Ion Exclusion Purification of Molasses

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The separation of ionic from non-ionic substances using ion exclusion is only a little over ten years old. Ion exclusion purification arose from the observation that at equilibrium the concentration of a strong electrolyte is lower within the aqueous portion of the resin phase than in the surrounding solution. The electrolyte is partially excluded from the water in the resin bead. Non-ionized or weakly ionized compounds generally have a relatively high concentration within the resin bead compared to highly ionized compounds. When the differences in relative concentrations inside and outside the resin bead are sufficiently large, two substances may be separated readily on a resin column.

Essentially ion exclusion purification is a chromatographic technique. The components to be separated are loaded on the column and washed through with water as the eluant. Compounds having a lower relative concentration in the resin bead will be eluted more rapidly and hence separate from components having a higher relative concentration in the resin bead. Non-ionized or weakly ionized compounds may also separate from each other if there is an adequate difference in their relative concentrations between the solution inside and outside the resin beads.

Recovery of sugar from molasses by ion exclusion offers a number of advantages over ion exchange. A cation exchanger is cheaper and more stable than an anion exchanger. Operation near pH 7 precludes sucrose inversion. There is no expense for costly regenerants as water elutes both the sucrose and impurities from the column. Fewer resin beds should be required as only one resin is utilized.

Wheaton and Bauman (1,2)[2] discussed theory of ion exclusion and its potential applications in 1953. Patents have been issued for the separation of ionic materials having different degrees of ionization (3) and for the separation of certain organic compounds (4). This latter patent (4), describes separations for glucose-acetone and sucrose-glycerol-triethylene glycol. A later article by Asher (5) discusses sugar purification by ion exclusion and gives examples of the separation of salts from dextrose or sucrose. Color and strong ionic materials present

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[2] Numbers in parentheses refer to literature cited.

in molasses or crude cane sugar were separated from the sucrose. A patent by Wheaton (6) on ion exclusion purification describes similar experiments including treatment of cane molasses to remove ionic compounds. Simpson and Wheaton (7) give a good resume of the effects of a number of variables that influence the efficiency of ion exclusion separation—particle size, flow rate, crosslinkage, and feed volume to column volume ratio —using ethylene glycol as a test compound. Simpson and Bauman (8) describe a procedure for recycling effluents from an ion exclusion separation of ethylene glycol from sodium chloride which could possibly be adapted to sugar liquor purification. A more recent publication by Norman, Rorabaugh, and Keller (9) discusses some of the advantages of ion exclusion as applied to sugar juice purification. They also postulate operating requirements for a continuous Higgin's contactor (10) which might be used to purify sugar beet thick juice diluted to 40 Brix.

None of these papers indicate any separation of reducing sugars, i.e., glucose or fructose from sucrose and one (4) specifically states that glucose cannot be separated from sucrose using ion exclusion. However, papers by Jones *et al.* (11,12) and Carruthers *et al.* (13) demonstrate the feasibility of separating mono, di and trisaccharides for analytical purposes on Dowex 50 W, (2% DVB, 200-400 mesh, Li form) using columns 100-150 cm long and 1-2 cm diameter. These analytical conditions would be impractical industrially. Cations in the sugar liquors would displace lithium and the load and rate of elution are too low.

There is little information in any of these papers to indicate whether the impurities other than salts and color present in sugar liquors, such as amino acids, salts of weak acids, saccarides and others, may be separated from sucrose by ion exclusion. It seemed possible that, in addition to separating strong salts and color eluted before sucrose, other impurities might be eluted after sucrose enabling further purification. This paper describes a number of experiments using cane and beet molasses that show the separation of some molasses components by ion exclusion.

Materials and Procedures

The resin was Dowex 50 W, 50-100 mesh. The potassium form of the exchanger was used since this form of the resin would most nearly approximate the form that would develop during factory operations on beet molasses. Studies compared the efficiency of X-4 and X-12 crosslinkages at room temperature and at 90°C. Two Pyrex glass columns were joined to coarse

sintered glass funnels: one for use at room temperature was 90 mm tubing 135 cm long containing 6500 ml of resin 115 cm high; the other was 50 mm tubing 115 cm long jacketed for operation at 90°C and containing 1800 ml of resin 100 cm high. Work with columns of this size is generally considered suitable for scaling up to industrial sized units. Temperature in the second column was maintained by pumping hot water through the jacket while loading with hot molasses and using hot water for elution. The normal flow rate of 1 ml/cm²/min was controlled with a capillary outlet; minor adjustments in rate being made by raising or lowering the effluent reservoir. Load volumes were 15% of the resin bed volume, 975 ml for the large column and 270 ml for the smaller column. Contraction of 5-10% in the resin bed during loading and subsequent expansion during elution do not interfer with column operation. Effluent fractions equal to 1/20 of the bed volume were collected and analyzed.

