Results of Long Term Storage of Molasses Desugarization Extract

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Introduction:

American Crystal Sugar Company (ACSC) has two molasses desugarization (MDS) facilities. One facility is at East Grand Forks (EGF), Minnesota, commissioned in the fall of 1993. The EGF facility is a "standard" simulated moving bed (SMB) separator. In January of 2000 ACSC commissioned a second MDS facility at the Hillsboro (HLB), North Dakota, factory location. The separator utilizes displacement chromatography along with simulated moving bed technology (1). It has been the practice of ACSC to store the extract juice from each desugarization facility for up to 10 months, and then process the stored extract juice after completion of the beet processing campaign. At Hillsboro we will also co-process (blend extract with beet thick juice) during part of the beet campaign. This paper will review past challenges and the resolution of problems. Specifically, this paper will focus on the production and storage of extract at Hillsboro's MDS facility.

The Hillsboro separator was brought on line in January of 2000. By July of 2000, the separator attained expected performance. Overall color removal on a mass basis was 85 to 88 percent, resulting in extract color that was 16 to 20 percent of feed molasses color. Purity of the extract was 93 to 94 while sucrose recovery through the separator was above 90 percent.

The first extract from Hillsboro's MDS plant was processed starting in June 2000. Referring to Table 1 below, note the change in extract that occurred from the time it was sent to storage until it was processed. There was a large increase in color, a drop in pH, an increase in invert, and a slight decrease in purity. Raffinose concentration in the feed was up to 3.0% on solids and up to 1.4% DS in extract.

Table 1

2000 EXTRACT CAMPAIGN RESULTS	
EXTRACT SENT TO STORAGE	EXTRACT AS PROCESSED
88.5 to 91.5 IC purity*	88.0 to 91.0 IC purity*
10,000-12,000 color	10,000 to 30,000 color
9.0 to 9.3 pH	7.5 to 9.0 pH
Invert 0.3 % on DS	Invert up to 2.0% on DS

*IC purity refers to purity determined by ion chromatography.

When the extract was brought into the sugar end for processing, numerous problems were encountered that lead to poor recovery. Recovery was 5.3 cwt per ton standard molasses versus the expected 7.6 cwt per ton.

Storage parameters for Hillsboro extract had been set initially to those of EGF product; RDS of 68.5, temperature below 25°C, pH target of nine. After the first extract campaign, changes were

made to the MDS operation in August 2000 to improve the stability of extract in storage. Tighter filter media was used for the molasses feed filtration. Temperature of the extract to storage was reduced to a target temperature of 15°C. The minimum pH of extract sent to storage was 9.5; adjusted with caustic as required. RDS of the extract was 69 or higher.

Pilot plant work done on the extract completed in months prior to the second extract campaign produced good recovery of sugar. However, during the second extract processing campaign that started May 2001, many of the same problems plagued the sugar end that had been experienced in the prior campaign. Recovery through the sugar end was low at 6.1 cwt/ton standard molasses.

Table 2

2001 EXTRACT CAMPAIGN RESULTS	
EXTRACT SENT TO STORAGE	EXTRACT AS PROCESSED
90.0 to 94.0 IC purity*	89.5 to 93.5 IC purity*
8000-9000 color	8000 to 20,000 color
9.4 to 9.6 pH	9.1 pH
Invert 0.1 % on DS	Invert up to 2.9% on DS (1 tank)

Further investigation into the storage and production of extract was initiated. Extract quality indicators such as lactic acid, pH, apparent purity, RDS, and microbial counts standards used for the EGF MDS extract, seemed inadequate.

In reviewing data, it was found that invert levels in the extract had increased in storage. Invert levels were found to be higher in the Hillsboro extract entering the factory than when the extract went into storage. High extract color was a major issue in processing the extract. Biocides such as formaldehyde, hops beta acids, and sulfur dioxide had no impact on stored extract stability. Investigation into the extract processing/storage issue proceeded along several paths.

In order to evaluate conditions required to store Hillsboro extract, a comprehensive study was conducted to look at the impact of various variables on the stability of the Hillsboro extract. An accelerated storage study was completed using coupled loop extract from Hillsboro and extract from our East Grand Forks facility. Samples were incubated at 50°C to accelerate reaction rates. Hillsboro extract was observed to decrease in purity and pH with an increase in color and invert with little change in microbial counts or lactic acid. Similar results had been observed in the tanks but occurred over a longer time frame.

