Sucrose Solubility Coefficients for Extract Derived molasses and Target Molasses Purities

Terry McGillivray, James Heggeness, David Groom American Crystal Sugar Company, 1700 North 11th Street, Moorhead, MN 56560

Introduction

During the last ten plus years, American Crystal Sugar has been recovering sugar from molasses with chromatographic separation systems. Chromatographic separators used at American Crystal Sugar Company include a simulated moving bed system and a coupled loop system, both developed by Amalgamated Research Incorporated. Both systems have been described in the literature. (1)

Regardless of the type of system used, the extract or sugar rich fraction has to be processed to produce crystalline sucrose. Different schemes can be devised for processing this material: co-process with juice from the sugar beet campaign or process in a separate juice campaign. In either case, the question commonly asked is "what is the amount of recoverable sugar per ton of molasses processed." The answer to that question may be confounded by processing problems unrelated to the ability to fully exhaust the molasses of sugar.

Molasses derived from extract will likely be different in composition from regular molasses due to the separation of chemical species during the chromatographic process. In addition to extract molasses being different from regular molasses, molasses from the two types of separators will be different in composition. For example, Rearick indicates that both glutamic and aspartic acids are present in much lower levels in the extract than in the feed molasses. Serine, tyrosine, and isoleucine are present at much higher levels in the extract than in the molasses. In beet molasses, typically 9% of the non-sugars are amino acids; in extract derived molasses, 31% of the non-sugars are amino acids.(2)

Work at American Crystal Sugar has shown that the two types of chromatographic separators can produce extract of significantly different composition with respect to purity, raffinose content, and betaine. There may be other compositional difference, but we have not analyzed samples specifically to examine those differences. Data in the table below show the compositional differences between extract produced from a SMB system and coupled loop type system.

Feed Molasses

Campaign 2001-02	East Grand Forks (SMB)	Hillsboro (coupled loop)
RDS	63.310	59.590
Raffinose	0.885	0.972
Betaine (% on RDS)	5.210	4.740
Purity	61.360	61.560

Extract

Campaign 2001-02	East Grand Forks (SMB)	Hillsboro (coupled loop)
RDS	71.31	69.95
Raffinose	0.38	0.60
Betaine (% on RDS)	2.57	0.94
Purity	89.1	92.59
Color	9434	10486

Note that the coupled loop system has been run in a manner that reduces the final concentration of betaine in the extract and hence in the molasses. The coupled loop system is less effective in removing raffinose than the SMB system.

Given the differential partition of different compounds between raffinate and extract, one might expect that molasses produced from extract would have a composition different from molasses produced from beet by conventional processing. Whether or not these compositional differences make any difference in the sucrose to non-sucrose ratio in the final molasses is a question of economic importance. The question is whether non-sucrose compounds present in the syrup are driving molasses purity in any manner.

Figure 1 shows the betaine concentration of feed molasses to the EGF SMB and the concentration of betaine in the extract produced. A concentration of 2.57 % on RDS in the concentrated extract would produce a molasses containing 9.1% on RDS. Molasses from the Red River Valley of Minnesota-North Dakota typically contains ~4-5 % betaine on RDS.

