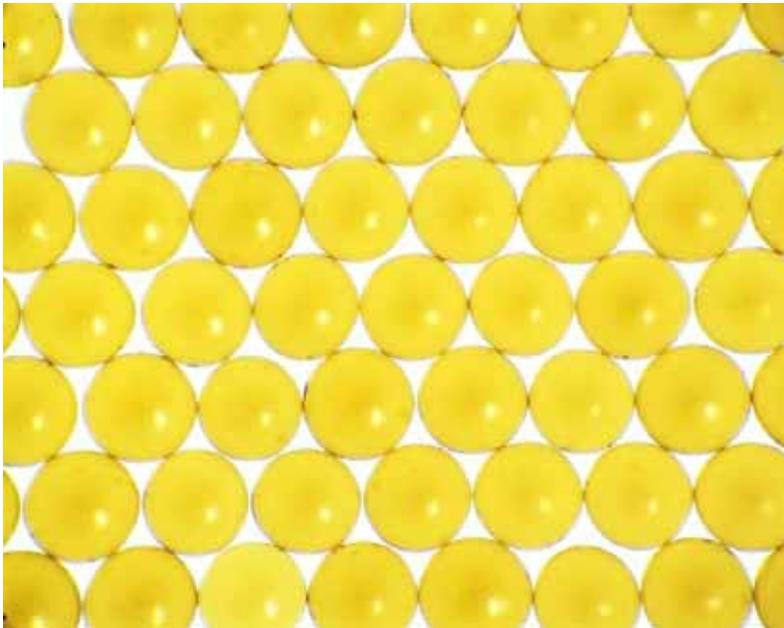
Larger molecules such as the DP2s, DP3s, DP4s, and higher oligosaccharides are not able to physically fit into some of the very small openings between polymer chains found in the gel resins. The mechanism of separating large molecules from small molecules by preventing some of the large molecules from getting inside the stationary packing is called size exclusion chromatography. Size exclusion chromatography takes 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 the column or column section first. This factor is only of secondary significance 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, or for removing higher saccharides from disaccharides.

¹ Chromatographic separation resins do not "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.

Table 1. Typical particle size distribution (HIAC) of DOWEX™ MONOSPHERE™ 99 Ca separation resins

	Microns		Microns
Nominal diameter	310	320	350
Volume median diameter (microns)	307	315 +/- 15	350 +/- 15
Broad range	min 90% 285-350		min 90% 315-380
Narrow range	min 75% 300-335		min 75% 330-365
Fine fines	max 1% <260		max 1% <280
Coarse fines	max 4% <280		max 4% <310
Fine coarse	max 4% >380		max 4% >410
Coarse coarse	max 1% >450		max 1% >480

Figure 1. DOWEX MONOSPHERE 99 Ca/320 chromatographic separation resin



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

The Effect of Resin Particle Size

Chromatographic separation is a rate-controlled and rate-limited process. The slow step is the diffusion of the glucose and fructose inside the resin bead itself. Slow diffusion kinetics (large bead size or a high crosslink resin) results in a broad, low, chromatographic peak. In process terms, the product cuts are lower purity and lower concentration, the recovery is lower and the water usage is higher. Chromatographic process efficiency is increased by the use of a smaller size bead. Diffusion paths are shortened, resulting in sharper peaks. The sharper peaks yield higher recovery, higher purity and/or lower elution water usage.

The tradeoff in the use of smaller size separation resin beads is a higher pressure drop. This effect is especially pronounced with those beads on the small end of the particle size distribution, since pressure drop is inversely proportional to the square of the particle diameter. The optimum results are obtained for a given system by using a separation resin of very uniform size distribution – as small as can be tolerated without exceeding the limits of tolerable pressure drop.

