Color Monitoring in Corn Syrup Manufacture

Corn Syrup Process

The discovery that starch could be transformed into a sweet substance is approaching 200 years old. In the mid 1800's, the starch industry in Europe developed mainly on potato starch, derived as by-product of a food crop, but in the USA it developed from corn (maize, sweet-corn, corn-on-the-cob). Starch extracted from corn is hydrolyzed to dextrose. Treatment by enzymes continues the conversion to other sugars such as glucose, maltose and fructose. Corn sweeteners now account for more than 55 percent of the US sweetener market.

There are many products resulting from these processes, and it may be useful to define them:

Corn Syrup (glucose syrup) is the purified concentrated aqueous solution of nutritive saccharides obtained from edible starch and having a dextrode equivalent (DE) of 20 or more.

Dried Corn Syrup (dried glucose syrup, corn syrup solids) is corn syrup from which the water has been partially removed, resulting in granular or powdery free-flowing semi-crystalline or amorphose solid products comparable in chemical composition to their liquid counterparts.

Dextrose Monohydrate is purified and crystallized D-glucose containing one molecule of water of crystallization with each molecule of D-glucose.

Dextrose Anhydrous is purified and crystallized D-glucose without water of crystallization.

Maltodextrin is a purified concentrated aqueous solution of nutritive saccharides obtained from edible starch in which a portion of the dextrose has been isomerized to fructose. It contains a minimum of 42% fructose on a dry basis.

High Fructose Corn Syrup (HFCS) is purified and concentrated D-fructose obtained from edible starch available in either anhydrous crystal or remelted liquid form.

Starch is separated from other parts of corn by the wet milling process. Cleaned, shelled corn (removed from the cob during harvesting) is soaked in water. It is ground and treated by hydro-cycloning to release the germ which is used for oil extraction. After further grinding, the hull is removed by sreening followed by centrifuging to separate the gluten from the starch. Starch is cleaned and concentrated in a series of hydrocyclones ready for conversion.

The most commonly used methods of conversion are acid process, acid-enzyme process and multiple enzyme process.

In the acid process, starch-water slurry is acidified and and reacted to dextrose under pressure. After the desired conversion, the process is stopped by releasing pressure and neutralization. The resulting liquor is clarified to remove suspended solids, decolorized and concentrated to finished density.

The acid-enzyme process is similar, but the slurry is only partially converted, with almost no dextrose production. The liquor is then treated with an enzyme and conversion continued until a 42 DE high maltose syrup is formed. The process is then stopped, the liquor clarified, decolorized and concentrated as for the acid process.

In multiple enzyme processes, starch is gelatinized and depolymerized by enzymes rather than acid.

High Fructose Corn Syrups

Dextrose solutions produced by acid-enzyme or dual enzyme process are refined by carbon and ion exchange columns before treatment with a purified isomerase (enzyme). The process is stopped at 42% fructose, purified and concentrated by evaporation. For high fructose production, the syrup is passed to ion exchange columns where the fructose is retained while dextrose passes through. Fructose is flushed from the column and blended with 42% feedstock to produce commercial grade 55% fructose syrup. The blend is further purified and decolorized by carbon and ion exchange processes.

Analyzer Applications

There are four measurements needed in these processes; continuous on-line color, turbidity, detection of organic material which will affect color and "brilliance".

Color Measurement

There are several points in the process where color is measured:

- Downstream of the filter presses, to determine the load on the color removal stage. Typical ranges are 0 to 5000 or 0 to 7500 color units.
- Downstream of the color removal stage for quality control, or as a way of determining when to take the color removal column off-line for regeneration instead of uneconomical time-based sequencing. In this latter application, there is usually one analyzer per bed. Typical ranges are 0 to 500 or 1000 color units.
- On the HFCS liquid fructose product line for quality assurance purposes prior to shipment to the beverage industry. It has also been proposed to install an analyzer on the tanker loading station to automatically provide a quality assurance certificate on loading. Typical ranges are 0 to 50 color units.

The industry standard color scale is defined by Corn Refiners Association (CRA) Method E16 where:

CRA number = A(450nm) - A(600nm) x 100/l

where

l = cell pathlength in cm

(The factor x 100 makes this scale closely approximate to the Lovibond yellow scale, which is still used by the wet corn milling industry.)