The following general analytical methods were used: Reducing sugars were determined by Munson-Walker copper reduction. Sucrose was determined by invertase inversion followed by copper reduction. Total nitrogen was determined by the Kjeldahl method and amino nitrogen by the Van Slyke procedure. Ash was determined by heating at 550°C and weighing the residue. Chloride was determined using an Aminco-Cotlove automatic chloride titrator. Color determinations were made with a Beckman Model B spectrophotometer measuring adsorption at 720 and 425 mμ and reported in arbitrary units.

Experiments and Results

An attempt was made to separate sucrose from glucose at room temperature using the large column with X-12 crosslinked resin. A solution containing approximately 190 g each of glucose and sucrose in 975 ml of water was loaded on the column and eluted with water. Two runs were made at flow rates of 1 ml/cm²/min and one-third that rate. The data for these runs are presented in Table 1 and Figure 1. This and other figures plot V_e/V_T (ratio of effluent volume to resin bed volume) against C_e/C_T (ratio of effluent concentration to original concentration). Results obtained using columns of different sizes may be compared directly on this basis. Although the separation of sucrose from glucose was not complete, nearly 50% of the sucrose was in the first three fractions at greater than 80% purity. The separation of salt from sucrose described by Asher (5) combined with these results demonstrate the possibility of separating cane molasses into a salt-rich fraction, a sucrose-rich fraction, and finally an invert-rich fraction.

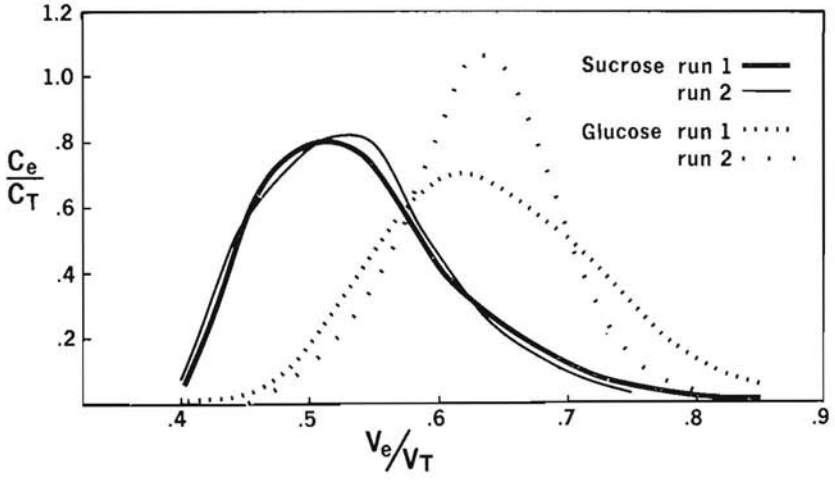

Figure 1.—Separation of sucrose and glucose using Dowex 50W (12% DVB, 50-100 mesh, K form) at 25°C. Run 1. Load: 190 g each of sucrose and glucose in 975 ml solution. Effluent rate: 1 ml/sq cm/min. Run 2. Load: 200 g each of sucrose and glucose in 975 ml solution. Effluent rate: ⅓ ml/sq cm/min.

Table 1.—Separation of sucrose from glucose at 25°C using Dowex 50 W(K) X-12.

	Percent of total					
	Sucrose		Glucose		Sucrose purity	
Fraction	Run 1	Run 2[1]	Run 1	Run 2	Run 1	Run 2
8	2.0	2.5	0.2	0.0	92.1	99.0
9	19.7	19.0	0.9	0.3	95.5	98.6
10	26.3	25.6	6.5	4.0	80.1	86.3
11	23.8	26.5	16.4	13.5	59.1	65.9
12	13.3	15.3	22.9	27.3	36.7	35.6
13	8.1	6.3	21.4	33.5	27.3	15.7
14	4.0	3.5	16.3	17.1	19.7	17.0
15	2.0	1.0	9.5	3.6	17.4	21.1
16	0.7	0.2	4.0	0.5	14.5	32.0
17	0.3		1.9		15.5	
Total g	188.4	203.6	188.8	201.6		

[1] Flow rate of 1/3 ml/cm²/min.

