OPTIMIZATION OF BETAINE RECOVERY IN A COUPLED LOOP MOLASSES DESUGARIZATION SEPARATOR

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Abstract:

Betaine recovered from American Crystal Sugar's molasses desugarization (MDS) plant has increased in value over the past few years. Maintaining product quality while maximizing recovery of the betaine-rich fraction has a higher rate of return than in the past. Techniques for optimization of the recovery and quality of the betaine fraction involve the use of a Foss NIRSystems Series 5000 benchtop spectrometer located on site at the factory lab. Data from the NIR has proven useful in monitoring the quality of the betaine-rich fraction on a daily basis. In addition, the NIR has proven to be a useful tool in troubleshooting and fine tuning control valve cut points. Data from the NIR has proven to be a very useful adjunct to the RDS and apparent purity data used to determine operating parameters. With the rapid availability of betaine data, adjustments can be made to the MDS trains to account for changes in feedstock. Data from comprehensive sampling around valve cut points can be used to enhance recovery while maintaining product quality of the betaine-rich fraction. This paper reviews the application of NIR betaine data in optimizing the operation of a coupled-loop separator.

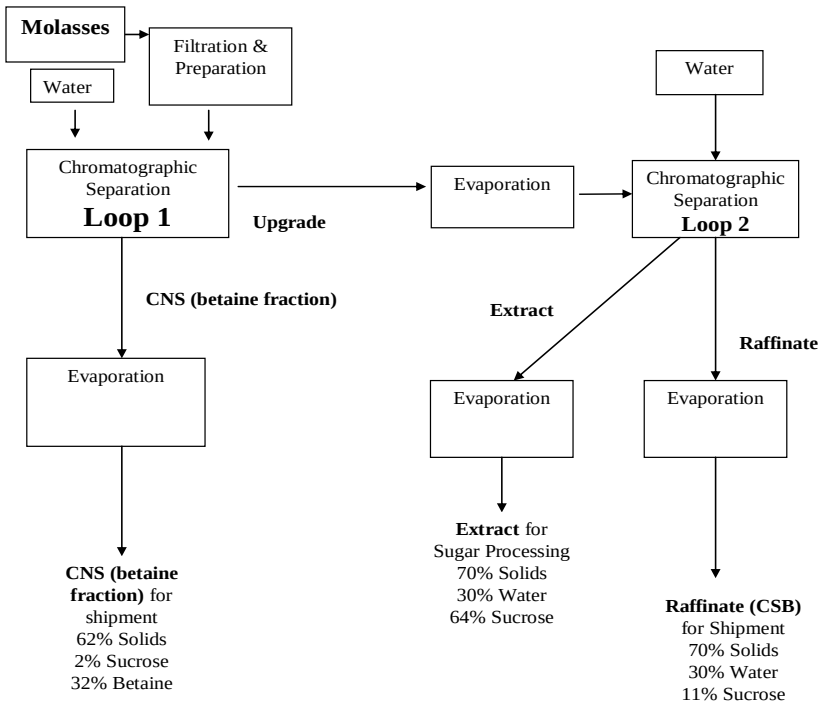
Introduction:

American Crystal Sugar Company (ACSC) operates two molasses desugarization (MDS) facilities. Both desugarization facilities utilize Amalgamated Research (ARi) separation technology. A "standard" simulated moving bed (SMB) separator is located at East Grand Forks, Minnesota. The other MDS facility and the focus of this paper is located at Hillsboro, North Dakota. The Hillsboro separator was brought on line in January of 2000 and attained expected performance by July of 2000. The Hillsboro separator is a "coupled-loop" technology that utilizes displacement chromatography along with simulated moving bed technology (Kearney, 1997). With coupled loop technology, a betaine-rich fraction can be obtained and sold to market. The betaine-rich fraction is typically referred to as the crossover nonsugars (CNS) stream in the Amalgamated separator. Initially, the CNS fraction from the first loop was combined with the raffinate stream produced in the second loop. The combined separator by-product (CSB) was sold into the animal feed market.

Coupled loop is also known as multi-component simulated moving bed. Coupled loop technology consists of two equilibrium curves established in the 1st loop. One curve consists of betaine and other amino acids (also called crossover nonsugars). This product is sold into the animal feed market. The other curve contains the salts and sucrose. Sucrose is separated from the salts in 2nd loop. In the past we focused on sugar end recovery of the sucrose-rich extract fraction produced in the second loop. With the increase in betaine use for animal feed and subsequent market demand, it became worthwhile to optimize the first loop for betaine recovery. Specifically, this paper will focus on the production of the betaine-rich CNS fraction produced at Hillsboro's MDS facility.