Ion chromatographic data indicated that concentration of invert was correlated with the degree of juice degradation. Increased concentration of invert in the stored extract was not correlated with increased microbial counts, lactic acid or other signs of microbial infection (3,5). Based on the prior mentioned observations, we investigated other causes for juice degradation including chemical and enzymatic activity. Sucrose inversion in the Hillsboro extract was found in the pH range of 8 to 10.0, negligible at pH 10.5, no activity noted at pH 11. High pH and pasteurization were found to mitigate degradation.

When the HLB extract was filtered through a 0.22 micron filter, added to a sucrose solution and heated to 75°C, invert level increased and purity dropped more rapidly than the control sample (sucrose only). Samples that were heated to 100°C were stable without regard to filtration treatment. The results pointed to the presence of a component that was not removed through 0.22 micron filtration. We hypothesized that an enzyme was present in the Hillsboro extract that was de-activated at temperatures above 75°C (5).

Recommendations to monitor invert in production and storage extract gave us sufficient early warning to process a tank in time to avoid significant loss. Even though microbial counts and lactic acid in the stored extract didn't seem high enough to indicate problems, tracking invert allowed us to indirectly monitor enzymatic (invertase) activity. Upon further investigation, high nitrite levels were found in the extract evaporator loop, indicating problems with the evaporators (Table 3). In our studies, elevated nitrite was associated with unstable extract. Elevated micro counts were found in the extract evaporator loop. Interestingly, microbial counts did not always correlate to high nitrite levels (4). It was suggested that the temps (50-55°C) in the extract evaporators were ideal for certain microbes to proliferate. A recommendation was made to raise the temperature in the extract evaporator loop to a minimum of 77°C. In addition, the pH of the extract prior to evaporators was raised to 10.5.

Table 3

NITRITE SURVEY				
SAMPLE	TEMP (C)	PH	RDS	NITRITE (PM)
Upgrade Evaporator	82	9.0	69.7	0
Extract Trains	84	9.6	27.0	0
Extract Evaporator Feed	81	9.6	20.8	2
Extract Evaporator out	56	9.6	69.4	800
Extract Product Tank	57	10.4	71.4	800
Extract to Storage	13	10.3	70.4	800
Hot Water Tank	72	9.8	0	0

Materials and Methods:

Sample collection: Samples were collected from various points in the MDS processing facility, extract storage tanks, and sugar end stations. Much of the data used came from samples collected by the factory staff for routine control and accounting analyses. Equal aliquots of each sample collected were placed into a container; the container kept in the freezer between sampling.

Samples for accelerated storage tests were collected using appropriate aseptic method and placed in sterile containers. All subsequent handling of accelerated storage samples was accomplished using sterile techniques. Accelerated storage test samples were placed in an incubator and kept at 50°C for the duration of the test period. Sub samples were taken periodically from the accelerated storage test containers via sterile pipette for analytical and microbial analysis.

Analytical methods, chemical analysis: Wet chemical analysis was completed using standard ICUMSA methods. Determination of pH was done by using a Ross combination electrode and an Orion pH meter. Apparent purity was determined on a Rudolph AutoPol 880 using 880 nm wavelength and a 10 cm cell. RDS was determined on a Bausch and Lomb refractometer. Color

was determined by measuring absorbance on a Milton Roy Spectronic 21D using a 1 cm cell. Samples were adjusted to pH 7 before absorbance was read. Water activity was measured with an Aqualab CX2; 0.78 N NaCl was used as a calibration standard. Invert (glucose and fructose) and sucrose concentrations were determined on a Dionex DX 500 Ion Chromatograph (IC) unit, using a Carbopac PA1 column an ED 40 detector in the PAD mode. The system was operated in isocratic mode at 22°C. Eluent was 200 millimolar sodium hydroxide kept under pressurized helium. Acetic, butyric, formic, lactic, and propionic acids were determined on Waters 500 series HPLCs using refractive index detection in isocratic mode. Eluent for the HPLC was a 5 millimolar sulfuric acid mobile phase; a BioRad Aminex HPX-87H column was used at 35°C. Betaine was determined with the Waters HPLC using a Bio-Rad Aminex HPX-87N column, eluent at 0.6 ml/minute 10 millimolar sodium sulfate and refract index detector. Nitrite concentration was estimated by using EM Quant test strips, samples were diluted with de-ionized water before reading.

