

Ion Exchange Applied to Sugar Juice Purification

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The process for recovering sugar from sugar beets has existed in its present form substantially unchanged since its inception over 100 years ago. There have been many improvements in technique and equipment but the essential methods have remained relatively the same. Now a new process of juice purification has been developed that promises to remove most of the non-sugars and permit recoveries of 95 to 96 percent without resort to the Steffenizing of the molasses.

The process makes use of the new synthetic resinous ion exchangers developed during the past 10 years. It is only with the advent of these new high capacity, durable, synthetic materials that the use of ion exchange has become practical and economical for sugar and many allied purification problems. This paper will discuss only the purification of the sugar juice, although the recovery of valuable by-products is possible and practical as indicated in some of our research.

The Dorr Company has been actively working on the application of ion exchangers to sugar juices and has cooperated with the Amalgamated Sugar Company in extensive experiments on a laboratory and pilot plant scale. As the principles and theories of ionic exchange reactions have been presented by others, they will not be discussed here.

Table 1 shows the results of the final 10-day run at the Burley Pilot plant in 1942. This table shows the results achieved on a continuous 10-day run. This pilot plant treated an average of 20,000 gallons of juice per day, which was equivalent to that from 560 tons of beets containing 16.3 percent sugar with 0.30 per cent beet-end losses.

This table is based on results achieved when treating second carbonation juice. From the quantities it is apparent that to remove 1 pound of non-sugars, there is required approximately 1 pound of 66° Be' sulphuric acid and 0.6 pound of soda ash (Na_2CO_3). This then is the direct chemical cost of treating a juice. From an average figure on elimination of non-sugars of 72.6 percent it is seen that per pound of non-sugars originally present, it will require about 1.4 pounds of 66° Be' sulphuric acid and 0.83 pound of soda ash to give this 72.6 removal. These results were with Idaho beets and will change slightly depending on the organic ash ratio of the non-sugars present in the juice. In general the organics have higher equivalent weights than ash constituents, and so per pound of chemical regenerants there will be more pounds of non-sugar organics removed than inorganics. Here it may be well to state that the general theory is that the ionic ex-

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Table 1.

	Feed to station			Finished juice								
	No. cycles on station	No. samples to laboratory	Brix	Apparent purity	Percentage invert on D. S.	Percentage conductivity ash on D. S.	Brix	Apparent purity	Percentage invert on D. S.	Conductivity ash percentage on D. S.	Percentage ash elimination	Percentage elimination based apparent purity and invert
1.	7	2	12.9	92.4	0.0	3.09	11.1	98.3	0.50	0.20	94.0	85
2.	18	9	12.9	92.1	0.0	2.89	11.1	98.0	0.50	0.20	94.0	85
3.	20	10	11.9	91.3	0.0	3.41	10.0	97.3	0.32	0.30	91.8	74
4.	22	11	12.1	91.3	0.01	3.32	10.3	97.3	0.19	0.28	92.0	72
5.	21	11	11.8	91.5	0.06	3.16	10.2	97.0	0.21	0.30	94.2	69
6.	23	11	11.2	91.3	0.15	3.09	9.9	96.2	0.59	0.30	92.4	63
7.	22	11	12.0	91.3	0.03	3.32	10.2	96.2	0.17	0.28	92.0	64
8.	25	12	12.0	90.9	0.21	2.96	10.3	97.1	0.31	0.30	90.5	73
9.	23	12	12.9	91.2	0.09	2.89	10.0	97.1	0.30	0.26	94.5	72
10.	24	11	12.5	91.6	1.00	3.32	10.4	97.3	0.34	0.28	92.1	76
11.	7	5	12.4	91.5								
TOTALS	212	105										
AVERAGE			12.2	91.5	0.05		10.45	97.14	0.34	0.257	92.5	72.6

Average gallons juice per cycle out—1,075. gallons
 Average tons beets per cycle 2.65. tons

12,000 pounds H_2SO_4 used
 7,350 pounds Na_2CO_3
 12,500 pounds impurities removed—calculated

change resins remove only those substances that ionize, although there is evidence that colloid and some other substances are removed also. This colloid removal, however, may be due to electrical charges borne by the colloids being neutralized by the exchanges or to the fact that pH changes occur during treatment.