As mentioned earlier, there are two distinct operations involved in the coupled loop or multi-component SMB molasses desugarization separator. What leaves the first loop impacts the second loop. One should not adjust operation of the first loop without regard to consequences on the second loop. Fortunately, we found that operating changes could be made on the first loop to optimize betaine recovery that has little impact on the second loop. Figure 1 below provides a basic overview of the coupled-loop separator. Note that properly treated molasses is fed into the first loop. Leaving the first loop are the CNS (betaine-rich) and Upgrade (sucrose-rich) fractions. The Upgrade goes into the second loop where it is separated into the sucrose-rich extract fraction and the raffinate fraction. White sugar is crystallized from the extract fraction. Raffinate is concentrated and sold as a by-product. The CNS from loop one is also concentrated and sold into the animal feed market.

Figure 1



In order to optimize loop one of the process it was necessary to have a laboratory method that provided rapid and reliable data on betaine concentration with minimal sample preparation. Since there was an available NIR instrument and the access to an HPLC instrument at the American Crystal Technical Services facility, the NIR was set up on site at the Hillsboro MDS laboratory. Adjustments to operating parameters on the separator were based on betaine data provided by the NIR.

Results and Discussion:

There are numerous items that need to be considered to optimize recovery of any product from a separator. Numerous control variables can be changed that influence and determine performance of the separator. The act of changing operating conditions of the separator is referred to as "tuning" at ACSC. Critical control variables include the volume of water added to the volume of feed (W/F ratio), the volume ratio of CNS fraction to the upgrade fraction (C/U ratio), the length of time for each step (step time), the internal flow rate (void setting), the volume ratio of extract to raffinate, and the throughput rate in gallons per minute (gpm) of molasses feed, among others.

Beside control settings, there are several other variables that must be addressed when optimizing the separator. These items include:

1. Resin in the cells must be uniformly distributed. There should be a minimum of broken beads or resin fines present in the cells.
2. Mechanical components such as hoses, distributors, fractal plates, and valves must be in good repair and operating properly. Flow meters should in calibration; pump and valve control loops must be properly tuned.
3. Loading of the separator must be appropriate for the volume of resin in the system; as the resin is overloaded, separation performance decreases.
4. Operating temperatures must be in the correct range to avoid microbial infections and ensure proper kinetics.
5. The pretreatment of the feed molasses must not be overlooked. Suspended solids must not be introduced into the system. All liquids entering the cells must be degassed. Molasses hardness must less than 3 meq/100 DS to avoid solids precipitation problems in the resin cells and evaporator trains. Typically we have had the best performance of the separator when feed molasses pH is adjusted to 8.5.

Resin and Distributor Assessment:

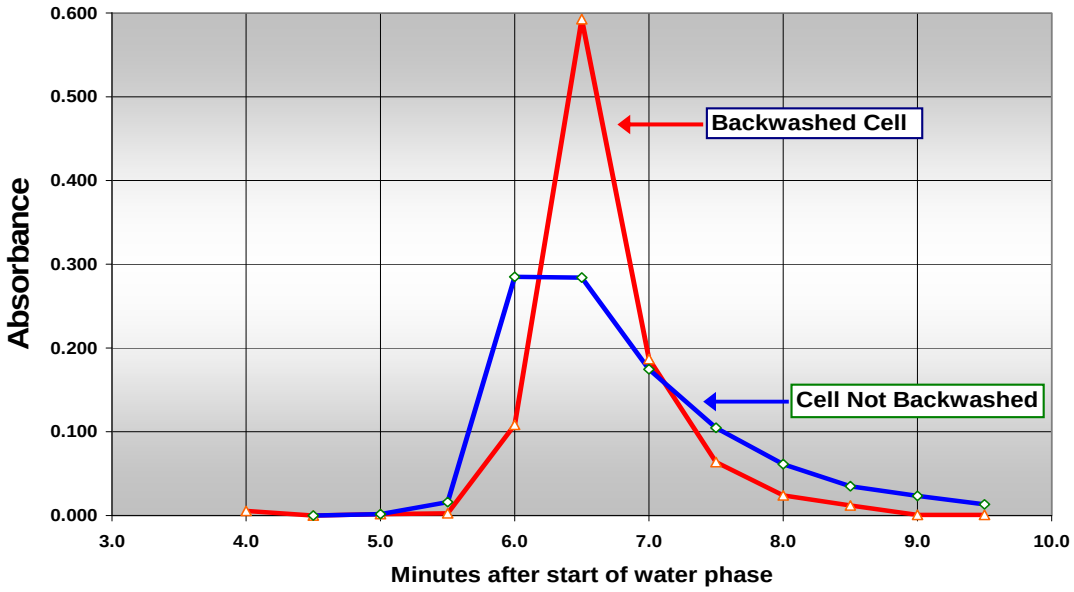
One of the ways we check the system for resin and distributor integrity is dye testing in conjunction with pressure drop monitoring and resin trap change outs. We used a modified dye test method introduced to ACSC by Amalgamated Research. A solution of Blue dye #1 was injected into a cell during the water phase. A series of samples were collected either at the end of one cell or across two cells and read in spectrophotometer at 628nm. Since it was difficult to control the amount of dye injected into a cell or across cells, the absorbance data was "normalized" then plotted so that peak area total were the same for each cell tested.