A series of experiments were conducted using X-12 resin at 25°C and 90°C and X-4 resin at 90°C. Dilute beet molasses, 40 RDS, was loaded on the large column containing X-12 resin and washed through with water at room temperature. The results of this experiment are shown in Table 2.1 and graphed in Figure 2. The curves for ash are omitted in this and other

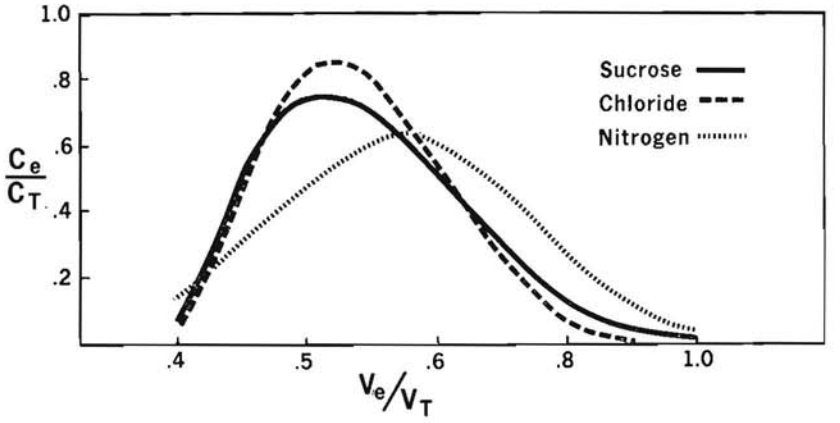

Figure 2.—Beet molasses purification using Dowex 50W (12% DVB, 50-100 mesh, K form) at 25°C. Load: 480 g 65 purity beet molasses in 975 ml solution.

Table 2.1—Purification of beet molasses at 25°C using Dowex 50 W(K) X-12.

	Percent of total						
Fraction	Sucrose	Non-sucrose solids	Nitrogen	Amino nitrogen	Ash	Chloride	Purity
8	2.6	3.3	4.7	2.0	3.3	2.2	61.5
9	16.9	15.9	10.6	9.7	18.8	15.5	67.8
10	24.6	21.8	15.7	13.6	26.8	27.2	69.1
11	23.0	21.8	20.4	17.7	22.8	26.2	67.6
12	16.7	18.5	20.2	18.8	16.0	18.1	64.2
13	9.8	11.4	15.2	16.9	9.1	8.3	63.1
14	4.0	4.9	8.2	11.9	2.6	2.1	61.8
15	1.6	1.9	3.7	6.9	0.5	0.3	62.6
16	0.6	0.5	1.3	2.5	0.0	0.0	69.9
Total g	262.0	132.3	7.9	1.2	56.4	8.4	

Table 2.2—Purification of cane molasses at 25°C with Dowex 50 W(K) X-12.

	Percent of total					
Fraction	Sucrose	Reducing sugars	Solids less sucrose & red. sugars	Nitrogen	Chloride	Purity
8	2.9	0.6	6.0	6.7	2.1	35.1
9	17.2	3.4	20.6	18.7	17.3	46.9
10	22.2	8.5	22.2	19 3	25.3	47.8
11	19.1	13.4	20.7	16.7	23.4	42.1
12	18.1	17.1	13.5	14.0	18.7	44.3
13	11.7	19.0	9.9	10.0	11.6	35.9
14	5.7	17.0	4.5	5.3	1.4	27.2
15	1.7	11.3	1.3	3.3	.1	16.7
16	0.8	6.3	0.7	3.3	....	13.8
17	0.5	3.5	0.6	2.7	....	16.2
Total g	148.7	98.9	124.7	2.4	9.5	

graphs since the ash values correlate very closely with the chloride values. There is only a slight separation of sucrose and non-sugars. The data from a similar run using 490 g of 40 purity refiners cane molasses shows essentially the same results except there is considerable separation of sucrose from reducing sugars (Table 2.2).

