DISTRIBUTION OF NON-SUGARS IN THE ARI COUPLED LOOP MOLASSES DESUGARIZATION SYSTEM

D. E. Rearick*, Cheri McKay and Alla Bagramyan
Amalgamated Research LLC, P.O. Box 228, Twin Falls, ID 83303

I. Introduction

In a conventional sugar beet molasses simulated moving bed (SMB) chromatographic desugarization system, removable non-sugars move ahead of sucrose during passage through a separation resin and are removed in a single raffinate fraction. Materials that, however, behave more like sucrose in interactions with the separation resin may be retarded and elute with sucrose in the product, or extract, stream. This class of materials generally includes lower molecular weight organic compounds that are less ionic in properties than, for example, inorganic salts. One group of compounds exhibiting this behavior are the nitrogen-containing components of sugar beet such as betaine and free amino acids.

In the ARi Coupled Loop chromatographic process, two separation loops are employed to separate two streams of non-sugars from sucrose.[1] The first loop is operated under conditions that increase the internal inventory of betaine and other less ionic components until sucrose is forced to move ahead in the separation profile. Sucrose is then removed from the leading edge of the profile in an Aupgrade@ stream, along with ionic materials that normally appear in the raffinate. The tailing fraction of more neutral (less ionic) substances is removed in a Abetaine@ fraction. The upgrade fraction containing most of the sucrose is then processed in a second loop, under conventional desugarization conditions, to produce a raffinate stream containing most non-sugars and an extact stream containing sucrose for recovery.

The removal of non-sugars in general during a conventional desugarization operation as well as the removal of amino acids in both kinds of separation systems have been discussed in previous papers.[2,3] This presentation will cover the removal of other non-sugars in the two non-sugar streams of a typical Coupled Loop system and will include additional data on amino acid elimination.

II. Results and Discussion

In this study, weekly factory composite samples of feed and all exiting streams (after concentration) from a normally operating factory Coupled Loop system were analyzed for sucrose, betaine, raffinose, common cations, inorganic anions, common organic acids, and amino acids. The system is generally operated to maximize crystallized sugar recovery rather than extract purity. Factory data for tons of material used or produced and refractometric dissolved solids were used in all material balance calculations, Elimination level for a particular non-sugar can be calculated in any of several ways including percentage of material entering that is eliminated or percentage of material exiting the separator that is eliminated in non-sugar streams. In general, elimination values given below were calculated as a percentage of the total leaving the separator; this avoids low elimination values for several materials that seem to be lost (possibly due to precipitation or equipment scaling) during separation or evaporation steps. Elimination values are dependent on the accuracy and precision of non-sugar analyses; substances present at low levels, like divalent cations and some of the amino acids, tend to give less reproducible or even obviously incorrect elimination values.

One question of interest in this kind of study is exactly how much of the total quantity of non-sugars present is being accounted for by all analyses. The following table gives, for each stream entering or leaving the system, total material accounted for, that is the sum of all analytical values, as a percentage of total non-sugars (100 - sugar).

Table 1. Total Material Accounted for by Analyses

Separator Stream	Total Material (%/NS)
Feed	63 - 65
Betaine fraction	75 - 76
Extract	67
Raffinate	58 - 61

Note that the percentage of total solids accounted for in all analyses is highest in the betaine fraction (which contains the highest proportion of betaine and amino acids) and lowest in feed and raffinate streams, which contain color components, high molecular weight compounds, and other unidentified materials..

During this study, sucrose was also determined on all samples, using gas chromatography. For comparison with non-sugar distribution, the percentage of sugar exiting the system as recoverable sugar in extract was 93 to 96%. Losses of sugar in the two non-sugar streams were 4 to 6% in the raffinate and 0.1 to 0.5% in the betaine stream.