Sharper absorbance peaks indicate better component separation, better overall performance, and it is possible to adjust or "tune" the separator for maximum performance. Broader peaks indicate poor internal flow characteristics resulting in a "smearing" of components; hence, poorer separation results. Figure 2 shows the results of dye testing on a cell before and after backwashing of the resin. In this example note the broader flattened out peak obtained from the cell initially. The resin was removed from the cell and backwashed to remove suspended solids and resin fines. After backwashing, the resin was returned to the cell; the cell was re-packed with resin after a few days of operation. In Figure 2, note the sharp peak obtained

from the dye testing after the resin had been backwashed and packed. The base of the peak is narrower, the peak height is higher.

Figure 2

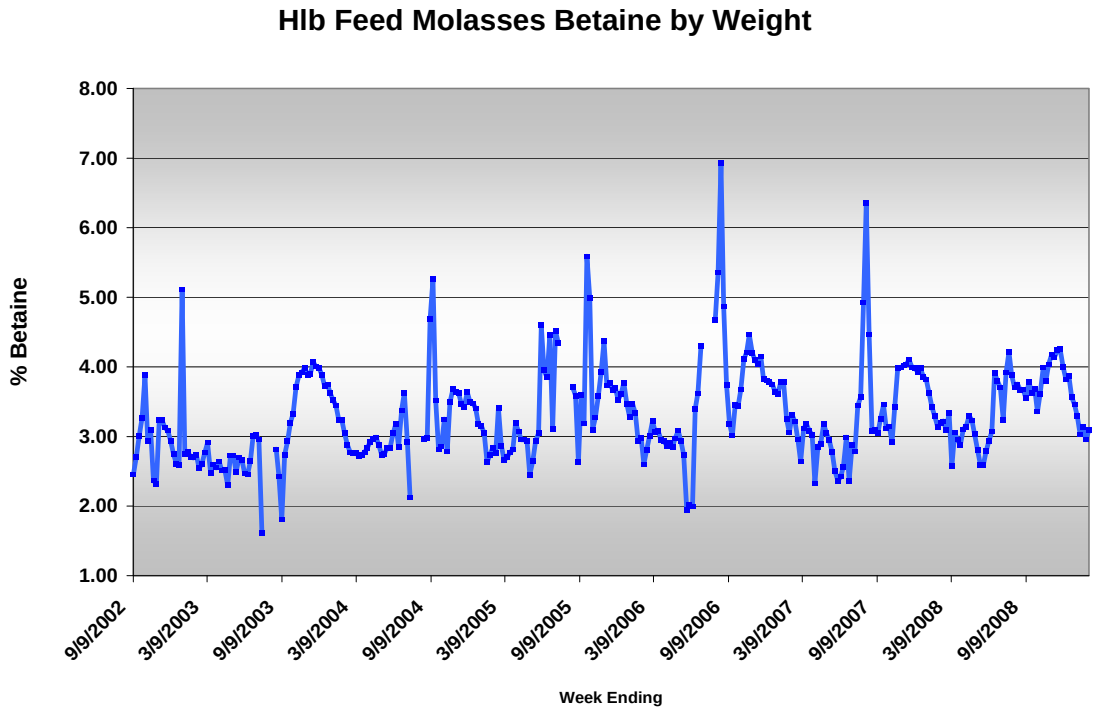
HLB-MDS Dye Testing



Betaine Concentration in Feed:

Figure 3 shows the betaine concentration in feed molasses at Hillsboro for 6 campaigns. Betaine concentration in the feed molasses varies from year to year and from season to season. The general trend is for betaine concentration in molasses to be highest in the fall, dropping to lower levels as the campaign progresses. The predominant reason the betaine concentration varies across the campaign is that molasses production on nonsugars tends to be lowest in the fall of the year. Molasses production tends to increase the longer the crop is stored; the trend reverses some when frozen beets are processed. Our data indicates that over 70% of the change in betaine content in molasses can be attributed to seasonal changes in the molasses production rate on beet. We've found that betaine on beet is relatively stable throughout campaign. However, as other nonsugars increase and molasses production increases, the betaine is "diluted", resulting in the lower concentration observed in early spring. Differences in betaine levels across campaigns are influenced by plant stress, growing conditions (sun, moisture and temps), beet variety and disease. Betaine levels are very elevated (almost double typical molasses) in secondary extract molasses produced from EGF MDS extract processing. The Hillsboro separated must be adjusted to successfully process secondary molasses.