There is an increase in the invert sugar content and as a corollary we may state a decrease in sucrose content of the treated sirup. This increase in invert sugar averaged 0.29 percent on dry substance for the final run. Inspection of the daily results will show results varying from 0.09 percent to 0.54 percent. Checks over isolated portions of the complete de-ionization station show that most of this inversion was due to bacterial action at the filter press and cooler. When these sections were kept clean, the inversion was minimized. The inversion due to the exchanger treatment was low and can be expected to be below 0.10 percent on sugar.

This subject of inversion is interesting. The pH of the juice (12-14 Brix) after passing through the cation exchange is around 2.0 and it is in the acidic state less than 3 1/2 minutes when operating on a 6-foot deep exchanger bed. Now a pH of 2.0 is equivalent to a hydrochloric acid solution of 0.01 normal which will cause inversion of the order of 0.02 percent or less in 3 1/2 minutes. The remaining inversion is due to the catalytic action of the cation exchange resin itself because the cation exchange resin may be looked upon as a solid acid with only its hydrogen ion in solution. Later results on inversion show that it may be kept below 0.1 percent on sugar with good temperature control and rapid treatment.

The dilution due to sweetening-off was calculated at 10 percent for the runs tabulated. This is higher than would be achieved in practice with the exchanger then used and would not normally be this much with that particular exchanger. However, because of operating conditions at the time it was not possible to control sweetening-off as well as desired. Newer exchangers of higher capacity will mean less dilution. Since dilution is due to sweetening-up and sweetening-off, it is a function solely of the volume of resins. Therefore, with a resin of higher capacity, more sugar sirups of the same non-sugar content can be passed through before they are exhausted and consequently less in the overall picture. The amount of dilution will be in inverse ratio to the capacity of the resin in question. Consequently the higher capacity resins will show better savings.

This dilution, however, does mean extra work on the evaporators. During the pilot plant run in 1942 dilution amounted to about 35 gallons of water per ton of beets. With newer high capacity exchangers, this will decrease to approximately 20 gallons per ton of

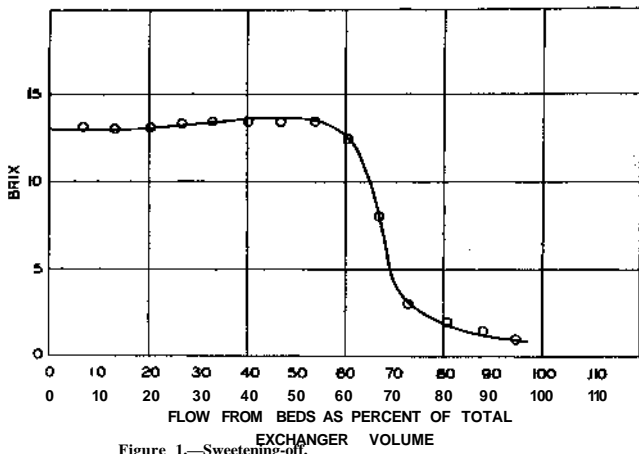


Figure 1.—Sweetening-off.

beets. The suggestion has been made to use the lower Brix sweet water in the battery at the third or fourth cell from the tail end. We do not believe this will bring any savings since water will still have to be used on the tail end of the battery to bring the pulp sugar losses down.

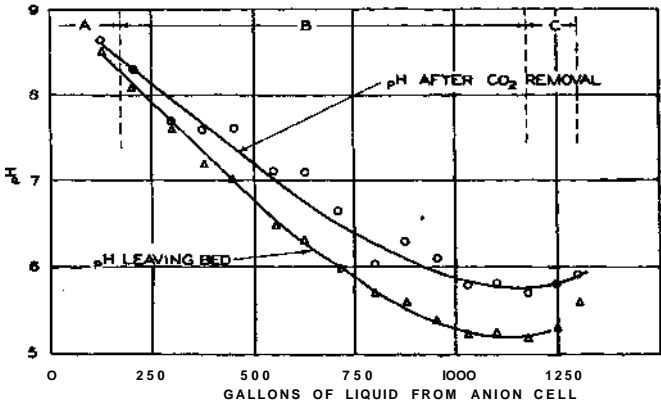
Graph 1 shows the results of sweetening-off on two typical runs. The ordinates show the Brix of the effluent of the pair of cells from the beginning of the sweetening-off step. The abscissae show the volume of effluent expressed as a percent of the volume of the cation plus anion exchanger. The total volume of both exchangers present was 36.5 cubic feet and it had treated juice equivalent to 2.65 tons of beets per average cycle.