Two of the major single non-sugar components of interest in Coupled Loop operation are betaine and raffinose which exhibit quite different separation characteristics. Betaine is quite efficiently removed from sugar and recovered as a byproduct in the Coupled Loop system. In this test the betaine fraction, which contained 60 - 65% betaine/DS, removed 75 to 88% of the total betaine exiting the system, depending on exact operating conditions. The extract stream still contained 3 to 10% of exiting betaine and the raffinate 8 to 13%. Elimination of betaine in the two non-sugar streams thus totaled about 88 to 96% of material exiting. Raffinose is a totally different story with one of the poorer eliminations of major non-sugars. The samples analyzed here showed 66 to 74% of exiting raffinose in the extract, 26 to 37% in the raffinate, and only 0.1 to 0.4% in the betaine stream. Elimination of raffinose is therefore only in the neighborhood of 30%. Distribution data for sucrose, betaine, and raffinose are given in Table 2.

Table 2. Sucrose, betaine, and raffinose distribution.

	Betaine Fraction (%/total out)	Extract (%/total out)	Raffinate (%/total out)	Elimination (%)
Sucrose	0.1 - 0.5	93 - 96	4 - 6	--------
Betaine	78 - 88	3 - 10	8 - 13	88 - 96
Raffinose	0.1 - 0.4	66 - 74	26 - 37	26 - 37

Due to juice softening, the only significant cations present in separator materials are sodium and potassium. Both are primarily removed in the raffinate stream at levels depending on exact operating conditions. The following table shows the distribution of monovalent cations based on total material out. Divalent cations are also present but at insignificant levels in the betaine stream and levels in the extract and raffinate too low to allow reliable elimination calculations.

Table 3. Monovalent cation distribution.

	Betaine Fraction (%/total out)	Extract (%/total out)	Raffinate (%/total out)	Elimination (%)
Sodium	1.9 - 2.6	23 - 28	69 -75	72 -77
Potassium	1.9 - 2.0	18 - 25	73 - 80	75 - 82

Inorganic anions are generally very efficiently removed in molasses desugarization although there does seem to be an exception. The following table shows distribution for the major anions, chloride, sulfate, phosphate, and nitrate. Of these, chloride, nitrate, and sulfate occur at the highest levels (0.5 to 1.0 %/RDS) in molasses with phosphate present at much lower levels due to its elimination in liming and carbonation. Note that chloride, phosphate, and sulfate elute primarily in the raffinate fraction and are eliminated reasonably well from the sugar stream. Nitrate is an exception, with 73 to 77 % still in the extract stream. Nitrate elimination this low has not been seen in previous data although nitrate elimination values were generally significantly lower than those for chloride or sulfate. It appears that nitrate ion may complex or associate with another species present in molasses to form a less ionic component that fails to be excluded from the resin. Phosphate also shows some unusual behavior in that, although it appears mostly in the raffinate, total phosphate coming out of the system is consistently only 45 to 50 % of the level entering with molasses. Since low levels of calcium are present in the molasses, some type of scaling or precipitation behavior may be responsible for the lower detected levels of exiting phosphate.

Table 4. Inorganic Anion Distribution.

	Betaine Fraction (%/total out)	Extract (%/total out)	Raffinate (%/total out)	Elimination (%)
Chloride	1.4 - 2.4	14 - 21	77 - 83	79 - 85
Phosphate	8.8 - 9.4	13 - 18	73 - 77	82 - 86
Nitrate	0.5 - 0.7	73 - 77	22 - 26	23 - 27
Sulfate	2.1 - 2.8	9 - 15	83 - 88	85 - 91

Elimination data for organic acid anions is given in Table 5. In molasses feed to the separator, lactate is present at the highest levels, 2.5 to 3.5 %/RDS in these tests due to both its occurrence and formation by invert destruction. The other organic acid anions are generally present at levels of 0.5 to 1.0 %/RDS with the exception of oxalate which is generally present at less than 0.1 %/RDS due to prior precipitation as the very insoluble calcium salt. Organic acid anion levels, particularly those for oxalate, are low enough that elimination results are somewhat variable. Data for individual acid anions is given in Table 5. Other than oxalate, which is at too low a level to measure very reliably, most of the simple organic acids are eliminated at reasonably high levels; PCA, or pyrrolidone-5-carboxylate, apparently has less strongly ionic character and is retarded somewhat by the resin causing significant elution in the extract.