Figure 3

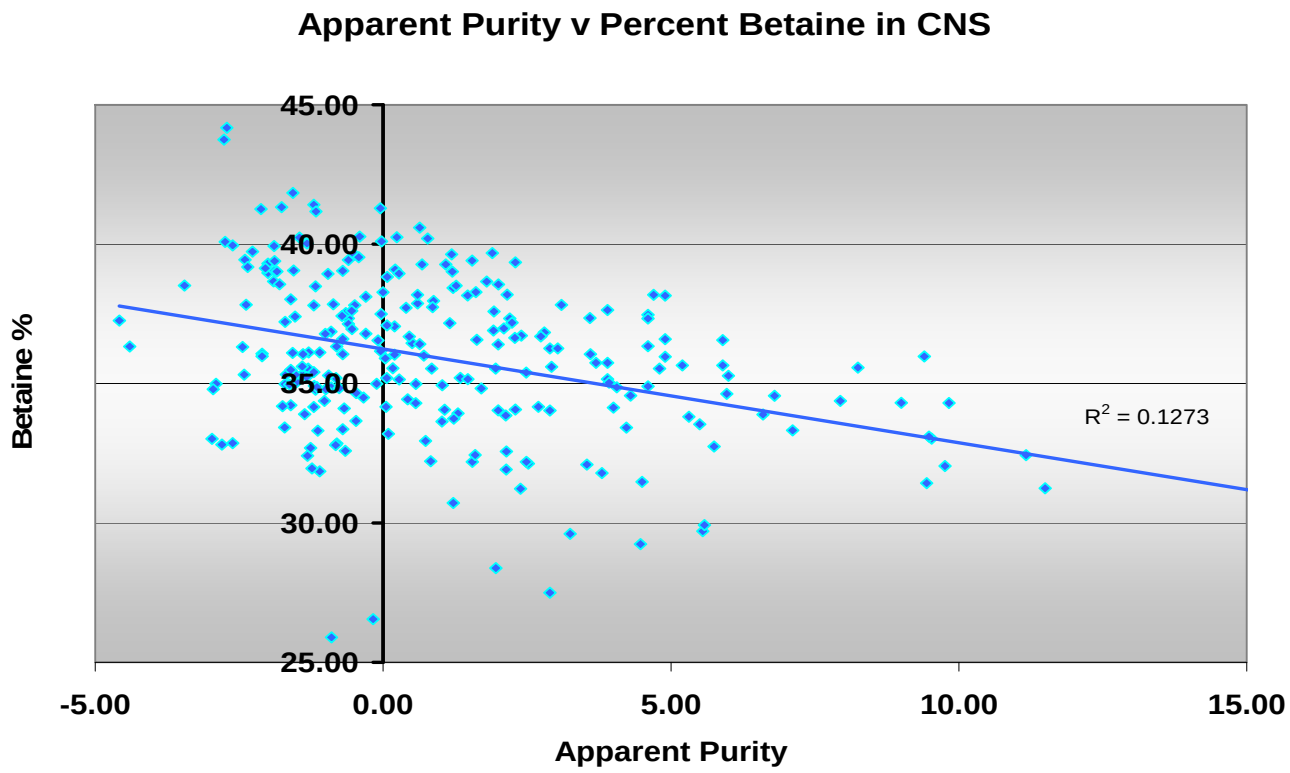


Control Data and the NIR:

One of difficulties encountered in optimizing betaine recovery was insufficient data on the betaine content in the CNS fraction. Before the installation of the NIR on site, the only available betaine information came from weekly composite samples that were analyzed on HPLC off-site. Given that the samples were weekly composites, process variation information was unavailable. Samples collected on a daily basis were infrequent and the turn around time was two days.

Prior to NIR installation, daily operating data used to control the separator consisted of obtaining RDS, apparent purity, and conductivity on the CNS sample. Apparent purity was obtained by running the CNS sample on an Autopol 880 and Index refractometer. During the optimization project, numerous betaine and apparent purity samples were compared. A correlation between apparent purity of the CNS and the betaine measured by HPLC in CNS was found to be very poor. Figure 4 is a plot of the apparent purity data obtained on a CNS sample plotted against the betaine % w/w as determined by HPLC analysis. Note the R-squared value of 0.1273, indicating that controlling the system with only apparent purity data will not be very effective.

Figure 4



Typically, operators of the separator were setting system controls to achieve a -2 apparent purity in the CNS fraction. Referring to Figure 4, one can see a very wide range (from 31% to 42%) of betaine concentration with a -2 apparent purity target. In order to ensure the guaranteed minimum of betaine in the CNS, the target concentration was set much higher than needed. With installation of the Foss NIRSystems Series 5000 benchtop spectrometer, data on betaine concentration was much more accurate. In the paper by Jarski, et al the NIR predicted betaine versus the HPLC betaine value was excellent with an R-squared of 0.9976.

