Ion Exclusion Purification of Sugar Juices

LLOYD NORMAN, GUY RORABAUGH, AND HAROLD KELLER[1]

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Preface

In preface to this article the authors would like to point out that ion exclusion as a commercial reality is not an accomplished fact. Both in the laboratory and the pilot plant it has been demonstrated that 50% or more of the impurities which escape carbonation can be eliminated by ion exclusion. The process as herein described is new—beset with the usual "bugs" (also mentioned) which threaten and could preclude development into commercial feasibility. Because the economic potential is so great, (as calculation of the value of recovery of 50% of the sugar lost in molasses will reveal), and because the need is so great (as the trend of sugar extraction in recent years will show), it is felt that the principles of ion exclusion and the machinery by which these principles may be applied will be of interest to all who are engaged in the production of sugar.

Introduction

Although the literature is replete with methods for purifying sugar juices, the basic, century-old system of clarification with lime (plus carbon dioxide in the case of beet juices) remains the accepted industrial procedure. This is not to say that others are inoperative, but the simplicity, the relative effectiveness, and particularly the economy of lime purification have so far withstood all efforts to replace it.

Despite its advantages, the process of carbonation has severe limitations. Such juice impurities as monovalent mineral salts and the anions of amino and certain other organic acids are present in large amounts, yet are relatively untouched by carbonation purification. Many are highly mellassigenic.

Decreased sugar recovery and increased molasses production over the past several years point to a need for better elimination of the impurity load we now process. Undoubtedly progress can and will be made on improving the quality of our beets in such areas as better varieties, better topping and storage, and more judicious use of nitrogenous fertilizers. But that is another story. As processing men, we must obtain the maximum sugar recovery from the beets as delivered. With other losses being normal, only improved impurity removal can accomplish this, and since car-

[1] Research Laboratory Manager and General Chemist-Director of Research, respectively, Holly Sugar Corporation and Assistant Research Director, Illinois Water Treatment Company.

bonation cannot presently be eliminated due to its inherent economy, supplementary purification seems to be indicated.

Shortly after World War II the new process of ion exchange seemed to be the solution to our problem. However, the process failed at that time, not because of technical inability to do the job, but because of such cost factors as rising regenerant costs, rising freight rates, cost of cooling the juice, and rising molasses value. Improvements in resins and development of new techniques make ion exchange worthy of continued consideration, although the newer process of ion exclusion reported here appears to have more promise.

Procedure

The process of ion exclusion has been known for several years, having been introduced by the Dow Chemical Company as early as 1953 (1)[2] and subject to a patent by this group (2). Early evaluation of the process, as applied to a fixed bed column, was discouraging because excessive dilution was indicated. Nevertheless, commercial utilization is being made of fixed bed ion exclusion for purification of such products as glycerine (3).

It remained for the advent of the Higgins continuous contactor (4) to bring about serious consideration of ion exclusion for purification of sugar juices. Holly Sugar Corporation in cooperation with the Illinois Water Treatment Company, and the Dow Chemical Company has conducted pilot-scale experiments with an 8-inch diameter Higgins loop.

Ion exclusion, while utilizing an ion exchange resin to effect a separation of both ionic and non-ionic materials, does not involve a true exchange reaction. A strongly acidic ion exchange resin, such as DOWEX 50W, is made by the nuclear sulfonation of styrene-divinyl benzene beads and variations can be made in these resins by changing and controlling the amount of cross-linkage in the resins. The degree of cross-linkage in a styrene-divinyl benzene bead refers to the amount of divinyl benzene it contains. A resin containing 4% divinyl benzene and 96% styrene would be said to have 4% cross-linkage. The amount of cross-linkage influences the physical-chemical properties of the resin. As the cross-linkage is increased the diffusion path becomes small enough to bar the entrance of large ions or molecules. By control of the size of these diffusion paths it then becomes possible to separate by size. If the cross-linkage of the resin is controlled to the right degree, the sugar molecule will enter the bead, but larger molecules, such as color bodies, will be excluded or screened out.

[2] Numbers in parentheses refer to references.

At the same time, ionizable compounds, such as sodium and potassium salts, amino acids, etc., are excluded because of the Donnan membrane effect. Ionic substances in equilibrium with resin will tend to have a higher concentration in solution, external to the resin bead, than that of the liquid phase inside the bead. The non-ionic substances will have the same concentration, both external and internal, or perhaps greater internal concentration due to adsorption. If an impure sugar solution is contacted with resin, such as DOWEX 50-W, in the salt form, the sugar concentration inside will be the same as or greater than outside, but the impurity concentration (ionic impurities) will be less inside than outside. If the beads are then eluted with water, purification will have been accomplished relative to ionic materials, even though the molecular size of the ionic compounds is smaller than the non-ionic sugar.

Ion exclusion offers a way of removing ionic constituents and separating large organic molecules from sugar solutions without the use of power or chemical regenerants. The separation can be shown graphically. If an impure sugar solution is passed through a column of resin in the salt form followed by a water rinse as shown in Figure 1, it will be seen that the salt is displaced from the column first with the purified sugar solution lagging behind.