Figure 1: EGF % Betaine on RDS 2001-2002

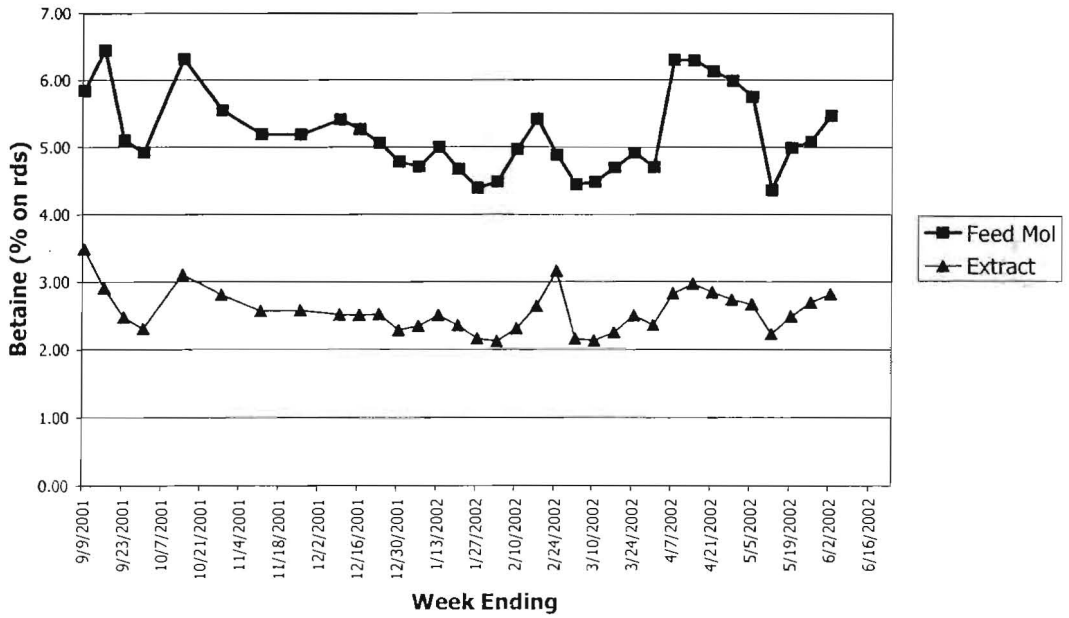
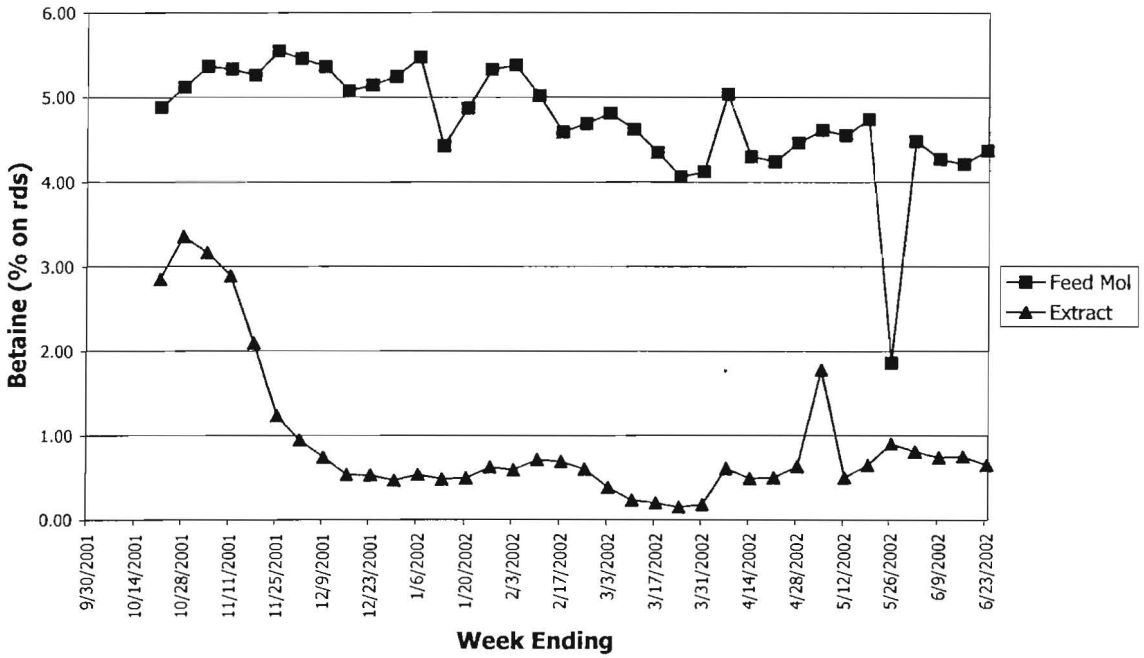