Microbial analysis included: Mesophilic, thermophilic, regular and osmophilic yeast and mold counts. In addition, flat sours, total thermophilic spore, along with thermophilic anaerobes producing H_2S, and thermophilic anaerobes not producing H_2S were counted. The methods used are described in detail by Samaraweera et al. (4).

Accelerated Laboratory Storage Testing:

Accelerated storage studies were started in July 2001 and continued in various forms until December 2002. Most of the studies ran from 6 to 10 weeks. All accelerated storage trials (AST) involved collecting extract from tanks or production extract to tanks and placing in sterile HDPP 1 or 3 liter containers. Samples were then incubated at 50°C. Aliquots were drawn for chemical analysis at regular intervals. Aliquots were also drawn from AST samples on selected trials and microbial analysis completed. Details of the microbial results are addressed by Samaraweera et al. (4). Method details of various trials conducted were discussed in an earlier paper by the authors (5).

Results:

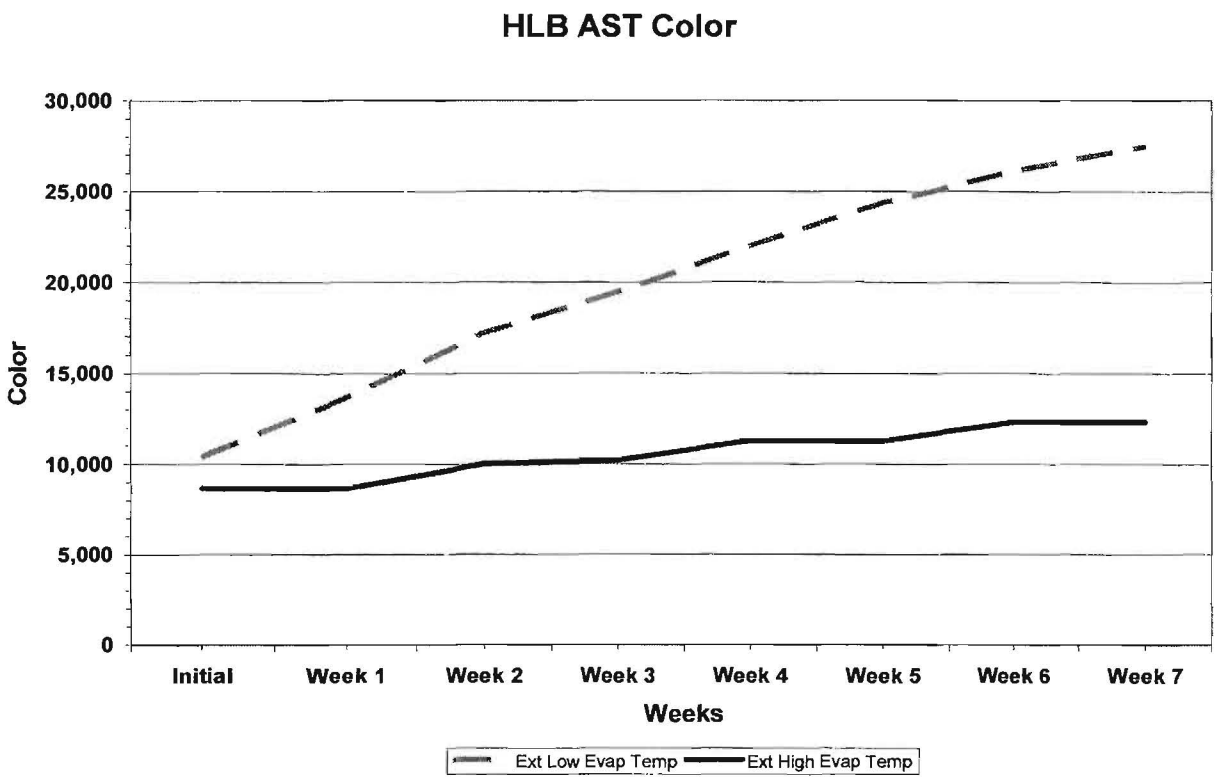
To confirm that changes made to the MDS operation improved stability of extract in storage, additional accelerated storage tests (AST) were conducted on the extract produced. As was outlined in a previous paper by Groom, et al. aliquots were pulled from the AST samples on a weekly basis (5). Samples were analyzed for invert, purity, color, nitrite, pH, and organic acids. The next four graphs display differences found between samples that had been placed in accelerated storage before and after changes were made to the MDS operation (elevating extract evaporator loop temperatures). The broken line is from data obtained from AST treatment of extract that had been produced when storage problems were encountered. This extract was produced when the extract evaporator loop was operated at 52-55°C. Extract was produced in August 2001. The solid line is data obtained from the AST treatment of extract that had been produced when the extract evaporator station temperatures were kept above 77°C. The later extract was produced August 2002.