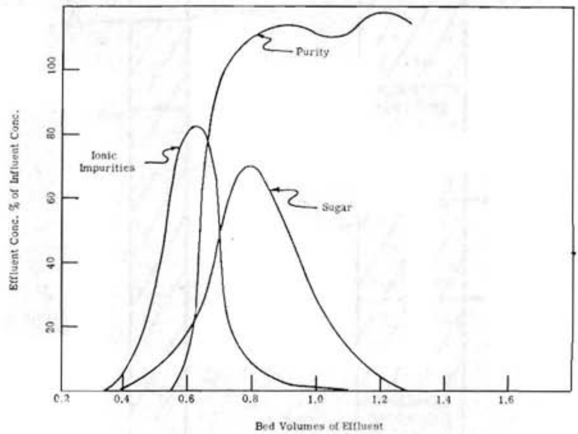

Figure 1.—Fixed bed exclusion of sugar juice.

It has been found that the sugar juices should be softened or converted to monovalent form prior to exclusion. This phase of the process has been patented by the Illinois Water Treatment Company (5). If this is not done the resin will eventually become loaded with multivalent ions such as calcium and the effectiveness of the process will be impaired. Fixed bed columns of DOWEX 50-W in the salt form are used for juice softening.

Figure 2 is a schematic diagram of the Higgins contactor as adapted for ion exclusion purification of sugar juices. The operation of the loop is semi-continuous or cyclic in nature. At the start of each cycle the loop is filled with resin from point A on the diagram clockwise all the way around to the valve at point V_1. Water fills the remainder of the loop between V_1 and A. In order to move or pulse the resin, valves V_1 and V_3 are opened with V_2 remaining closed. Water under a pressure of about 60 psi is introduced at point B. The resin is moved clockwise for a definite, pre-determined distance in slug type, positive displacement motion. The water displaced by the resin as it moves through valve V_1 is withdrawn at point C and can be re-used for subsequent

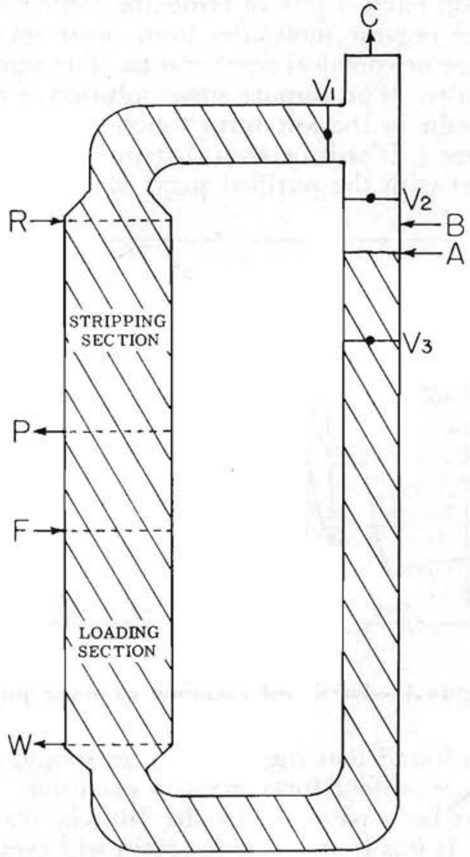

Figure 2.—Higgins continuous contactor.

pulses. When the pulse is completed, valves V_1 and V_3 are closed and V_2 opened to allow the resin to settle back to point A preparatory for the next pulse.

As soon as valves V_1 and V_3 are closed, the service cycle is begun. Feed juice is introduced at point F and rinse at point R, while product is withdrawn at point P and waste at point W.

Since a definite volume of resin is moved with each pulse, the maximum volume of feed is thereby determined because only a fixed amount of internal resin pore space will be available to accommodate the volume of feed. If more than this is fed, sugar will be lost in the waste stream. The degree of purification is also affected by the feed to resin ratio, so that an optimum must be sought with both volume throughout and purification being considered.

If the loading section between F and W is too short in length, sugar may be lost at W even though the ratio of feed to resin is satisfactory. This section length must also be a function of the flow rates involved, since the equilibrium considerations are a function of time.

Because the sugar preferentially penetrates the resin beads, it will move with the resin while the impurities move against the resin flow and separation is obtained. To recover the purified sugar solution it must be displaced from the resin interior. This, of course, is accomplished in the stripping section of the contactor by means of water introduced at point R. Only the minimum amount of water required to strip all sugar from the resin is added; any additional water will serve no purpose but will cause dilution. Adequate length in the stripping section is necessary to allow complete removal of sugar with the minimum water volume.

No transfer to or from the beads takes place in the center section between points P and F. However, as the resin is moved up, the void volume of juice between the resin beads is also moved up. Since the juice originally at point F is of feed composition it must be displaced back to point F during the service cycle or eventually the product at point P will be contaminated by juice of feed composition and purification will be impaired.

