

# Ion Exchange Process for Beet Sugar Refining

## I. Purification of Beet Diffusion Juice

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Before describing the technique known as the Assalini "A" Process, it is advisable to summarize briefly the conventional method for extracting sugar from beets as practiced in most of Europe. The procedure is outlined in Figure 1. European practice differs chiefly in that a raw beet sugar is produced. This sugar is remelted and passed through some decolorizing material and finally crystallized to obtain a refined sugar meeting the specific chemical and physical requirements of the particular country. As in the U.S., the greater demand in the European market is for refined sugar.

In the past 10 or 15 years, ion exchange resins have aroused considerable interest in the sugar industry in general, inasmuch as this technique showed considerable promise as a new method

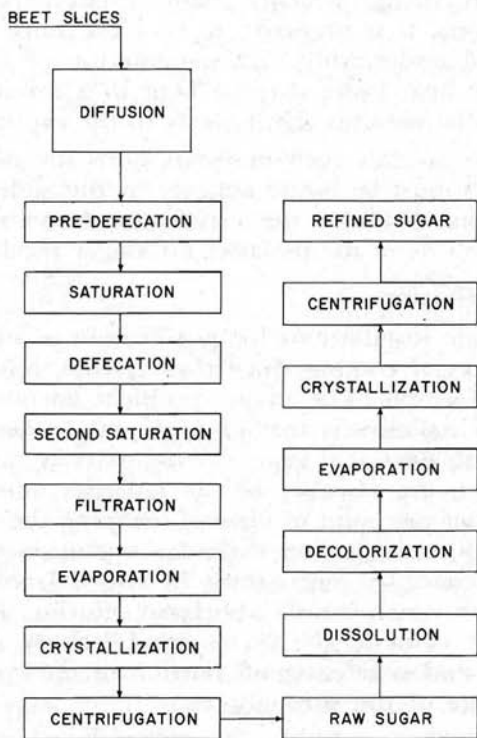


Figure 1.—European beet sugar process.

of purification which could be capable of augmenting crystallization as the purifying technique. As a first approach, the application of ion exchange resins was investigated either for the purification of thin juices to obtain greater sugar recovery or to purify the molasses to recover the sugar which is otherwise uncrystallizable.

In large measure, the application of ion exchange resins for deionization has not yet yielded the outstanding results originally hoped for. The reasons for this have been many and the difficulties might be summarized as follows:

### **Thin Juice Deionization**

When using conventional deionization for the purification of thin juice, it is necessary to cool the juice from 90° C. down to 10°-15° C. when using a strongly acidic cation exchange resin. This is necessary, of course, to avoid serious inversion of the sucrose during and immediately after the passage of the juice through the bed of cation resin in the hydrogen form. Inversion can be controlled by use of a carboxylic cation exchanger. Additionally, when using strongly basic quaternary ammonium anion exchangers, it is necessary to cool the juice to 60° C. or below to avoid undesirably high degradation of the functional groups. While heat losses may be kept to a minimum, a heat-exchange installation adds significantly to the capital investment.

Needless to say, all such expenses both for new plant and processing costs must be borne entirely by the additional sucrose extracted beyond that for the conventional method and must also cover the value of the molasses no longer produced.

### **Molasses Purification**

Ion exchange installations for purification of molasses would not require special cooling since these syrups could be treated during the off-season. The major problem encountered in the purification of molasses is that of dilution. In fact, for the deionization of molasses, it is generally necessary to make successive dilutions. First, the viscosity of the molasses must be reduced by dilution from the point of view of lowering the concentration of non-sugars so that the ion exchange operation is more easily controlled. Second, the sugar must be rinsed from the columns after exhaustion which entails additional dilution. Because of the high non-sugar content, the cycles are relatively short and the sweetening-on and sweetening-off portion of the cycle becomes a large percentage of the throughput.

In an attempt to simplify the conventional sugar recovery process along with increasing the quantity and quality of sugar

produced, it was decided to study the purification of diffusion juice directly by means of ion exchange with the elimination of all of the stages of defecation in the conventional process. Toward this end, a series of investigations were performed, initially in small columns on synthetic juice and later in a pilot plant capable of processing 180 gallons of diffusion juice per cycle. A schematic flow sheet of this plant is shown in Figure 2.

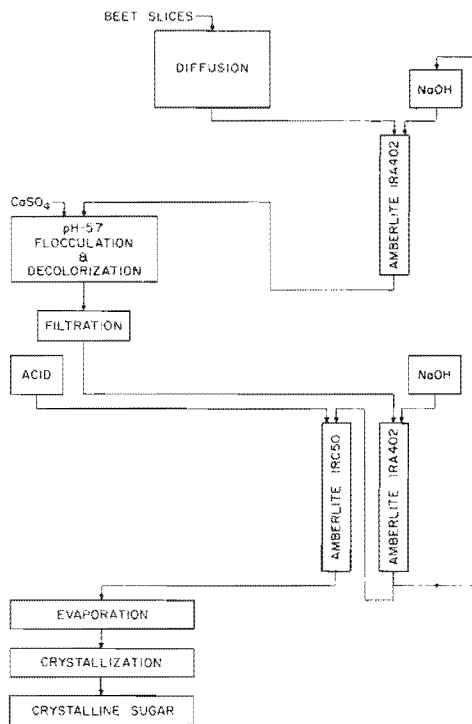


Figure 2.—Application of Assalini "A" Process to European beet sugar production.