Once the calibration of the NIR was complete, operators routinely ran samples to obtain information on the CNS stream. The use of CNS apparent purity was phased out for use in changing operating parameters than controlled betaine concentration in the CNS fraction. One advantage of the NIR is the ease of use for the operators. Ion Techs who run the process do not spend a lot of time in the lab due to other assigned tasks. One advantage of the NIR was that no special preparation beyond the routine wet chemical analysis already being done was required. The results are obtained from the NIR in under two minutes.

Apparent purity is still being obtained on CNS; however its primary use is to check on sucrose build up in the first loop. If sucrose build up is excessive, it will carry over into the CNS fraction. As sucrose carries into the CNS fraction, apparent purity in the CNS fraction will move from negative to positive. A positive apparent purity in the CNS is also accompanied with lower overall sucrose recovery. Current operation involves using NIR, apparent purity, and RDS data

to adjust separator parameters. With the rapid feedback provided by the NIR, drifting of the betaine concentration in CNS can be avoided.

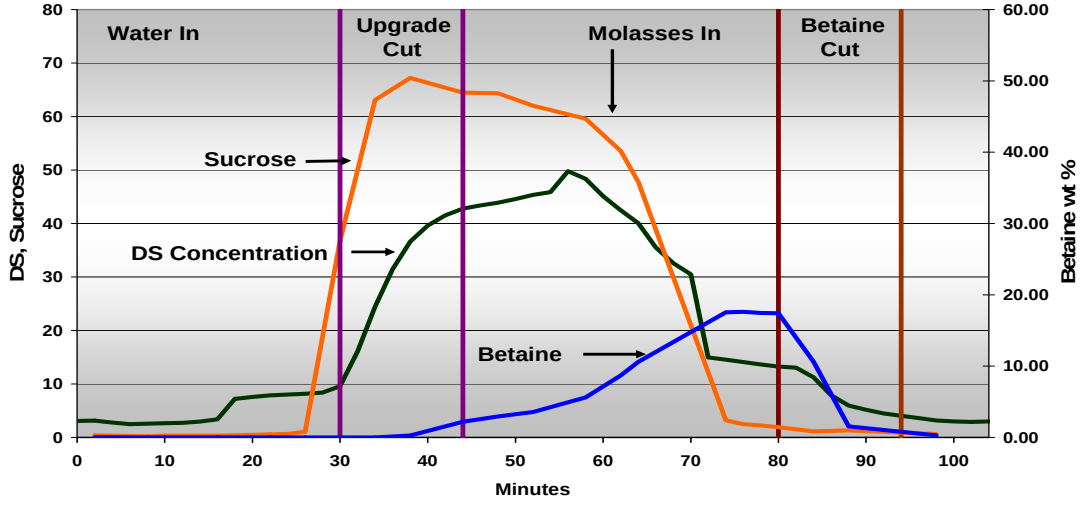
Major Component Profile and Optimization:

In order to optimize and troubleshoot the first loop, it is very useful to understand the relationships between the components being separated. As mentioned earlier, the coupled loop technology consists of two equilibrium curves established in the 1st loop. One curve consists of betaine and other amino acids (also called crossover nonsugars). The material in this curve leaves the first loop as the CNS fraction. The other curve contains the salts that move with sucrose, which leave the system (first loop) as the upgrade fraction.

Loop one, the part of the separator were the betaine-rich CNS fraction is produced, contains two trains. Each train has 4 cells that contain resin. In order to understand what is happening internally, a set of samples were pulled across one complete cycle on a train. A cycle is complete when each cell (all 4 cells in a train) has gone through a reference step such as the feed step. A re-circulation phase occurs between each step also. Figure 5 is a graph of the major components we are concerned with in loop one. The data for the graph were obtained by pulling a sample every 2 minutes from the same point through a complete cycle. Samples collected were analyzed with an ion chromatograph and HPLC. The sucrose leaves the first loop in the upgrade cut. Trailing the sucrose is betaine which will leave in the betaine cut (also referred to as CNS). The cut points occur when selected valves open and the products are removed from the train.

Figure 5

Loop One Profile



Adjustments can be made to influence the size of the cuts. The result is a change in volume of the material being removed. Since flow of water and molasses in must equal flow of upgrade and CNS out, volume changes to upgrade result in a change to CNS and vice versa. In Figure 5, note that some betaine is present in the upgrade cut. Some of the betaine at the time of