From the foregoing discussion it will be seen that the cycle of operation is divided into two parts: 1. the pulse in which the resin is moved and 2. the service cycle during which liquid flows are accomplished. Careful control of resin movement as well as liquid flows is necessary to maintain separation and throughout at optimum conditions.

The positive values of ion exclusion to the sugar processor are several. We would like to enumerate these and discuss each briefly:

1. Ion exclusion can eliminate ionic impurities not removable by carbonation. Sugar extraction can be increased. The degree of purification (about 50%) will be such that some buffer capacity in the juice will be maintained.

2. Considerable color is removed from the juice. Improved sugar color should thus be realized.

3. Because calcium is removed in the softening step, scaling of evaporator tubes should be eliminated.

4. Possible improvement in crystallization is anticipated, since many impurities of high molecular weight are eliminated.

5. The process can be operated continuously with the Higgins contactor. It can be made completely automatic with a minimum of supervision necessary.

6. Operation is at high temperature – no costly cooling and reheating required.

7. No regenerant chemicals are required. Only water is necessary to strip the sugar from the resin.

8. High throughput rates may be possible with resultant savings in equipment cost. Operation is at 40 Brix. More solids per gallon also help lower equipment size and cost.

9. Dilution is minimized. Countercurrent flows and high Brix feed keep added evaporation costs low.

10. Resin employed is most stable type known. This allows operation at high temperature and minimizes attrition losses. Mesh size of resin is 50-100. This also helps keep resin losses and make-up at reasonable levels.

Just as with demineralization by ion exchange, the process of ion exclusion will purify commercial juices. We need only develop the equipment and technique to do the job economically enough to be commercially feasible. Juice throughput must be high to keep down equipment size and capital costs. Degree of purification must be kept at a high figure to realize maximum benefits. Losses of sugar must be minimized. Dilution must be kept at low levels to prevent excessive re-evaporation costs. Water and waste quantities must be within reasonable limits to allow efficient and economic handling thereof. Obviously, simultaneous maximization of all these objectives is incompatible, so that compromise must be made to optimize operating conditions.

Our pilot plant studies have encountered the usual problems. Most of these have been mechanical in nature. In order to maintain control of physical conditions inside the contactor loop all flows must be precisely controlled from cycle to cycle. Resin flow in particular has been difficult to control. Pressure drop across valves and past internal obstructions such as distributors has been a major factor in erratic resin movement. Resin expansion and contraction due to temperature variations and juice flow changes is thought to be another factor. Wall effects of the loop itself may be still another.

Control of all fluid streams into and out of the loop is extremely important, not only from the effect on steady state conditions of the exclusion phenomenon, but also because of the effect on resin flow just mentioned. The solution of flow control in our pilot contactor has not yet been found, though we feel that progress is being made and that the answer will be found.

At the present state of development many problems still remain to be solved before ion exclusion purification can become a commercial reality. We feel that the following operating conditions must be met:

Flow Rate—3 gpm/ft^2 of contactor cross section (with 40 Brix juice)

Separation—50% removal of impurities

Dilution—10% or less

Sugar losses—undetermined, but as low as possible

Water requirements—no more than 300% by volume on juice flow

Waste—roughly equivalent in volume to water requirements

Some of these conditions have been achieved in our pilot plant operations; some have not, but our experience leads us to believe that these objectives can and will be realized.

We have focused our attention on application of this new process to factory thick juice. This is the logical point of attack if full benefits are to be realized throughout the entire sugar end of the factory. However, the dictates of optimum economic return require the examination of other possibilities. Processing of high greens or machine syrups—or even molasses—may in some circumstances prove more economical, depending on such factors as pan capacities, purity considerations, and equipment costs. For instance the quantity of machine syrup for any given factory would be much less than thick juice. If an equivalent amount of impurities can be eliminated at this point, the low raw load and molasses production could be equally reduced with extraction correspondingly increased. Equipment cost would be less, though facilities would be required to handle the recycle juice at the purity and Brix attainable.

Also, we have mentioned little about ion retardation, a process similar to exclusion in which the ionic impurities would travel with the resin movement while sugar would travel counter to resin flow. An advantage of increased throughput may be gained by using retardation. Exclusion is favored at this time because a special, more costly resin is required for retardation, a resin which may not have the stability of the strong acid cation used in exclusion. Furthermore, little or no color removal is expected with retardation, a benefit of exclusion which is difficult to evaluate economically, but which will undoubtedly be of much value in some areas.

We have briefly described the process of continuous ion exclusion as it might be applied to the sugar industry. It will be supplementary to, but will not eliminate carbonation. Hopefully, it can increase sugar extraction and quality by eliminating melassigenic impurities and color from juice, while requiring no regeneration reagents other than water. Necessary equipment is complex, but automatic in operation and relatively high in potential throughput, with reasonable labor and capital costs being indicated. The need for a process which will economically allow increased sugar extraction from juices continuing to deteriorate in quality from year to year is clearly indicated. Ion exclusion promises to fill this need.

References

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