Figure 2 shows the concentration of betaine in the feed to the coupled loop system compared to betaine concentration in the concentrated extract. Compared to the EGF separator, the Hillsboro separator is more efficient in removing betaine from the molasses. Betaine concentrations in molasses produced from Hillsboro extract would be expected to be lower than concentrations in the feed molasses. The values for Hillsboro are 4.74 % on RDS in the feed molasses compared to 3.3 % on RDS in molasses produced from Hillsboro extract.

Figure 2: HLB% Betaine on RDS 2001-2002



Raffinose is not as effectively separated from the Hillsboro separator as at EGF. As a result, molasses produced from extract at Hillsboro is expected to have more elevated raffinose levels than molasses at EGF. EGF is expected to have ~3.6% raffinose in molasses from extract compared to current campaign YTD concentration of 2.02%. Hillsboro will have raffinose in extract molasses at 4.4% compared to YTD molasses concentration of 2.2%.

Rearick's work shows, and is verified by our experience at ACS that high levels of tyrosine can result in precipitation in the stored syrups. Determination of sucrose solubility coefficients has been made more difficult due to the precipitation of organic materials in the molasses in particular, making separation of the syrup from the crystals difficult. (2)

Background

The method used for the evaluation of molasses purity at a given temperature is the Polish Test. The method provides results that are used as the basis of calculations including: degree of saturation, target molasses purities at different temperatures and supersaturations, and financial impact of changing process parameters. Wicklund as reported in Genotelle found that the saturation coefficient for molasses can be expressed by the equation.(3)

$$K_{SAT} = \frac{NS}{W} \times a + b$$

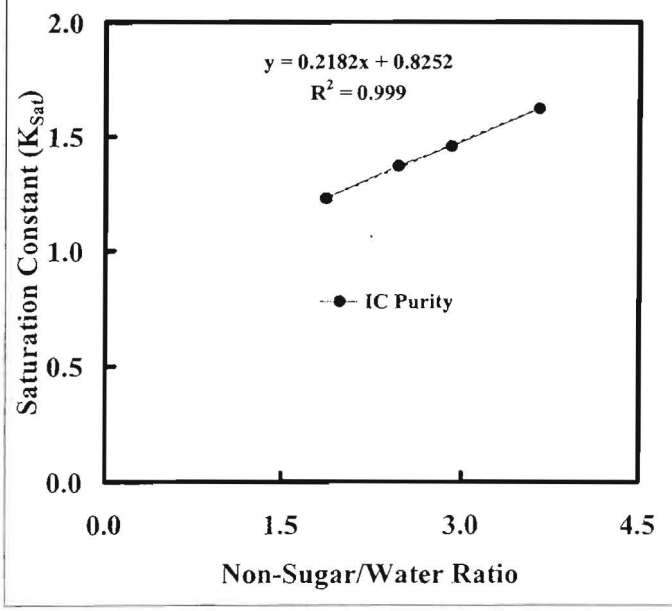
This equation is generally valid for NS/W ratios greater than 1.5. An equation containing an exponential term was found by Vavrinecz that covers the lower NS/W region. The constants of the equation depend only on the nonsucroses and are independent of the relative amounts. For the work reported here, the linear equation has been used. (4)

$$K_{SAT} = \frac{NS}{W} \times a + b + (1-b) \times e^{-c \times NS/W}$$

Method and Procedures

The method used for determination of equilibrium molasses coefficients is the procedure referred to as the Polish Test. The procedure is based on the work of Wagnerowski with modifications reported by McGinnis, Smith, Vavrinecz, and Schoenrock.(5,6,7,8)

Figure 3: Sucrose Solubility Coefficients: CRK Molasses (4/1/01). Based on IC Purity.