The juice to be treated was cooled by passage through a heat exchanger and a cooler in series until it was at 20° to 22° C. The cooling in the heat exchanger was done by means of the treated juice from the de-ionization station with subsequent cooling by cold water in the cooler. In this way some 80 to 85 percent of the heat can be recovered.

No pH correction of the juice leaving the station is needed. The juice at the start of the cycle is slightly alkaline, around pH 9.0, and drops to pH 5 to 6 at the end of a cycle. The resulting mixture when boiled a few seconds gives a solution of pH 7.0 to 7.2. The alkalinity

at the start of the cycle is due to the basicity of the anion exchanger converting traces of unremoved cation salts to the corresponding bases and/or carbonates depending on whether the bed was regenerated with NaOH or Na_2CO_3 . The acidity at the end of the run is due to the poor capacity of the anion resins for weakly ionized acids such as H_2CO_3 . A short boiling of the juice drives out the CO_2 and the pH rises to around 7.0 to 7.2.

Graph 2 shows the pH of the juice throughout a complete cycle as it leaves the anion cell. The lower line shows the trend of pH as this juice leaves the anion cell. The upper line shows the pH of the juice after it had been degasified to remove CO_2 . This degasifying was done at room temperature and, therefore, CO_2 was not completely removed. Better removal of CO_2 is accomplished if the juice is boiled. Inspection of the graph 2 will show that the average pH is about 7.0. The explanation of this pH range logically follows when it is realized that an anion exchanger is weakly basic. At the start of a treatment cycle the resin is freshly regenerated and in this state can convert a small portion of the cation salts that leak through the preceding ca-



- A WATER DISPLACED FROM BEDS
 B NORMAL JUICE CYCLE
 C EXCESS JUICE DISPLACED FROM BED

Figure 2.—pH of exchanger juice.

tion cell to bases such as hydroxides or carbonates. The exchanger was previously regenerated with a Na_2CO_3 solution which converted it to the basic form and perhaps to a carbonate base. Now when a trace of unexchanged cation with its anion such as KNO_3 passed through the bed the stronger acid radical NO_3 would displace the OH or $1/2/\text{CO}_3=$ radical from the exchanger and give a basic reaction in the effluent. As the cycle progressed the exchanger would not remove weak acids such as H_2CO_3 and other weak organic acids because as it becomes exhausted its basicity is lowered. Beet sugar juices after second carbonation have as much as 20 percent of their equivalents of anions present as $\text{CO}_3=$ and this with weak organic acids actually leak through and are even displaced from the anion resin by stronger acid radicals towards the end of the cycle. This accounts for the progressive lowering of the pH. The thin juice boiler will remove the CO_2 and raise the pH.

The exchangers, as shown in the table, removed 92.5 percent of the ash constituents in the juice. The overall removal was calculated on the basis of purity increases. On several runs the nitrogen removal was determined by running Kjeldahl nitrogen tests on the juices periodically during the run. On a typical run the average nitrogen removal over the whole run was 90.8 percent. No time was available to determine what specific nitrogen compounds were removed.

The capacities of various exchangers are discussed by Thompson for water treatment. These ratios will hold for sugar solutions within reasonable limits. Certain exchangers exhibit better stability and higher capacity. Certain others can be regenerated to give an equivalent removal and/or capacity with less regenerant consumption. Others give better color removals. The judicious selection of the resinous materials best fitted to all cases is the subject of considerable study upon the part of the Dorr Company, and we are continually testing new exchanger materials as they become available from the various manufacturers.

The acid consumption given in the table 1 is for single stage regeneration. Since that time we have developed methods in our Westport Laboratories that will greatly reduce regenerant requirements.