Runs were made using X-12 and X-4 resins at 90°C with both beet and cane molasses. The results of the run using beet molasses on X-12 resin in the small column are presented in Table 3.1 and Figure 3. X-12 separates beet molasses components slightly better at 90°C than at room temperature but not sufficiently better to be industrially significant. The higher

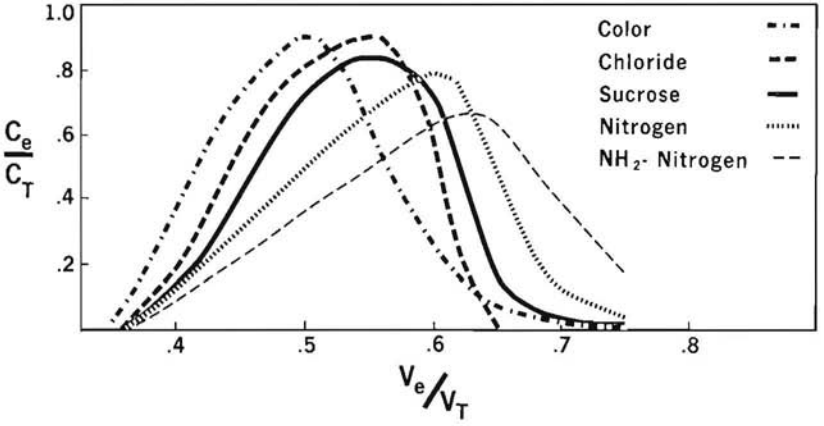

Figure 3.—Beet molasses purification using Dowex 50W (12% DVB, 50-100 mesh K form) at 90°C. Load: 133 g 65 purity beet molasses in 270 ml solution.

Table 3.1—Purification of beet molasses at 90°C using Dowex 50 W(K) X-12.

	Percent of total							
Fraction	Chloride	Sucrose	Non-sucrose solids	Nitrogen	Ash	Amino nitrogen	Color	Purity
7	0.2	...	0.2	0.2	....	....	....	....
8	6.0	3.9	.05	3.7	5.6	3.1	0.6	....
9	19.0	14.8	16.2	10.6	16.8	8.9	13.0	64.8
10	27.3	23.9	23.8	16.7	25.9	12.5	24.5	66.9
11	30.2	28.2	26.3	21.1	30.5	15.6	30.0	68.4
12	17.4	23.3	23.2	26.5	20.5	21.1	19.3	67.0
13	....	4.5	7.7	15.3	0.7	20.6	9.1	53.8
14	....	1.0	1.7	4.1	0.1	12.7	2.0	55.6
15	....	0.5	0.4	1.9		5.5	0.9	....
16	....	....	....	....	....	....	0.6	....
Total g	2.3	75.4	37.4	2.3	15.2	.4	50.7[1]	....

[1] Arbitrary color units at 425 mμ.

temperature slightly increases the maximum concentration of the individual components, but there is little other advantage. Table 3.2 presents a similar run using 141 g of 40 purity cane molasses. The results for cane molasses is also poor except for the separation of reducing sugars from sucrose.

The most successful separations were made with X-4 resin at 90°C. Runs were made with diluted beet or cane molasses using the small column. The analytical results for the run made with beet molasses are presented in Table 4 and Figure 4. Nearly 50% of the sucrose was eluted at 80 purity or higher.

Table 3.2—Purification of cane molasses at 90°C using Dowex 50 W(K) X-12.

	Percent of total						
Fraction	Sucrose	Reducing sugars	Solids less sucrose & reducing sugars	Chloride	Nitrogen	Color	Purity
7	0.0	0.0	0.2	....	0.4	0.2	0.0
8	4.4	1.0	9.7	7.1	12.1	15.9	31.6
9	19.1	2.4	22.4	23.5	22.5	27.8	46.5
10	26.4	7.1	26.3	29.2	25.0	29.3	47.8
11	27.9	18.5	23.8	28.4	21.4	20.3	44.5
12	18.0	32.2	12.7	11.7	10.7	5.4	34.1
13	3.4	29.7	3.2	0.1	4.2	0.5	12.3
14	0.7	7.9	1.2	....	2.3	0.3	8.8
15	0.1	1.4	0.5	....	1.6	0.3	7.7
Total g	42.7	31.0	38.5	2.8	0.6	327.6[1]	

[1] Arbitrary color units at 425 mμ.