The Effect of Resin Crosslinking

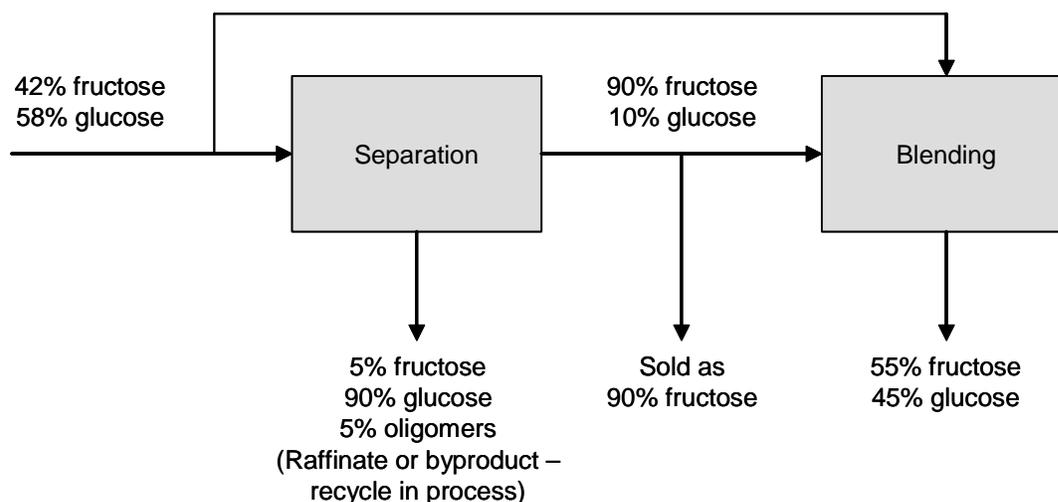
Lightly crosslinked resins (high water retention capacity) have fast diffusion kinetics. In small scale chromatographic separation tests, high water resins can perform well. However, while faster kinetics can be achieved by using a separation resin with a high water retention capacity, high water resins do not yield higher production capacity because the equilibrium capacity of the resin is reduced and the operating pressure drop is increased. This type of resin may be suitable for the more difficult separations, but it is not as robust for producing HFCS 55.

The Engineering Mechanism

If a mixture of glucose and fructose dissolved in water is pumped through a fixed bed packed with a gel resin in the calcium form, the fructose, being more strongly attracted to the calcium on the resin beads, spends more time immobile inside the beads. The glucose is attracted less and therefore spends more time outside the beads, in the flowing stream of liquid in the voids between the separation resin beads. The net result is that glucose moves (on average) down the bed of resin more rapidly than the fructose.

If a stream of liquid is withdrawn from the column earlier than the peak of total dissolved solids (TDS) or farther down the column than the peak of TDS, that stream will be enriched in glucose compared to the feed (Figure 2). A stream removed later than or higher in the column than the peak of the TDS will be enriched in fructose. A single packed bed of resin can be used in this way to purify or enrich fructose from the 42 stream. More commonly, the process is carried out in continuous equipment operating under the simulated-moving bed (SMB) principle.