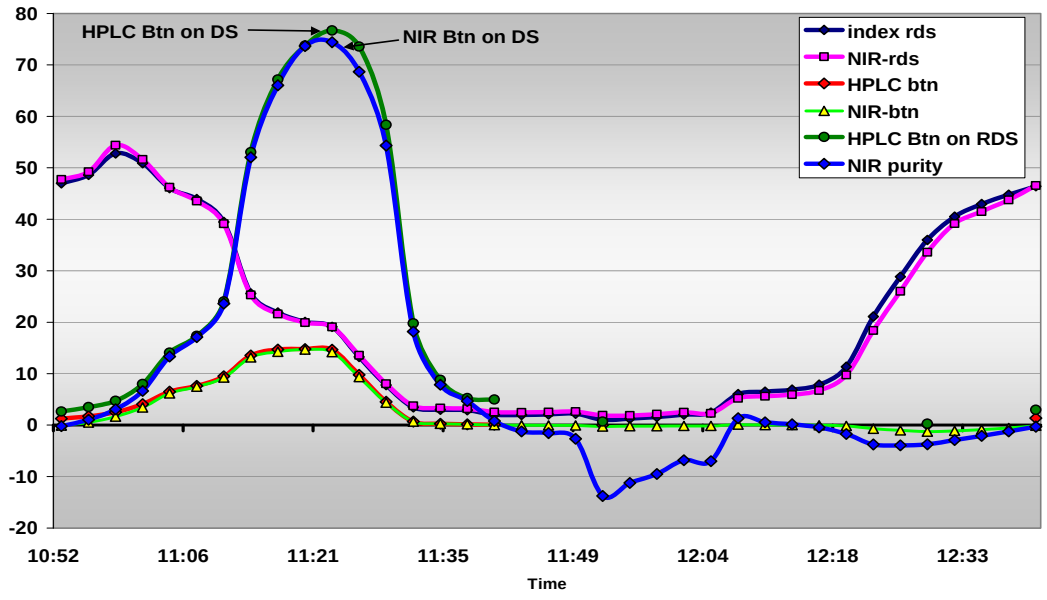
sampling was leaving in the upgrade, resulting in less overall betaine recovery in the saleable CNS product. Adjustments to the system are typically done to keep betaine in the upgrade fraction to a minimum.

Use of NIR for Optimization:

Obtaining profiles can be very useful in troubleshooting and optimizing the separator. The data graphed in Figure 5 took a considerable amount of time to obtain. Collecting samples over almost two hours was just the beginning. Samples had to be prepped and run on analytical instruments such as the HPLC. One of the goals in using NIR was to reduce analytical time required for extraordinary sample analysis. The major focus was to be able to obtain betaine and DS profiles rapidly. With the NIR, profile data can be obtained the same day samples are collected at the factory; a complete profile can be accomplished in just over 4 hours rather than a day and half to two days required prior to the use of NIR. The graph below (Figure 6) illustrates the utility of using NIR to obtain component profiles. On the left side of the graph, our primary focus point, note that the HPLC and NIR betaine data overlap in the CNS cut (between time 11:21 and 11:35). The NIR was not calibrated for betaine in the water phase (time 11:49 – 12:33) so the correlation is poor in that region. However, dissolved solids determined by NIR overlap the dissolved solids obtained by refractometer through the whole profile.