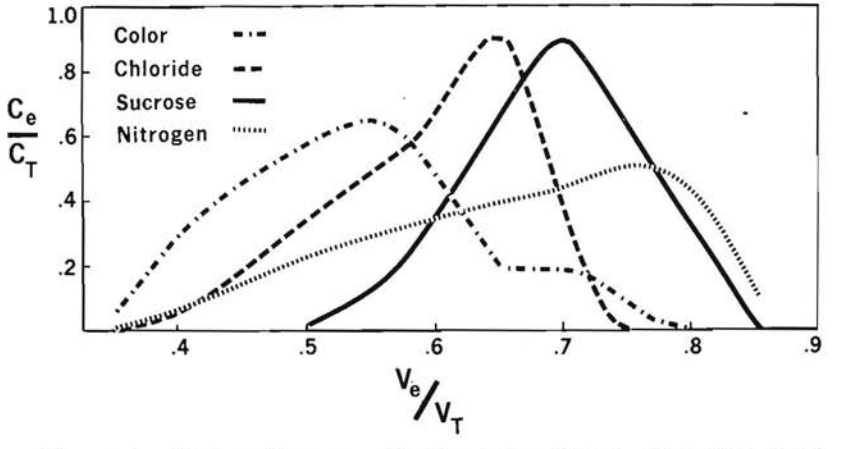

Figure 4.—Beet molasses purification using Dowex 50W (4% DVB, 50-100 mesh, K form) at 90°C. Load: 133 g 65 purity beet molasses in 270 ml solution.

Table 4.—Purification of beet molasses at 90°C using Dowex 50 W(K) X-4.

Fraction	Percent of total							
	Sucrose	Chloride	Non-sucrose solids	Nitrogen	Amino nitrogen	Color	Ash	Purity
7	....	0.2	0.3	0.4	0.1	1.7	0.3	....
8	....	1.7	3.0	2.3	1.6	10.1	2.9	....
9	....	5.9	6.9	4.8	4.3	15.0	7.3	....
10	0.6	11.6	10.7	7.4	7.2	19.2	12.6	9.1
11	3.9	16.8	14.3	10.1	9.8	21.7	16.9	34.3
12	12.1	22.1	17.0	11.7	12.1	15.5	21.1	57.4
13	21.9	29.7	19.6	13.2	12.7	7.0	25.8	68.0
14	29.5	12.0	11.7	14.7	19.0	6.4	11.6	82.7
15	19.6	....	8.4	16.9	11.8	2.4	1.1	81.5
16	12.1	....	6.8	14.5	12.4	0.8	0.3	77.0
17	0.2	....	1.2	3.8	9.2	0.3	0.1	27.6
Total g	76.2	2.3	40.2	2.2	0.3	48.7[1]	15.0	....

[1] Arbitrary color units at 425 mμ.

Most impurities are eluted before the maximum sucrose concentration, but some appear later. Impurities eluted later are principally amino acids and other nitrogen containing compounds.

This experiment was repeated using cane molasses, (Table 5 and Figure 5). More than 65% of the sucrose was eluted at 68 purity or higher. This purity is a considerable improvement over that obtained using X-12 at 90°C where the best fraction had a 48 purity. It is likely that the substances shown in the

Table 5.—Purification of cane molasses at 90°C using Dowex 50 W(K) X-4.

Fraction	Percent of total							
	Sucrose	Reducing sugars	Solids less sucrose & reducing sugars	Chloride	Nitrogen	Ash	Color	Purity
7	....	....	1.3	0.4	1.6	0.7	3.8	....
8	....	....	6.8	2.4	8.8	4.2	12.3	....
9	0.1	0.8	11.5	7.6	14.5	10.3	18.4	1.4
10	1.0	1.1	16.2	15.1	17.6	16.7	21.8	6.6
11	6.7	1.5	18.9	22.1	17.9	22.3	27.2	29.3
12	17.8	1.5	19.0	28.4	13.8	23.9	7.1	52.3
13	32.9	3.8	16.2	23.7	11.6	20.6	6.0	68.1
14	34.0	19.8	2.9	0.1	6.3	0.6	1.0	68.6
15	7.5	36.9	2.9	....	3.5	0.3	0.8	21.7
16	0.1	30.1	2.4	....	2.5	0.2	0.6	0.3
17	....	4.3	1.1	....	1.9	0.2	0.5	....
18	....	....	0.8	....	....	....	0.4	....
Total g	45.6	30.5	36.3	2.8	0.6	15.9	323.0[1]	....