Follow up microbial and nitrite data indicated a decrease in microbial activity in the extract prior to storage. Nitrite concentration in the extract sent to storage was less than 4 ppm, usually less

than 1 ppm. With increased temperature in all loops, we have not observed sliming of the water check filters. This action has resulted in a further reduction of the microbial load to the trains.

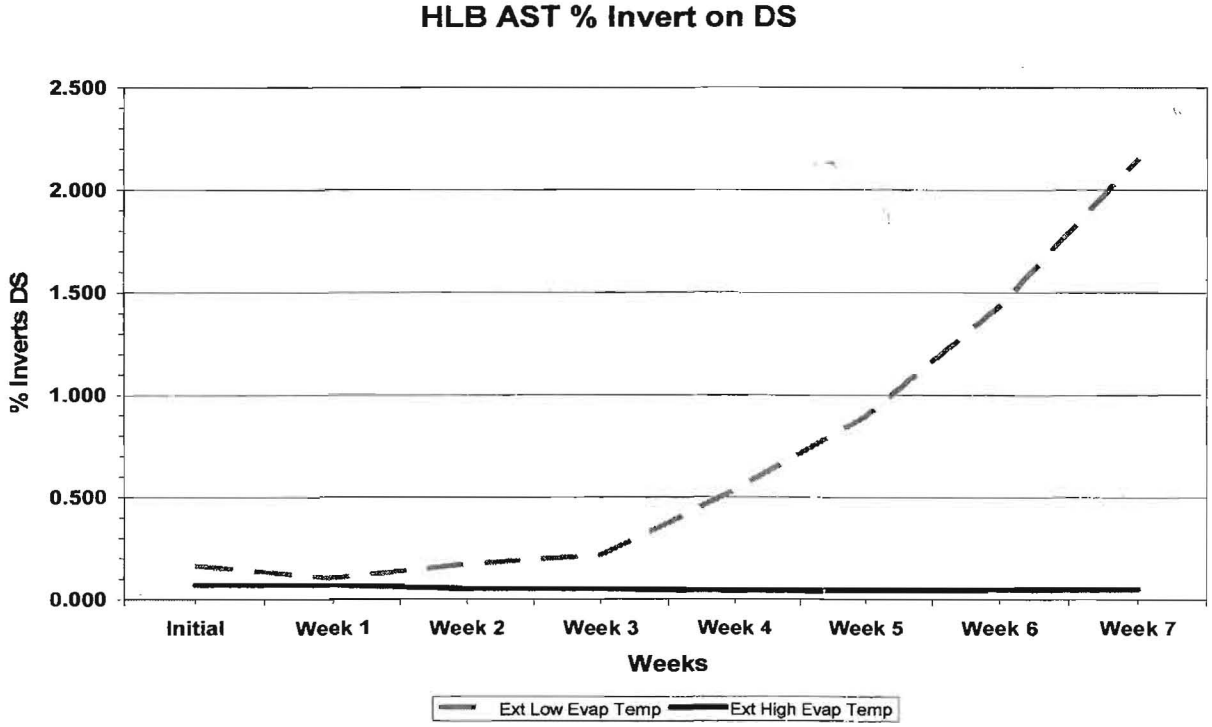
Figure 1 below illustrates the difference in color stability of extract produced in August 2001 when the extract evaporator station was running below 55°C and August 2002 when the temperature was raised to a minimum of 77°C. The graph represents data obtained from AST samples over a 7 week period. Note that color increased 165% for the low evaporator temperature sample in contrast to a 42% increase for extract produced at a higher temperature.