Sucrose solubility coefficients were completed at 80 °C using NS/W ratio in the range of 1.5-4.0. Samples were analyzed for purity by pol and by ion chromatography. Samples were concentrated under vacuum to attain the higher NS/W ratios. Course sugar was added to each trial to ensure the sample was saturated. Samples were mixed for 24 hours prior to analysis.

Results and Discussion

A typical plot showing the saturation coefficient and the NS/W ratio is shown in figure 3.

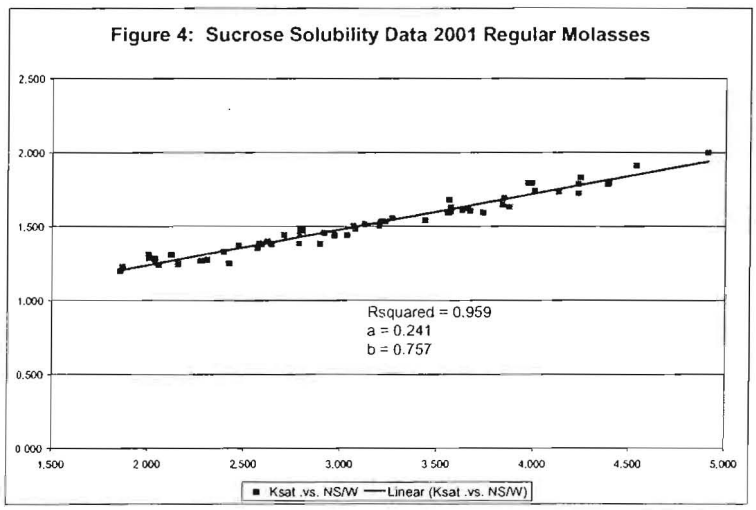
Sucrose solubility coefficients have been determined since

1995 with emphasis on normal beet molasses prior to 1999. Due to problems with storage and processing of extract during the last campaign (2001-02), additional time has been spent on evaluating whether the higher than normal molasses purities produced at the two extract producing facilities are due to in part to melassigenic properties of non-sucroses in the extract or due to other processing issues.

Sucrose solubility values measured during the last two campaigns on molasses made from normal show some variation in value, but average values of the coefficients are close enough between campaigns to be used for prediction of target molasses purities.

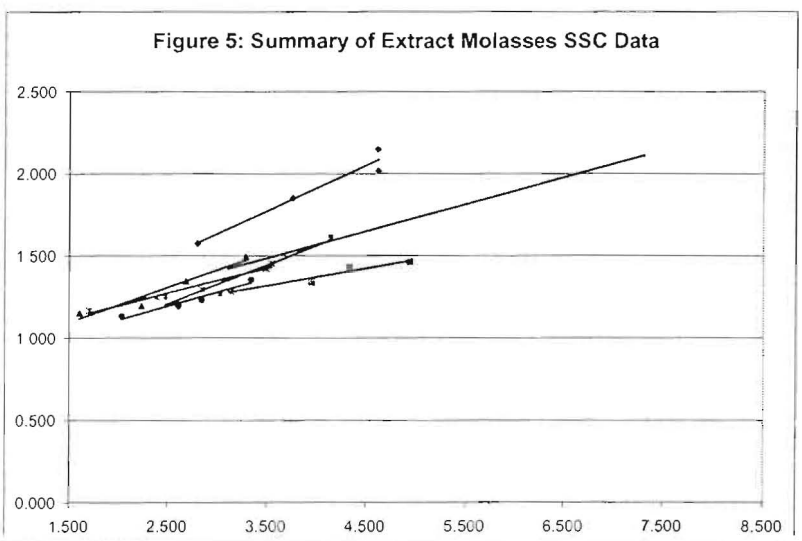
Sucrose solubility coefficients

Year	a	b
2001-02	0.253	0.747
2002-03	0.259	0.689



When the data for the 2001 campaign are examined, one can see that there is a reasonable regression fit between the saturation data and the NS/W ratio. It is reasonable to suggest that the coefficients do not vary significantly during the course of the year.