[1] Arbitrary color units at 425 mμ.

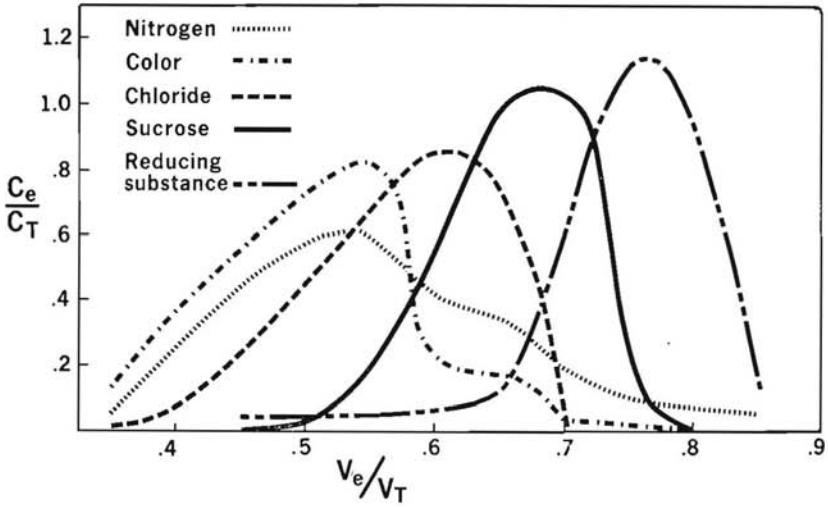

Figure 5.—Cane molasses purification using Dowex 50W (4% DVB, 50-100 mesh, K form) at 90°C. Load: 141 g 40 purity cane molasses in 270 ml solution.

early portions of the reducing sugar curve are not reducing sugars but higher molecular weight compounds or salts that exhibit reducing properties. Comparison of the color curves for the beet and cane molasses runs shows that both depart considerably from a smooth curve at fractions 12-14. This anomaly is due to some colored substance that is excluded less from the resin than the majority of colored compounds.

The difference in the nature of the nitrogen compounds present in beet molasses from those in cane molasses is shown by a comparison of the separation of beet and cane components on Dowex 50 W (4% DVB, 50-100 mesh, K form) at 90°C. Most of the cane molasses nitrogen compounds are eluted in the first half of the run, but most beet molasses nitrogen compounds are eluted in the later half. The late elution of beet molasses nitrogen compounds is primarily due to the presence of relatively larger amounts of amino acids and betaine. The separation of reducing sugars from other material is quite good. More than 70% of the reducing sugars can be obtained at 78 purity compared with an original 27 purity. More than half of the non-reducing fraction is sucrose so that the total sugar purity (no. 15-18) is 90.

Conclusions

Examination of the results of these experiments indicates that X-4 resin at 90°C gives the best purification. Under these conditions 50% of the sucrose in beet molasses was separated at 80 purity or higher. On a commercial scale these fractions could be returned to intermediate pans using liquors of this purity for crystallization and sucrose recovery. Fraction 16, 77 purity, containing 12% of the sugar could be returned to the low raw pans but fractions 12-13 containing 34% of the sugar are of such low purity that under present practice they should not be returned to the sugar end of the factory. Most of the sugar in these fractions may be recovered by using them to dilute fresh molasses for the next column load. The impurities returned to the sugar end would of course form some molasses and later be recycled through the column. Using ion exclusion it would not be necessary to obtain only highly purified fractions. High purity fractions would be returned to the sugar end of the factory for concentration and crystallization, fractions high in salts and low in sucrose would be discarded, and fractions intermediate in purity would be used to dilute fresh molasses and recycled on the column.

The results of these experiments show that static ion exclusion columns of Dowex 50 W (4% DVB, 50-100 mesh, K) can be used to recover sucrose from beet and cane molasses and invert from cane molasses.

Operation of the columns at 90°C gives the best overall separation of molasses constituents, the highest concentration of solids, and lowers the possibility of fermentation taking place during purification.

Acknowledgment

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Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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