Figure 1



In Figure 2, the concentration of invert in the AST samples is shown. Over the 7 week trial, invert in the extract produced at lower evaporator temperature increased 1232%. In contrast a slight decrease in invert was observed in the sample produced with higher evaporator temperatures.

Figure 2



Referring to Figure 3 below, note that pH was more stable in the high evap temp extract. In contrast, the pH dropped 22% in the extract produced at lower evaporator temperature.

Figure 3

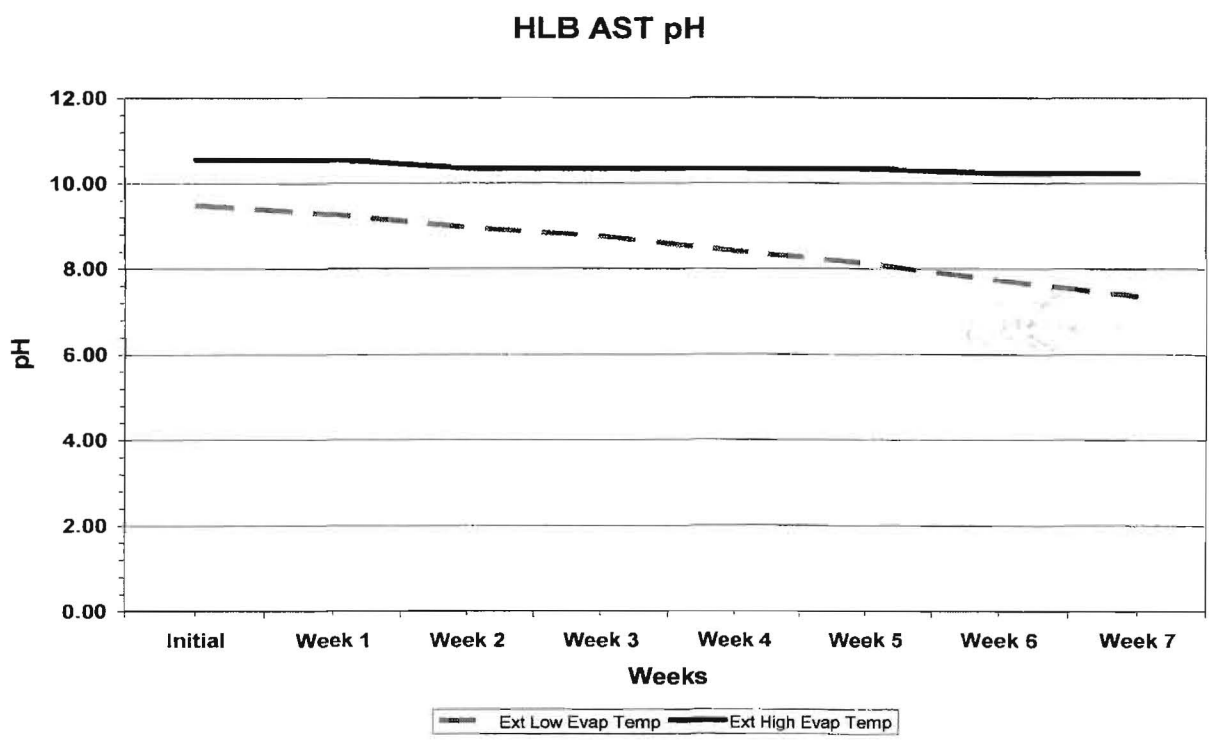


Figure 4 illustrates how extract purity was more stable when higher evaporator temperatures were used in production. Extract produced August 2001 (at lower temps) decreased in purity by 4 points. While initial extract purity values were different, work conducted determined that initial purity in of itself had little influence on stability of extract in storage within the typical operating range.