Figure 2. HFCS enrichment

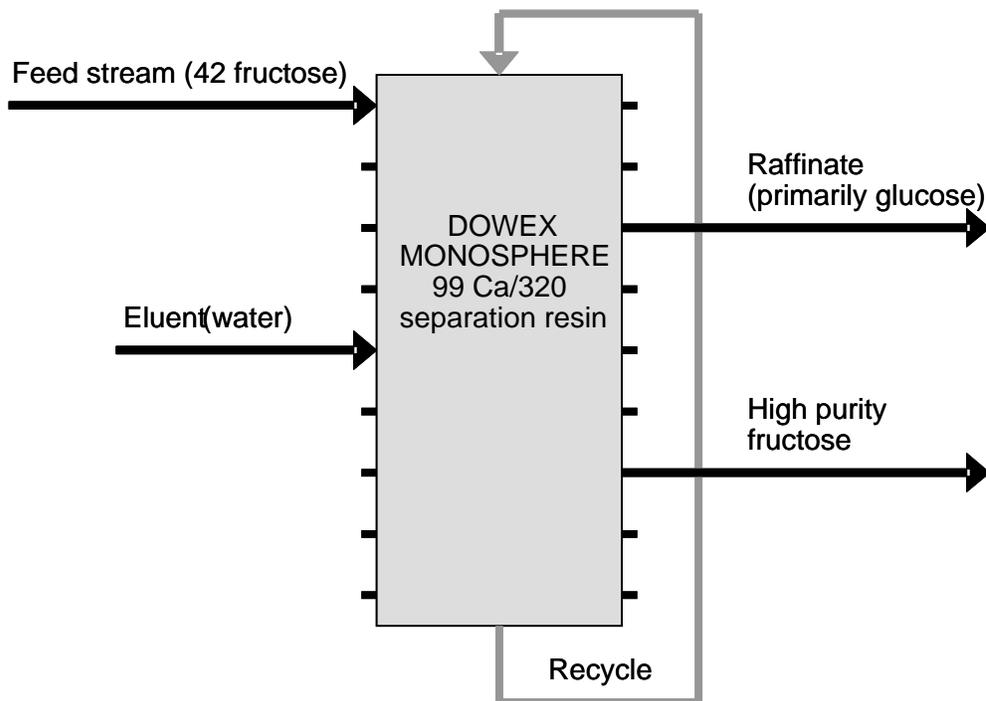


Simulated-moving Bed Separator Operation

In service, 42% fructose syrup is added to a column or set of columns containing the resin (Figure 3). As the syrup stream moves down the column, fructose moves more slowly (on average) than glucose. This results in separated bands of higher purity of each component within the column. Precise computer operation follows these bands as they move down the column and controls 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. Recycle flow internal to the process is 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 high purity (80-90%) fructose is blended with 42-45% fructose.

Figure 3. Chromatographic separation with a simulated-moving bed system



This simplified diagram represents the simulated-moving bed operation commonly used in corn sweetener production. The loop (represented as a single box above, can consist of a single column with dividers between sections, or it can be multiple columns piped in a loop), filled with resin beads, has multiple inlets and outlets. Feed stock (42% fructose) and eluent (water) are continuously added at various inlets as dictated by a sophisticated computer control system. At the same time, high purity fructose (75-95%) and enriched glucose (raffinate) are withdrawn from the zones of high purity that result as the syrup moves through the column loop.

The Need for Uniformity – Flow and Resin

In an SMB separator, product cuts are taken based on position relative to the feed port. Since the cuts depend on the separation profile being at that particular place in the separator at that time, **consistent flow rate control is critical**. Calibration of process flow meters is extremely important. Hydraulic balance should be checked at least once per week. (The sum of inlet flows should equal the sum of outlet flows.) Section-to-section uniformity is also important so that the extract and raffinate cuts are taken at the correct time. Section uniformity has several aspects. Resin levels in each section should be the same. Each section should have the same volume (including connecting piping wherever possible). The resin in each section should have the same characteristics.

Resin uniformity from section to section is important. Several different resins can test well in laboratory tests, yet perform poorly together when installed in an SMB separator. The two ways to insure the uniformity of resin in each section are to mix all the lots of resin together thoroughly before loading the separator or to have a very narrow allowable range on all chemical and physical properties of the separation resin used.

Operating Costs

The major variable cost in separator operation is the cost of evaporating water from the product cuts to bring them to the desired % total dissolved solids (% TDS). When a separator is new, we recommend that the owner document the operating performance in terms of capacity of 55% fructose produced per unit volume of separator and water used per pound dry substance of 55% fructose. These numbers will give you a benchmark to compare the operating efficiency of the separator. Calculate the annual costs of evaporating the water needed. Small increases in recovery and purity can yield very large economic savings in evaporation costs. The most common problem in uneconomical operation is not knowing how much extra water is being evaporated, compared to what could be achieved.

Maintaining Long and Short-term Performance

Separator Tuning

Simulated-moving bed separators are complex. There are many, many variables. It is not a surprise that most operators don't change things unless there is a dramatic problem. A small imbalance resulting from operating parameters which are very slightly off the optimum can cause large performance deficiencies. Careful and proper tuning can keep performance at the optimum and minimize production costs of HFCS-55.

Performance Declines

Most short-term performance declines are related to hardware or operating parameters. There are many things which can be slightly off here and cause operating difficulties.

Separation efficiency is enhanced by:

1. Correctly and precisely operating computer controlled operating/monitoring devices.
2. Optimum tuning of the separator control parameters.
3. Precise calibration of all flow meters and tuning of flow control loops.

Separation efficiency is reduced by:

1. Poor feed flow distribution, which causes backmixing.
2. Increased system void (dead) volume which causes backmixing and product dilution.
3. Poor operating parameters, especially in regards to the steptime.
4. Aging of the resin caused by oxidative attack.
5. Low resin levels.
6. Variable flow rates.