Figure 6

HLB MDS - NIR and HPLC Profile

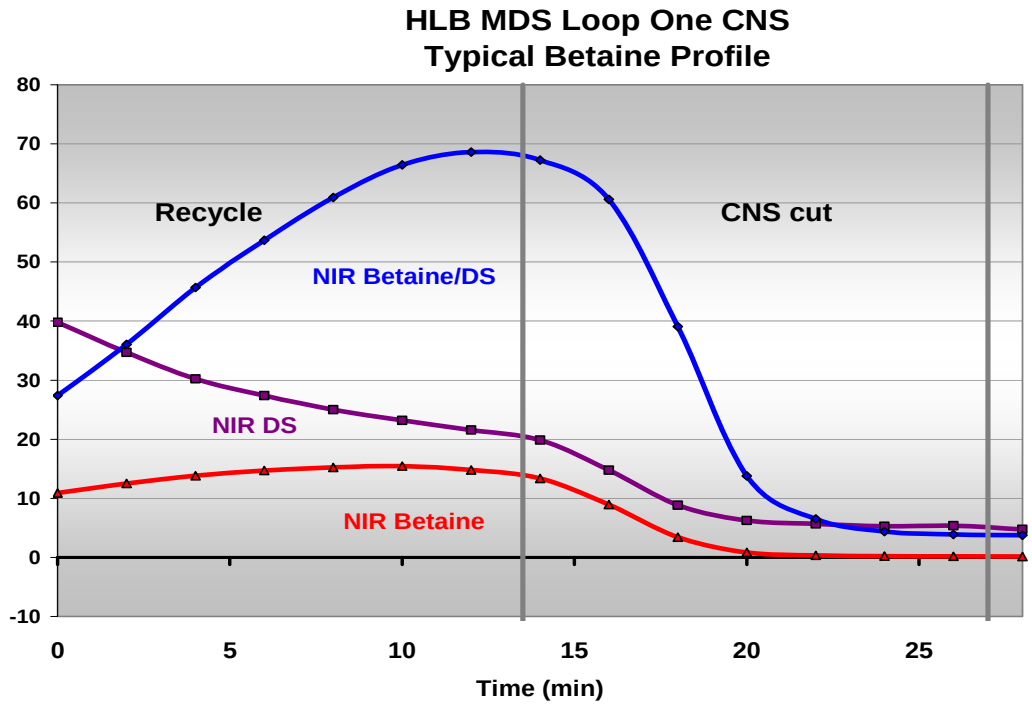


Another use of the NIR involves obtaining data for a partial or "pick" profile. In the pick profile, samples are collected in the recycle phase and the CNS cut only. Since the majority of betaine is "located" in the recycle and CNS cut, the pick profile is typically all that is required for troubleshooting and fine tuning the system. Figure 7 below is a recycle-CNS pick. The

component curves are what we would expect to see in a properly operating system. Betaine should drop off sharply in the middle of the CNS cut along with dissolved solids. Dissolved solids at the beginning of the recycle phase are typically around 40%. An increase in the dissolved solids at that point indicates excessive inventory build up in the separator and adjustments are required. With the NIR, samples can be pulled from the separator and analyzed in 2 hours with two people.

In addition to a recycle and CNS pick, the operators will take a 3 point sample pick. The "3 point pick" is obtained by pulling a sample at the beginning, middle, and end of the CNS cut. While the 3 point pick data are less descriptive of the process, information can be obtained on potential operating drift.

Figure 7



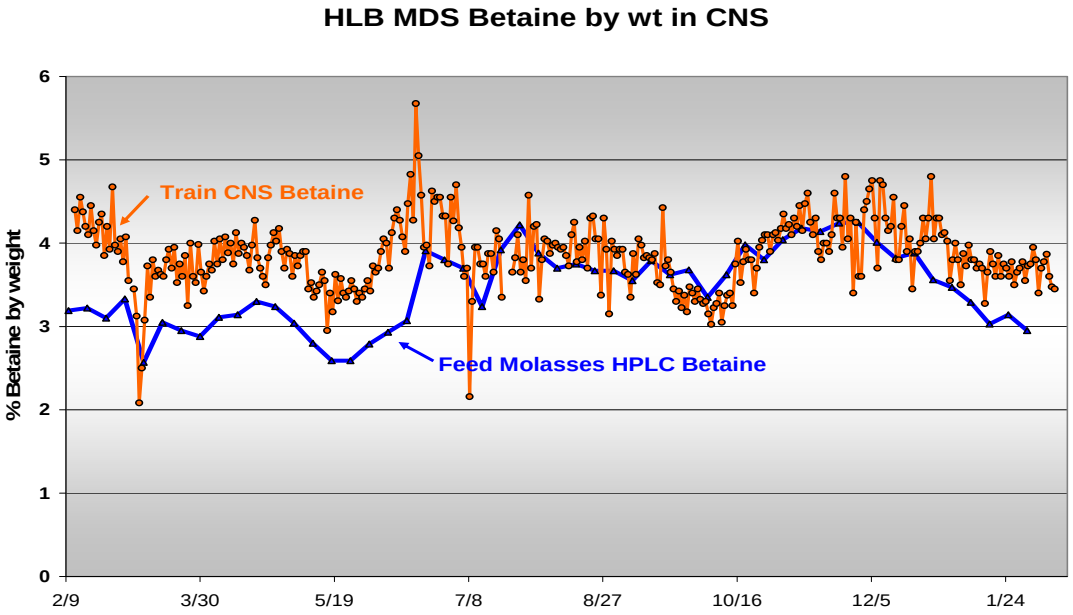
Results in Operation:

Given the timely availability of data obtained by using the NIR, variability in the betaine-rich CNS fraction has decreased. With up to date information available, tuning changes to the separator can be made quickly, rather than waiting for weekly composite sample results. In addition, the weekly data obtained does not yield information on process variability unless it is extremely high.

One of the issues the Hillsboro MDS plant has struggled with is the variability of betaine content in the feed molasses. The Hillsboro plant receives molasses from 5 different factories. Not only is the molasses feed from 5 different factories, the molasses coming into the facility can be from different times of the year. As was mentioned earlier, betaine content in molasses

changes through campaign. Prior to using the NIR, the content of betaine in the CNS followed the content in the incoming feed molasses. In Figure 8, note the left and right sides of the graph. On the left side the NIR was being evaluated and not used for daily process control. Betaine content in the CNS followed betaine content in the molasses. On the right side of the graph, note betaine content in CNS leveled off at the target value despite the continued drop in betaine of the incoming feed molasses.