By contrast, plots of data from determinations of sucrose solubility data on extract derived molasses show considerably greater variation. The reasons for the variation may be partially due to procedure, sample purging problems due to precipitated organics such as tyrosine in the molasses, and possible changes in the molasses composition.



Although there appears to be more noise in the data from extract molasses samples, the grouping of the data suggests general agreement within the data. When the equilibrium molasses purities are calculated

using the individual coefficients, the predicted purities are generally not higher than those predicted for regular molasses. A set of predicted purities are shown if the next table.

Year	Sample	a	b	Predicted Mol Purity
2002-03	EGF Extract Molasses	0.245	0.799	58.68
2002-03	HLB Extract Molasses	0.23	0.696	56.27
2002	EGF Extract Molasses	0.277	0.64	57.98
Sum 2001	Extract Molasses	0.215	0.769	56.61
2001-02	All beet molasses samples	0.253	0.747	58.33
2002-03	All beet molasses samples	0.259	0.689	57.77
1999-Spr 01	All beet molasses samples	0.243	0.74	57.69

Data from the table above indicate that predicted purities for extract molasses are not greater than for molasses solely from beet. (All results are based on 55 C° final temperature, SS of 1.1 and NS/W ratio of 3.5.)

Sample	a	b	Predicted Mol Purity
PP extract molasses from HLB extract	0.315	0.686	60.52
PP extract molasses from HLB extract	0.229	0.746	57.00
PP extract molasses from HLB extract	0.164	0.912	56.03
HLB production extract molasses	0.237	0.616	55.32
HLB production extract molasses	0.159	0.859	54.84
HLB production extract molasses	0.229	0.775	57.47
HLB COWS Week 30-35 extract molasses	0.280	0.579	57.22
PP extract molasses from HLB extract	0.196	0.740	54.99
PP extract molasses from HLB extract	0.155	0.842	54.29
EGF Tank #1 extract molasses	0.310	0.647	59.78

The table above shows target molasses purities predicted for molasses produced from a variety of extract sources.

Conclusions

The target molasses purities from beet during the last two campaigns (2000-2002) averaged 58.05; all extract derived target molasses purities with two exceptions are less than beet derived molasses purities. Given those data, it is difficult to argue that high molasses purities during extract processing are due to the non-sucrose composition of the extract. The data suggest that extract derived molasses should have a purity equal to or lower than that of molasses derived solely form beet.

It is worth noting that Vaccari's work on cooling crystallization of East Grand Forks factory extract resulted in a final molasses purity of 42.1% compared to a final molasses purity of 51.8% from the cooling crystallization of raw juice that had an initial purity of 87.6%. Final molasses purity attainable from extract has been shown to be as low as or lower than molasses from regular factory syrups.(9,10)

Difficulties in obtaining low molasses purities are not due to non-sucrose components in the extract, but more likely due to purity and color profiles across the pan floor. The colors of extract are generally two to three times higher than those of thick juice. The coupled loop system is capable of producing extract with purities greater than 95%, which can result in poor sugar recovery in a traditional three boiling system. Both color and purity profiles can be major issues in the processing of extract.

In addition, the purity profile on extract from a coupled loop system may be skewed due to the relatively poor ability of that type system to separate raffinose, resulting in a higher apparent purity extract than would be measured by HPLC or GC. This problem would be increased accentuated during poor storage years.

Betaine, raffinose, and other non-sucrose compounds present in extract may change the kinetics of approaching the equilibrium molasses purity. Raffinose is known to affect the crystallization rate and betaine may increase viscosity in the low raw crystallization. Both of these effects would likely result in higher molasses purities due to kinetic reasons. Using a different crystallization tactic may allow the factory to achieve the target molasses purities. Our results indicate that the equilibrium extract molasses purity should be as low as that achieved with molasses produced from beet.

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