Additional economics in acid consumption can be realized by operating two more pairs of cells in series. This has two advantages. One is that a cell can be operated to exhaustion instead of breakthrough, which is advantageous since it takes almost as much acid to regenerate the cation cells less completely with less acid and still get good eliminations because the second pair removes what the first pair does not. For example, take a single case of NaCl removal from a solution. With a certain exchanger the cation will remove 96 percent

of the sodium ion when regenerated with 350 percent theoretical acid required to remove the cations on a bed. However, if two pairs are operated in series each cation cell may be regenerated with only 250 percent theoretical to give 80 percent removals and then with two pairs in series there will be an 80 percent removal in each cation cell or an overall removal of 96 percent at a 28.4 percent savings in acid costs.

This series method of operation has, however, some disadvantages also. There has been mentioned the subject of the catalytic inversion of sucrose by the cation exchanger. With two pairs of cells in series this is more than doubled and so makes for a sacrifice in sugar recoveries, and as a result the savings are decreased. In addition it means that in any given installation the number of pairs installed has to be increased by the number of pairs operated in series minus one. Thus first cost of the plant is increased. It is obvious that the advantages and disadvantages of the two methods of operation must be given judicious study.

Table 2 shows the results of boiling and crystallization tests on ion exchange treated sugar juice. These tests were made in cooperation with the Western Sugar Refinery on exchanger treated second carbonation juice from the Woodland factory of the Spreckels Sugar Company. The crystallization steps began with a pilot size pan 30 inches in diameter and ended up in beakers. Manipulative difficulties were severe because after a few crystallizations the removal of samples seriously upset yield figures. However, the results show the purities obtainable in final molasses, although quantities were impossible to calculate with accuracy on the final samples.

To Table 2 is appended a tabulation of a typical refinery blackstrap molasses for comparison. There is quite close agreement on the analysis of the two final products, indicating that the final molasses from an ion exchange plant can be reduced to low purities.

On the basis of numerous tests made on second carbonation juice it is possible to make the following comparison of the estimated recoveries for a straight house versus an exchanger house. The estimates have been made by taking analyses figures midway between the results shown in tables 1 and 2. For an example, a factory slicing 2,000 tons of beets per day with a net sugar to the sugar-end of 16 percent on beets, a feed purity of 90.91 for second carbonation juice, and a finished purity of 97.15 for the ion exchanged juice has been selected. These, as can be seen by inspection of tables 1 and 2, are less attractive economically than those indicated by the maximum purity rises determined in the test work. The intention is to be conservative, although higher purities can be expected with quite a reasonable degree of assurance.

Table 2.—Crystallization tests.

Item	Original 2d car- bonation juice	Solution before organo- liting	Organo- lited solution	First filmas	First syrup	Second syrup	Third syrup	Fourth syrup	Fifth syrup	Sixth syrup	Seventh syrup about 7/15/42	Seventh syrup about 10/15/42	Typical refinery black- strap
R. D. S.	57.0	15.8	14.1	82.5	68.0	57.2	72.4	75.6	78.0	81.4	85.4	82.4	
A. P. C.	.892	.898	.985	.985	.974	.965	.949	.918	.867	.790	
Total weight	709.0	121.0	74.59	37.97	18.31	8.46	4.32	1.60	*	
Weight sugar	98.5	98.5	49.25	24.62	12.59	5.86	2.98	1.03	
Weight non sugar	1.5	1.5	1.28	0.91	0.68	0.53	0.40	0.27	
Weight water	609.0	21.0	24.06	12.44	5.04	2.07	0.90	0.30	
Calc. yield of sugar crystals	49.24	24.63	12.63	6.73	2.93	1.90	
A. P. C. of sugar found977	.986	
A. P. C. of sugar calc.982	.977	.969	.965	
ANALYSIS OF SYRUP													
Color	600	17
pH	7.1	7.0
Sugar by Polz.	50.200	14.05	13.900	80.60
True sucrose	82.2	42.4	36
Invert	.092	.020	.055	0.26	6.5	7.8	20
Moisture	43.900	84.340	85.830	18.00	14.6	17.6	24
Ash	1.890	.541	.937	0.18	3.2	3.9	8
Raffinose	7.6	9.2
Organic	4.018	1.040	.178	0.96	15.9	19.1	12
True purity611	.514	47.4

*NOTE:—Separation of sugar crystals unsuccessful; sample of syrup recovered for analysis and further crystallization on long standing in beakers.