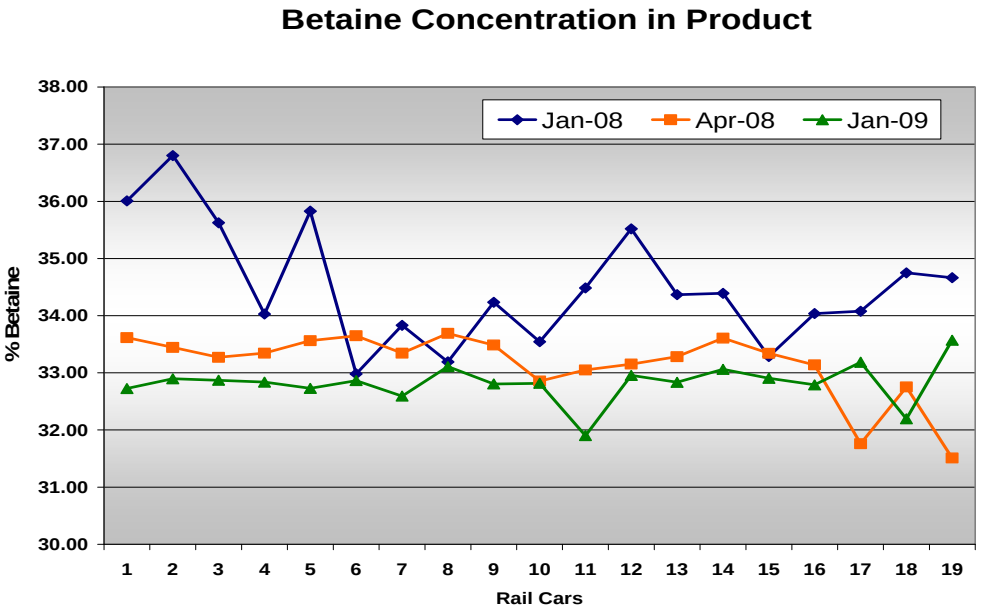
Figure 8



By using NIR we have been able to reduce CNS product variability. By producing a CNS with more consistent betaine content, the target concentration of betaine can be reduced. In the past, the betaine target value in CNS was artificially high to ensure all product produced met the minimum guaranteed betaine level. Since no premium was obtained with higher betaine concentrations, the additional betaine in CNS was essentially being given away. With up to date betaine information, the focus shifted to improved betaine recovery; more tons of CNS could be produced per ton of standard feed molasses. With improved monitoring of the process, another benefit is that very little betaine is moving into the extract.

In Figure 9 below, the reduction in CNS variability is evident. The graph below is based on rail car data. Three separate two week periods were compared. In January 2008 the betaine content in the cars as shipped varied from 33 to 37 percent. In April 2008, the use of NIR was in its early stages, betaine in cars varied from 31.5 to 33.5 percent. By January 2009, variability in the CNS product was reduced further. The range of betaine was 32 to 33.5 percent. With the reduction in variability note the overall average of betaine in the CNS dropped, yet the minimum level of betaine was maintained.

Figure 9



Continuous improvement has been achieved in reducing CNS betaine variability. The table below lists the betaine content in the CNS product as shipped. In fiscal (starts September 1) year 2007 the average content of betaine was 37.6%, the range in content was 9.8 points. In 2008, the average fell, but the range in betaine content was 11.6 points. The asterisked 2009 value represents data collected beginning January first.

Table I
Betaine Variability in CNS Product

Fiscal Year	Avg %Betaine	Low	High	Range
2007	37.6	32.7	42.5	9.8
2008	35.6	29.8	41.4	11.6
2009	34.4	30.1	38.6	8.5
2009 *	34.8	31.8	37.9	6.1

Conclusions:

Successful separator optimization is a multi-variate process. Numerous contributing factors need to be considered.

- Loading of the resin must be correct. Excessive nonsugars load decreases separation performance. Operating parameters such as step time must be adjusted for the appropriate nonsugars load.

- Variability in the molasses feedstock must be considered. Separator "tuning" parameters must be adjusted to account for changing betaine concentration in the feed molasses.
- Use of the NIR has allowed for more timely and accurate analytical feedback for the operators. Adjustments to the C/U ratio and void settings can be accomplished before a large drift in CNS betaine content is observed.
    - With more timely operating adjustments, variability in the saleable betaine-rich CNS product has been reduced.
    - With lower product variability, betaine target values have been decreased allowing for a greater yield of CNS per ton of molasses.
    - Overall recovery of betaine has improved, reducing the amount of betaine going to the extract.
    - Out of spec product production has been reduced significantly.

Acknowledgements:

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References:

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2. *Jarski H.; Groom, D.; McGillivray, T.* (2009): Use of NIR Spectroscopy for On-Site Betaine Measurement in the ACS Hillsboro Molasses Desugarization Plant. Presented at ASSBT Meeting, Orlando, Florida, February 26-March 1, 2009.