The laboratory analysis for color is very labor intensive. The spectrometer used is a single beam unit, requiring standarization against reference potassium dichromate solution. It is too slow and too expensive to be used for process control, and yet it is!

Application development work carried out in conjunction with Tate and Lyle, Silvertown Refinery, London, showed:

- The 4000 split beam technique measured color accurately.
- The measurement is totally independent of turbidity, up to at least 1200 ppm, so filtration is not necessary.
- Reliability is extremely high, with zero maintenance required over many months of on-line service.
- Stability is so high that zero adjustment is only done when the plant is shut down for maintenance.

Although we use the 436nm mercury line for color measurement rather than 450nm specified in the standard, the error is very small, linear and is corrected during factory calibration. The 436nm line gives greater accuracy, lower drift and greater linearity than 450nm generated by a wide band source and interference filter combination.

Also, we use the very intense 546nm mercury line as a reference wavelength instead of the 600nm specified. The error in background between 546nm and 600nm is negligable, and has one important advantage. There is a measurement requirement known as "brilliance" which is equal to the percent transmittance at 550nm. By taking the output of the reference channel, we can give this measurement as a direct output. It can be seen that the lab has to take three measurements - 450, 550 and 600 nm, while we can do all that is required directly, on-line, continuously.

Turbidity Measurement

Usually, low particulate levels in a filtered liquid would be monitored by a forward scattering turbidimeter such as the Model 4030, or a nephelometer. The Model 4030 is too expensive to have many opportunities in this industry. However the most likely application is monitoring the performance of the filter presses, where color measurement is also a requirement. Remember that the virtue of the Model 4000 split beam technique is that if particles are present, they reduce the amount of light equally in both measuring and reference channels, so the color measurement is unaffected by the amount of light transmitted through the cell. Hence, by monitoring the amount of light loss in the reference beam, we can establish a correlation between light intensity and turbidity. (The lamp output is sufficiently stable that zero drift is not a problem.) In this way, we can monitor both color and turbidity in the same analyzer, with very little increase in cost, which makes both measurements more attractive, especially when there is no installation cost for the second measurement.

Turbidity measurement downstream of the filter presses is important, because the next stage is color removal, and particulate carryover is filtered out in the color removal beds, causing pluggage and high regeneration/maintenance costs. The filter presses are actually multiple "plates" of cloth and operate by first recirculating the solute continuously around the press until a sufficient layer of filtered "cake" is built up on the cloth surface to create an efficient filter bed. Hence, it is the solids removed and left on the cloth which actually does the filtering. A press room contains many presses, all connected in parallel. When the pressure drop across the filter becomes too high due to build up of cake, the filter must be stripped down, the cake removed, re-assembled and new filter bed established. This is very labor intensive. It has been shown that although on a time-averaged basis, the filtered liquor may only show a particulate level of 10-20 ppm, there are periods at start-up and break-through of individual presses when the levels are as high as 500 ppm.

Organic measurement

In addition to measuring product color exiting the decolorizing stage, of whichever type, it is possible to monitor for the organic compounds at 365nm (outside the visible spectrum). These are the compounds which affect color. By using this measurement, the process can be more economically operated by waiting until breakthrough is apparent (although still not being measured as color) rather than operating the process on a timed sequence as is usually the case.

Who to Contact

Plant Manager. Will be interested in anything which saves money, but will more than likely introduce you to:

- **Works Chemist.** This person is vital to have on your side. He is responsible for all quality matters. He has the job of assisting the process people in improving the processes, it is in his interest, but he cannot afford the resources. He will most likely tell you that no color analyzer can stand up to the environment in a sugar refinery, but he has never worked on a sulfur plant or off-shore rig.
- The unit **process engineer**.

Sales Aides

Basic 4000 brochure and "Monitoring Product color with the Model 4000 Photometric Analyzer" for description on how the 4000 works, and why it is the most reliable analyzer in the world.

"On-line monitoring of colour and turbidity in sugar process liquors" by Plews, Mead and Day. Also available in Spanish.

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Application Note

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