Table 5. Organic acid anion distribution.

	Betaine Fraction (%/total out)	Extract (%/total out)	Raffinate (%/total out)	Elimination (%)
Oxalate	4.7 - 21.0	30 - 44	49 - 64	57 - 70
Citrate	4.0 - 5.1	11 - 16	80 - 84	84 - 89
Malate	3.0 - 3.7	19 - 22	75 - 78	78 - 82
Lactate	1.9 - 2.4	13 - 19	79 - 85	81 - 87
Formate	2.0 - 2.5	16 - 23	75 - 81	77 - 83
Acetate	2.4 - 3.4	6 - 10	87 - 91	88 - 94
Pyrrolidone-5-carboxylate (PCA)	1.6 - 2.2	38 - 45	52 - 60	54 - 62

Data on free amino acid elimination was also developed in this study, although results on the Coupled Loop have been reported previously. Table 6 gives values for elimination on amino acids present at high enough levels to give somewhat reliable results. Most of the amino acids, however, occur at levels of 0.05 to 0.2 %/DS in molasses so some elimination data is not consistent. The amino acid with the highest level in most samples, γ-amino butyric acid or GABA, occurs at levels only as high as 0.3 g/100 DS. Unlike the other groups of non-sugars, amino acids show significant elimination in the betaine fraction with values of up to 40 % for alanine, leucine, and proline. Betaine fraction samples may contain amino acid levels of over 1.0 %/DS for several of those more highly eliminated in that fraction. As is usually observed, glutamic acid and aspartic acids are eliminated mostly in the raffinate and serine is not significantly eliminated in either non-sugar fraction.

Table 6. Free amino acid distribution.

	Betaine Fraction (%/total out)	Extract (%/total out)	Raffinate (%/total out)	Elimination (%)
Aspartic Acid	3.4	39 - 44	53 - 58	56 - 61
Glutamic Acid	5.3	0	95	100
Serine	3.6 - 4.0	80 - 81	16	20
Glycine	16	49 - 53	31 - 35	47 - 51
γ-amino butyric acid (GABA)	19 - 20	43 - 46	35 - 37	54 - 57
Alanine	36 - 39	35 - 39	26	62 - 65
Proline	16 - 36	24 - 63	21 - 40	37 - 76
Tyrosine	14	51 - 56	30 - 36	44 - 49
Isoleucine	15 - 16	56 - 59	26 - 28	41 - 44
Leucine	40	27 - 32	28 - 32	68 - 72

III. Experimental

Cations were determined by atomic absorption spectrophotometry. Organic acids and inorganic anions were determined by ion chromatography with conductivity detection. Amino acids were analyzed by conversion to phenylthiocarbamyl derivatives by reaction with phenylisothiocyanate. Derivatives were analyzed by high performance liquid chromatography (HPLC) using the Waters Pico Tag™ method (trimethylamine/sodium acetate/60% acetonitrile gradient). Sucrose was determined by gas chromatography after conversion to a trimethylsilyl derivative. Betaine was determined by HPLC on a sodium-form cation exchange column with refractive index detection.

IV. Acknowledgments

The authors would like to thank Diane Patterson for the gas chromatographic determination of sucrose in all samples.

V. References

1, Kearney, M., V. Kochergin, K. Petersen, M. Mumm, L. Velasquez, and W. Jacob, Proceedings from the 30th Biennial Meeting, American Society of Sugar Beet Technologists, Orlando, FL, Feb. 10-13, 1999, Operations, p. 187-189.

2. Rearick, D.E., Proceedings from the 28th Biennial Meeting, American Society of Sugar Beet Technologists, New Orleans, LA, March 8-11, 1995, Operations, p. 25-29.

3. Rearick, D.E. and C. McKay, Proceedings from the 34th Biennial Meeting, American Society of Sugar Beet Technologists, Salt Lake City, UT, Feb. 28-March 3, 2007, Operations, p. 82-87