Figure 4

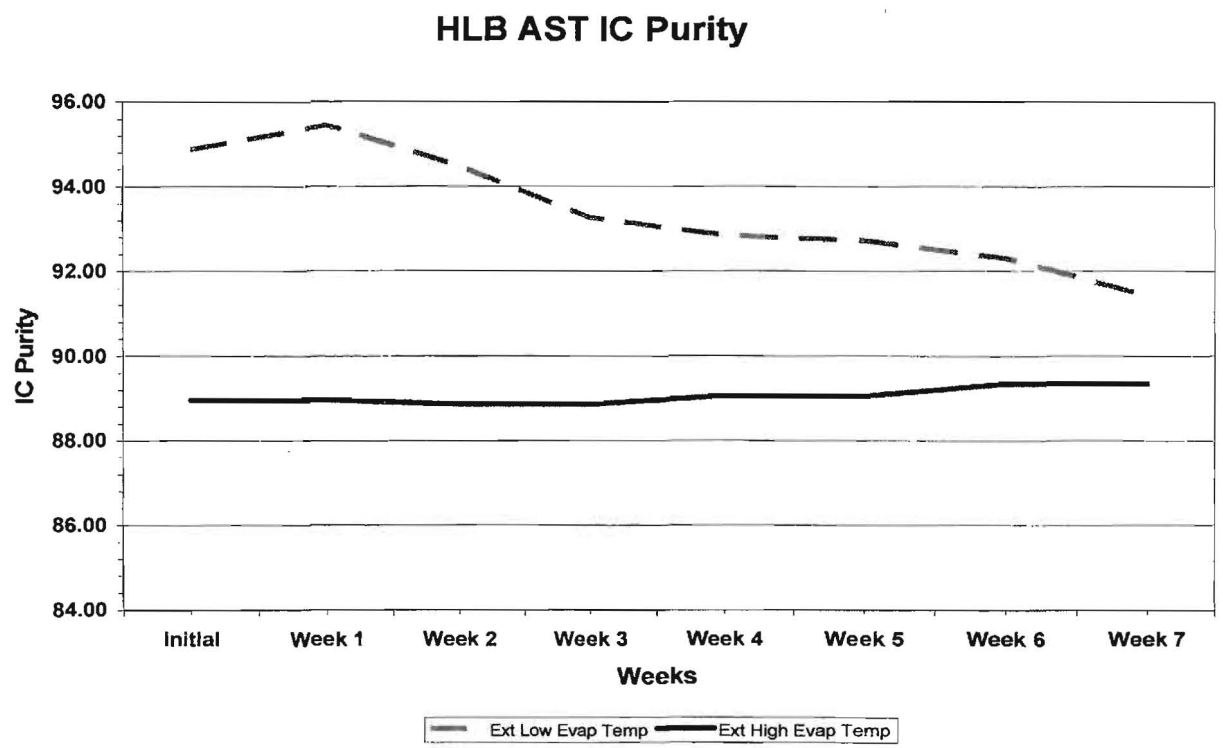


Table 4

AST DATA FOR EXTRACT PRODUCED AT HIGH AND LOW EVAPORATOR TEMPERATURES				
	COLOR	INVERT % DS	pH	IC PURITY
Low temp initial	10380	0.165	9.5	94.9
Low temp final	27480	2.155	7.4	91.4
High temp initial	8660	0.071	10.6	89.0
High temp final	12330	0.049	10.2	89.3

Factory operating data confirmed what was observed in the AST work. Extract sent to storage after the operating temperatures were increased in the MDS facility stored well and processed better. In Table 5 below, note that the extract as processed changed little in storage. In contrast to the data shown earlier in Tables 1and 2 invert critical values such as purity, pH, invert, and color were relatively unchanged. The extract processed had been in storage from 4 to 10 months.

Table 5

2003 EXTRACT CAMPAIGN RESULTS	
EXTRACT SENT TO STORAGE	EXTRACT AS PROCESSED
90.0 to 94.0 IC purity*	90.0 to 94.0 IC purity*
8000-9000 color	9000 to 12,000 color
10.5 pH	10.4 pH
Nitrites < 2 ppm	Nitrites < 4 ppm
Invert < 0.2 % on DS	Invert < 0.2 % on DS

Discussion:
The major issues regarding extract were increased color in storage, high color in sugar end processing, low buffering capacity, decreased purity in storage, and increased invert levels.