Long-term Resin Protection

Two important factors govern the chemistry of chromatographic separation using resins as the chromatographic packing. First, the resin must be in the correct ionic form. For fructose purification, the resin must be in the calcium form. Second, the resin must be protected from premature aging in order to preserve the good separation performance available when the resin is new. The predominant mechanism of aging is oxidation. Oxygen attacks organic compounds, including the organic polymer chains which make up the backbone of a resin, by a free-radical chain mechanism. The final result is a scission or cutting of the chain. With fewer connections holding the bead together, the resin absorbs more water and swells up in size. The process of increasing in size and increasing in water retention capacity (WRC) is termed decrosslinking, because the physical properties of the resin will look like they would if the resin had a lower crosslink level than what the resin originally possessed. As discussed previously, resin WRC and resin particle size have very large effects on separation process performance.

Preservation of the separation resin's performance depends on understanding the two important factors above and preventing the reactions from happening. In order to keep the resin in the calcium form:

1. Keep the pH in the proper range and minimize iron and other metals in the separator feed. Control pH to separation resin from 4.0-4.5. At low pH, H⁺ can displace Ca⁺⁺ from the resin. Hydrogen ion on the resin can also catalyze 5-hydroxymethyl-2-furfural (HMF) formation and can increase the susceptibility of the resin to the decrosslinking reaction. At high pH, the high temperatures in the separation system will cause fructose degradation and by-product formation.
2. Keep iron (Fe) and other metal levels at a minimum. Poorly deashed separator feeds can contain sodium, magnesium and iron. Sodium, magnesium, iron and other metals can displace calcium and reduce the separating capability of the separation resin. Fe can catalyze decrosslinking of resins. Keep low ash levels in the feeds to the separator. If the resin has been analyzed and it can be demonstrated that hydrogen or metal ions have displaced calcium from the resin, then recalcification of the resin can be very beneficial. However, unless it is known that ions other than calcium ion are present, "recalcification" may not improve the resin performance more than a thorough backwashing of the resin would.

Long-term performance decline of a separator is usually caused by oxidation of the resin, as described above. To maximize resin life, control dissolved oxygen to less than 0.5 ppm, preferable less than 0.1 ppm. Oxygen is the one factor which can be controlled to prevent the decrosslinking. Decrosslinking can severely shorten the life of the separation resin. At high oxygen levels separation resin has been destroyed in as little as six months. Resin can last 7 years or more if the dissolved oxygen is kept below 0.1 ppm. Resin can still be functioning, but be causing high operating costs if decrosslinking has increased the water retention capacity (WRC) of the resin to or above 63% (WRC is measured after conversion to the hydrogen form).

Controlling HMF and Microbiological Growth

Controlling HMF

One of many UV-absorbing species found in corn syrups is 5-hydroxymethyl-2-furfural or HMF (also known as 5-hydroxymethyl-2-furancarboxaldehyde). It is thought to be a color precursor or a color marker, which indicates when a syrup could have a high heat color. HMF results from acidic dehydration of fructose. Its formation is promoted by high temperature and low pH. It can also be produced via reactions involving one of the pathways of the Maillard reaction. HMF is created in a normally operating chromatographic separator. The conditions for HMF formation are present in every chromatographic separator: the temperature in a separator is high, there is fructose present in high concentration, the pH is below neutral and the average residence time in the separator is long. Measuring the HMF levels in and out of a separator under normal process conditions can assist in troubleshooting at times of a process upset. Control of the pH to the separator is especially important to prevent HMF formation inside the separator.

Controlling Microbiological Growth

Separators are normally maintained at 140°F (60°C) or above to keep viscosity and pressure drop down, but even more importantly, to keep microbial growth to a minimum. The TDS concentration inside the separator column varies with time and position in the column. There will be times and areas of low TDS where microbial growth could be very rapid if the temperature is not kept high. For short-term shutdowns, the high temperature will inhibit microbial growth. For shutdowns exceeding 12 hours, separators need to be sweetened-off very thoroughly. In addition, some chemical addition may be needed to prevent microbial growth in separator resin which is not in service for an extended period of time.