Table 3.—Comparative estimated recoveries.

Per day	De-ionization	Straight
Pounds sugar to sugar-end.....	640,000	640,000
Purity to sugar-end.....	90.91	90.91
Pounds non-sugars to sugar-end.....	62,000	62,000
Pounds raffinose to sugar-end (1 pound/ton beets).....	2,000	2,000
Pounds invert former (0.2 percent on sugar).....	1,300	300
Purity of juice to pans.....	97.15	90.91
Pounds sucrose lost in sweeten-off (0.091 percent on sugar).....	606	
Pounds non-sugars to pans.....	15,470	61,700
Pounds sucrose to pans.....	638,165	639,715
All invert to molasses.....	1,300	300
All raffinose to molasses.....	2,000	2,000
Sugar to molasses—1.5 to 1 on NS.....	23,200	92,550
All non-sugars to molasses.....	15,470	61,700
Total solids in molasses.....	41,970	156,650
Pounds molasses at 82 D. S.....	61,200	191,000
Net sugar to buy.....	614,965	547,105
Cubic feet white massecuite.....	18,400	16,900
Cubic feet hl-raw massecuite.....	1,500	5,500
Cubic feet lo-raw massecuite.....	820	2,320
Recovery increase—pounds sugar.....	67,800	
Molasses decrease—pounds at 82 D. S.....		139,800
Percentage recovery on sugar to sugar-end.....	96.09	85.49

It is realized that calculations of production or extraction from juice purities cannot be as accurately foretold as the estimates indicate. However, both straight house and exchanger house are estimated on the same basis so the comparison is fair.

Table 3 indicates an increased recovery of 67,800 pounds of sugar per day and a decreased production of 139,800 pounds of molasses per day.

Table 4 shows the estimated debits and credits for the two types

Table 4.—Estimated savings with de-ionization based on 100-day campaign.

	Debits	Credits
Increased sugar value: at \$4.25/100.....		288,150.00
014,905—547,105		
Loss in molasses sales at \$18/ton.....	125,820.00	
191,000 pounds—61,200 pounds		
Sulphuric acid at 16 pounds/ton beets 1c/pound.....	32,000.00	
Soda ash at 13.1 pounds/ton beets 1.4c/pound.....	38,680.00	
Extra fuel at 10c/ton. 15 tons/day.....	9,000.00	
Extra labor on D-1 station—2 men.....	4,200.00	
Decreased labor at centrifugals—1 man.....		1,930.00
No sulphur burned at 1c/pound and 0.5 pound/ton beets.....		1,000.00
No carbon at 10c/lb. and 0.1 pound/ton beets.....		2,000.00
No boiling chemicals, estimated.....		6,000.00
Exchanger replacement at 10 2/3 percent.....	13,800.00	
	221,000.00	209,070.00
	Net savings	77,470.00
Per ton beets \$0.8673		

of houses with a resulting estimated increased monetary return of \$72,470 per 100-day campaign or a net return of \$0.3873 per ton of beets. From this return it will be necessary to pay for the plant and pay taxes, insurance, and fixed overhead.

No credit has been taken for the very probably increased value of exchanger molasses nor for the increased efficiency of the sugar-end because of clean scale-free heating surfaces. Molasses prices are now higher than the \$18 per ton figure used in calculations, but pre-war prices were considerably lower so the estimated value as taken is thought to be more than fair.

Summary

As a summary it may be stated that an exchanger house promises:

1. Increased recovery of 10.5 percent on sugar processed.
2. Low ash white sugar.
3. Higher operating efficiencies in the sugar-end.
4. Elimination of the use of sulphur and carbon.
5. Elimination of boiling out during campaign.
6. Higher quality final molasses.

This will mean increased financial returns to the sugar processor. The use of the new exchanger process is practical and economic and offers a major technical improvement to the sugar industry.

Grateful acknowledgement is extended to the Amalgamated Sugar Company through whose cooperation on pilot plant tests the greater part of this work was made possible and to the Western Sugar Refinery for the tests on the crystallization of sucrose from ion exchanger treated beet juices.

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