Early in the campaign 2001 recommendations were made to keep RDS above 69.5, the pH at 9.5, and temp to storage less than 20°C. Sargent indicated that stability was noticeably improved if juice was stored at 10°C (3, 7). With improved cooling equipment we were able to target and hold 15°C to storage. To prevent potential microbial loading into the system, finer filter media was used for filtering the feed molasses. Recommendations were considered the usual target values for juice storage in the sugar industry. While these measures may have helped stabilize the extract somewhat, they were insufficient to maintain desired extract quality in storage.

Based on initial AST studies, a recommendation was made to raise the pH of the extract sent to storage. Raising the pH to 10.5 suppressed enzymatic and microbial activity. While the course of action did not address the root cause, the juice was more stable in storage. Invert levels were held in check with the high pH treatment.

The extract degradation reactions can be classified into two major types: the first set involves destruction of sucrose and production of invert sugar, due to the presence of invertase produced by microbes; the second set involves increased color formation due to an increased invert level (8, 9). Raising extract pH to 11 with caustic or heating the extract to 100°C stopped invert production in lab studies. A relatively modest increase in invert can lead to very high color in the extract and cause difficult processing in the sugar end. In solutions (particularly those with low buffer capacity) invert reacts under alkaline pH conditions to form color and various acids (9, 10). This reaction can occur in the absence of microbes. The color formation reaction was observed in sugar end processing in Hillsboro and was reproduced in controlled lab studies at Tech Services. Color in extract is different than color found in beet thick juice (11). Any additional color loading in the sugar end makes it difficult to make white sugar that meets color specifications.

Production of invert is typically due to microbial activity; microbes need to be present at some point in the process to create the invertase and subsequent invert formation. Loss of sucrose in storage was caused by microbial contamination in processing and storage with subsequent enzymatic activity resulting in increased invert production. The traditional chemical markers were not good early indicators of a problem in the extract. Lactic acid levels (total and L form) did not change significantly while the extract deteriorated as determined by an increase in invert.

Our tests indicated that enough invertase was present to degrade extract juice with little detectable microbial contamination. Based on our studies, we believe microbial contamination in processing and/or storage resulted in invertase activity that subsequently resulted in increased invert production.

One potential source of invertase may have been microbial activity in the HLB MDS evaporator train loop. While that prior hypothesis was not directly proven, raising the temperature and pH in the extract evaporator loop mitigated the problem. Extract produced since operating temperature were increased in the MDS extract evaporator has been more stable as measured by pH, IC purity, invert, or color.

Conclusions:

Enzymatic activity in the stored extract resulted in lower purity, increased invert levels, and high sugar end colors during processing of extract. Increased invert levels created high color issues in sugar end processing. Biocide treatment with formaldehyde, beta hops acids, and sulfur dioxide had little impact on HLB extract stability in storage. Removal of microbes by filtration through a 0.22 micron membrane did not ensure juice stability. Since filtering through a 0.22 micron membrane did not result in stable juice, all observations were consistent with the hypothesis that an enzyme was responsible for degradation. Enzymatic activity was not influenced by filtering or any of the biocides used (5).

Based on our observations, we believe that invertase played a major role in extract storage and processing problems at Hillsboro. The HLB extract contained an active enzyme that was not completely destroyed with 75°C treatment, but was inactivated at 100°C. Elevating the pH to 11 also stopped enzymatic activity. We believe the invertase was due to microbial activity in the MDS extract evaporator loop. We did not observe elevated lactic acid level normally associated with a microbial infection of the juice.

Investigations lead to the discovery of elevated microbial counts and increased nitrite level in the extract evaporator loop at HLB. Raising the temperature to a minimum of 77°C and pH above 10 in the extract evaporator loop reduced storage losses to near zero. Counts have been consistently lower in the extract after the above actions were taken. In addition, nitrite level is typically less than 4 ppm, most of the time it is 0. Invert level in extract has been less than 0.2% on dissolved solids; typically less than 0.1% on solids. We have processed several tanks since the temperatures in MDS were increased and have only had occasional problems with surface infection. Invert concentration, pH, color, and purity have remained stable in juice that has been stored up to 10 months before processing.. Extract coming out of storage is essentially unchanged from what was put into storage.

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