The scheme of this process could be summarized as follows:

### First Stage

This consists of passing the diffusion juice, as it comes from the measuring tanks, through a bed of strongly basic anion exchange resin principally in the hydroxide form. This resin should be of the porous variety such as Amberlite IRA-401S or, preferably Amberlite IRA-402. The mineral salts present are converted as in normal ion exchange with the adsorption of the anion and the conversion of the cation to its corresponding

hydroxide. The complex organic salts are partly dissociated by the exchange reaction which results in an increase in pH due to the conversion of the mineral cation to its hydroxide. The pH of the diffusion juice, originally between 5.5 and 6.5, reaches a value around pH 10 after passage through this resin column thereby eliminating the immediate possibility of serious inversion.

### Second Stage

(Chemical treatment and filtration)—The sugar juice, which has already been partly defecated by the ion exchange treatment, is subjected to a chemical treatment with an inorganic salt which is able to form a "floc," and thus further defecate and decolorize the juice. This particular phase of the process required a very large number of experiments in order to determine the most suitable salts for the floc formation which was optimum from the point of view of analytical, technical, and economic requirements. It was found that a most efficient flocculation of the organic substances present, along with nearly complete decolorization, could be obtained using a 30% solution of aluminum sulfate. This treatment must be effected with special care since a pH of 5.7 must be obtained to form the aluminum hydroxide floc. This pH value is optimum from the point of view of best defecation, easiest filtration and minimum dissolution of aluminum sulfate into the juice which would, of course, increase the ash content. Even under these conditions, however, filtration is rather difficult and commercially practical filtration rates can be obtained only with vacuum filters. This treatment is also more expensive than those which will be described below but it is interesting to observe that, at a relatively low pH for a sugar juice, no increase in invert content was observed even at rather high temperatures.

The use of calcium chloride for this flocculation was also investigated. This has given very good results from the point of view of analyses and economy. In this case, the juice from the first ion exchange column is treated with a 30% solution of calcium chloride. With the beet juice under investigation, it was found that optimum defecation was reached when a quantity of calcium chloride equal to about 0.03% of juice was employed. Flocculation was excellent as was the decolorization. Moreover, the filtration of the suspension was easier than that resulting from the aluminum sulfate treatment. Naturally, the juice defecated in this way undergoes a further increase in purity. However, it is necessary to avoid using excessive amounts of calcium chloride because of the obvious increase in ash content which would result from this very soluble salt. Economically,

the use of calcium chloride was considerably more desirable than the aluminum sulfate treatment because of the small quantities employed.

It was found that calcium sulfate is the salt which yields the most interesting results from the industrial point of view especially from the viewpoint of lowest cost. The amount of anhydrous calcium sulfate which proved to be optimum on the juice investigated was 0.3 to 0.4% based on juice. Addition of the calcium sulfate was done from a slurry of calcium sulfate. The addition was made to a sugar liquor having a pH of 9.9. The final pH was adjusted to 7.7 for ease of handling. The flocculation was almost complete and the decantation of the precipitate was very rapid. This would permit the use of thickeners already present in the factory and the filtration of the thickened slurry presented no special difficulties.

Ordinary sand filters have been employed for these filtrations since they were found entirely suitable. It should be noted that, in the case of the calcium salts, the juice does not reach an acidic pH since the hydroxides formed after passage through the anionic resin in the first stage remain either substantially unchanged or are only partly converted to the corresponding sulfate.

### Third Stage

After the filtration indicated above, the juice still contains amounts of soluble minerals and organic substances. In order to complete the purification and decolorization, the juice is sent through two further beds of ion exchange resins. The first is a porous anion exchange resin in the hydroxide form, preferably Amberlite IRA-402, and the second is a weakly acidic cation exchanger in the hydrogen form, preferably Amberlite IRC-50. After this two-bed deionization, the juice has a very high purity, is virtually colorless and yields sugars equivalent in quality to the products achieved by the refining process used in Europe as described previously.

During this final ion exchange treatment, the pH never falls below 7 but it is possible to obtain a final juice with a higher pH value by reducing the level of regeneration of the Amberlite IRC-50. However, this was found to be unnecessary during the entire investigation. Since the carboxylic cation resin is weakly acidic, its regenerant consumption for sulfuric acid is only slightly higher than theoretical. While the use of a strongly acidic cation resin might give a higher purity with the removal of betaine, this substitution would naturally give rise to significant inversion.

The anion exchanger in the first stage is regenerated with the excess caustic recovered from the regeneration of the anion exchanger in the third stage. This technique is important, firstly, from the point of view of economy since it permits a high regeneration level of the anion exchanger in the deionization stage, which gives maximum purity, while the excess hydroxide ion can be utilized in the first stage anion exchanger to bring about the necessary pH rise. Secondly, the regenerant effluent from the second anion exchanger contains a large quantity of various sodium salts in addition to the excess sodium hydroxide which serves as the actual regenerant for the first anion exchanger. These sodium salts serve to remove the great bulk of the organic material adsorbed by the first anion exchanger which treats the diffusion juice directly.