Resin Properties

Table 2. Typical resin properties for DOWEX™ MONOSPHERE™ 99 Ca/320 separation resin

Resin type	Strong acid cation
Ionic group/backbone	Sulfonate/gel polystyrene-DVB
Ionic form	Calcium
Physical form	Spheres
Total exchange capacity, min, meq/ml	1.5 (H ⁺ form)
Water retention capacity (WRC), %	57-61 (H ⁺ form)
% Conversion to indicated form, (min)	99
Whole uncracked beads (WUBs), min, %	98
Color throw, APHA, max	20
Acidity, pH	7.0-8.8
Metallic impurities (Fe, dry, max, ppm)	30
Excess surface moisture, max %	1.0
Typical densities	
Particle	1.27 g/cc
Apparent bulk (BS&D)* **	48-51 lbs/cu ft (770-820 kg/m ³)

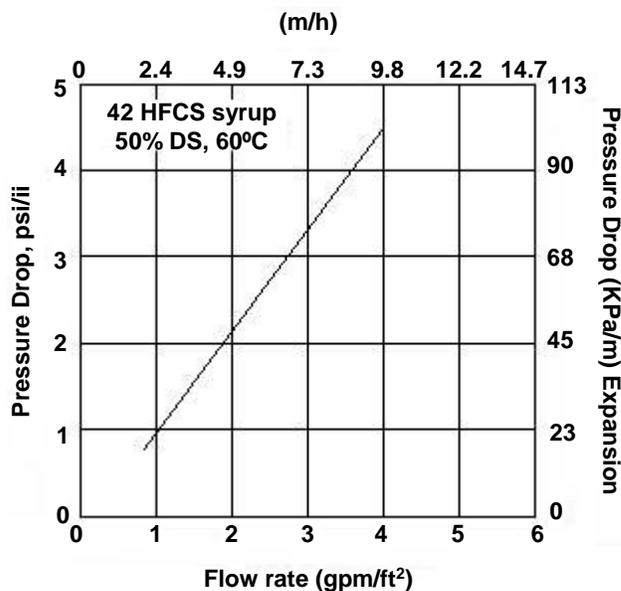
* This is a BS&D (Backwashed, Settled & Drained) density. More resin will need to be installed than one would calculate using this value, since resin will "settle in" during use.

** As per the backwashed and settled density of the resin, determined by ASTM D-2187.

Table 3. Typical operating conditions for DOWEX™ MONOSPHERE™ 99 separation resins

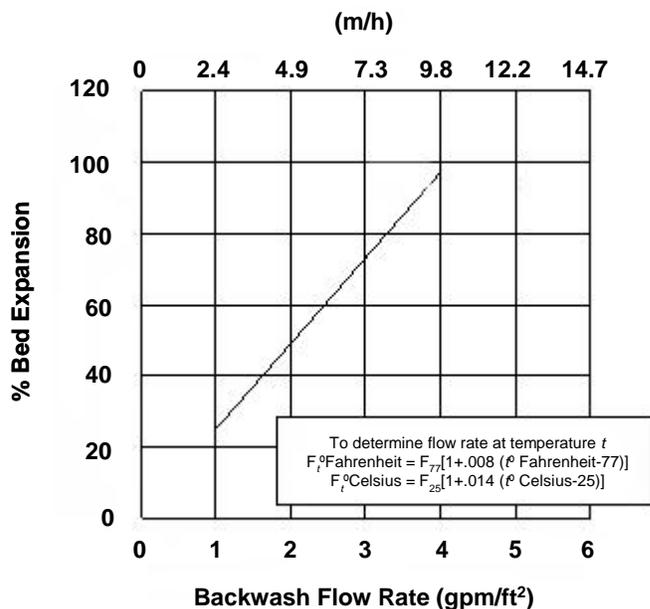
Syrup temperature	140-160°F (60-71°C)
Maximum dissolved oxygen concentration	0.5 ppm
Recommended dissolved oxygen concentration	<0.1 ppm
Simulated-moving bed operation	with optimized tuning

Figure 4. Pressure drop with DOWEX MONOSPHERE 99 resins



This graph is provided to help you determine pressure drop across beds of DOWEX MONOSPHERE 99 resins.

Figure 5. Backwash expansion of DOWEX MONOSPHERE 99 Ca/320 resins



This backwash expansion curve is provided to help you determine the expansion of your beds at a given temperature and flow rate. Colder water will expand the resins higher in the bed for a given pump rate. Thorough backwashing of new chromatographic separation resin prior to first use is highly recommended. With good operation (adequate feed filtration and good control of dissolved oxygen concentration), backwashing of Dow's chromatographic separation resin is rarely required. Excessive expansion may lead to resins escaping the bed.

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Notice: 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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