The anion exchanger in the first stage need not be regenerated to high levels, since even if all of the salts in the diffusion juice are not converted to the corresponding hydroxide, there is always a good increase in purity and the pH rises to a point such that flocculation, either with aluminum or calcium sulfate, is easily brought about and is quite efficient.

As regards the analytical and economic data obtained from the various experiments, the following summaries indicate the experimental results obtained using the process described above. Incidentally, the analytical data used for the calculation of technical and economic balances, have been obtained enzymatically as regards the sucrose and by a solids balance as regards the non-sugars. The yields and extractabilities were obtained by means of direct weights. These results were in agreement with calculations made according to the usual extractability formula.

Table 1.—Analytical Data on Assalini "A" Process.

	Diffusion Juice	Final Juice "A" Process
Enzymatic sucrose—%	15.50	15.40
True dry substance—%	18.23	15.80
Enzymatic true purity—%	85.0	97.5
Total non-sugars—%	2.73	0.40
Ash—%	0.61	trace
Chlorides—%	0.043	trace
Invert—%	0.033	0.036
Color (Stammer units—100% solids)	360	0.097
pH	5.80	7.70

The juice obtained with the application of the "A" Process, on evaporation and crystallization, produces a thick juice and a first product massecuite with the same characteristics but with a

slight increase in the purity due to the removal of volatile non-sugars during evaporation. This resulted in a slight decrease in pH due to the volatilization of nitrogen compounds. A comparison of yields between the Assalini "A" Process and conventional European practice is given in Table 2.

Table 2.—Operation Results.

	Conventional European Practice	Assalini "A"
Sucrose—%	16	16
Losses up to raw juice—%	0.50	0.50
Lime process losses—%	0.10	
Resin and filtration process losses—%	.....	0.10
Sucrose in juice—%	15.40	15.40
Purity—%	90	97.5
Total non-sugar - %	1.71	0.40
Sucrose in molasses (purity 60)	2.57	0.60
Extractible sucrose	12.83	14.80
Extractible gained 100 lbs. beets		1.97

Table 3.—Operating Costs-Assalini "A" Process (Based on Chemical Prices in Italy).

	Cents/100 lbs. Beets
<b>Reagents</b>	
Sulfuric acid (66 Be) 0.44 lbs.	0.580
100% caustic soda 0.70 lbs.	2.860
Calcium sulfate 0.300 lbs.	0.971
	3.511
<b>Other Expenses</b>	
Steam 7 lbs.	0.819
Labor for ion exchange -0.01 hour	0.293
Labor for filtration 0.01 hour	0.293
	1.405
<b>TOTAL</b>	4.92 cents

Table 4.—Economics of "A" Process.

Raw and Crystalline Sugar	
Abolition—Lime Process	2.20 cents/100 lbs. beets
Cost "A" Process	4.92 cents/100 lbs. beets
Net Cost "A" Process	2.72 cents/100 lbs. beets
Processing Cost per Pound Sugar Gained	1.38 cents/lb. sugar
Value of Sugar in Molasses not Produced	2.31 cents/lb. sugar
Cost of Sugar Gained	3.69 cents/lb. sugar

## Economics

### Raw and Refined Sugar Production

The economics of the "A" Process have been evaluated in Table 4. Here again the values are based on Italian sugar practice.

### Production of Refined Sugar

From a syrup with a purity of 97.5 to 98% and 0.5 Stammer units per 100 solids, at least 50% of refined sugar is obtained in Europe directly from the first massecuite. The second and third products would be sent back to the refinery. Taking the cost of refining at 0.73¢/lb., we have:

Table 5.—Production—Refined Sugar.

Expense with the conventional process	$0.73 \text{ cents} \times 12.83 =$	9.4 cents
Assalini "A" Process expense	$\frac{0.73 \times 14.80}{2} =$	5.4 cents
Saving for 100 lbs. beets		4.0 cents
Saving for each lb. of additional sugar:	$\frac{4.0 - 2.72}{1.97} =$	0.64 cents/lb.

The cost for a plant to process 2000 tons of beets per day has been estimated in Table 6. The economic evaluation has again been based on European practice.

Table 6.—Plant Economics—"A" Process.

Basis—2,000 tons beets per day		
Installation: \$210,000—Resins		
	\$113,000—Equipment	
	\$323,000—TOTAL	
Amortization Rate—5 campaigns—300 days		
	<b>Crystalline</b>	<b>Refined</b>
Destroyed Molasses	2.310	2.310
Amortization	1.242	1.242
Operating Expenses	1.386	.....
TOTAL	4.938	3.552
Lowered Cost	.....	0.637
Total Cost—1 lb. additional sugar—produced, cents	4.938	2.915

At this date, extensive testing has not been completed to give an accurate field estimate of exchanger life but the above value is believed to be realistic.