

METTLER TOLEDO APPLICATION NOTE

pH Measurement In Corn Wet Milling

BACKGROUND

Corn wet-milling is the most common method used to process corn in the U.S. In this process, corn kernels are separated into their component fractions and then further treated to yield cornstarch, corn sweeteners, corn oil, and animal feed. This process consumes over 1.3 billion bushels of corn each year in the U.S. alone. Each 56-pound bushel of corn requires at least 40 gallons of water, so large volumes of water must be treated, used, and then (perhaps) treated again before disposal. Tight monitoring and control of all this water captures the maximum from every bushel — this is where pH measurement of the process water comes in.

THE PROCESS

The cleaned corn kernels are "steeped" at 50°C (120°F) in a mild (0.1 to 0.2%) sulfurous acid solution to loosen the hull, soften the gluten, and dissolve some constituents of the kernel. The steeping phase lasts between 24 and 48 hours at 4 pH and causes the kernels to swell to double their normal size. Sulfur dioxide gas is added to the water to break chemical bonds in the gluten and prevent the growth of bacteria in the steep tanks. Water used in steeping is later concentrated and used as animal feed.

After steeping, the corn is coarsely ground to free the germ. The lighter corn germ is separated from the corn slurry by cyclone separation or by gravity in a settling tank. The germ, which contains 85% of the oil, is further washed over screens to remove any starch that may be adhering to it. Mechanical pressure and solvent extraction are used to remove the corn oil. This oil is then clarified and filtered before delivery as a final product.

The corn/water slurry (minus the germ) is then finely ground to release the starch and gluten from the kernel. This mixture flows over screens that capture the fibrous kernel but allow the starch and gluten to pass through. The fiber is collected, rinsed to reclaim the starch, and then used for animal feed. The gluten is then

removed by centrifuge, and the remaining starch is washed several times until reaching 99.5% purity. At this point, the process will change depending on the desired final products.

Starch is basically a polymer of glucose sugar units. The long chain starch molecule itself is very versatile and is used as a thickening agent in foods, as a raw material for ethanol and plastics production, and as a coating agent in the paper and textile industries. The properties of starch depend on the extent and nature of the bonds in the molecule and can be changed by various preparation methods that involve acids, bases, sodium hypochlorite, and enzymes. These methods yield products such as modified starch, unmodified starch, dextrans, cyclodextrins, and starch derivatives. These products are generally dried to a powder as a final product.

The starch molecule is also used as the raw material for making all kinds of sugar syrups. For these products, the starch slurry is combined with acid and enzymes called amylases that break the starch molecules into dextrose (glucose) and other sugars. The kind of enzyme, reaction time, and process conditions are varied depending upon the product requirements for different kinds of sugars. The product syrups are identified by a Dextrose Equivalent (DE) value that represents how far along this reaction (starch conversion) has gone.

The product syrups are neutralized and then ion-exchanged to remove salts. Dextrose is the simplest sugar, but not the sweetest. Converting dextrose to fructose doubles its sweetness and is very economical. This step is called isomerization and uses the isomerase enzyme at a specific pH value. The direct product of isomerization is 42% fructose syrup, but later fractionation processes are used to produce 90% fructose or even crystalline fructose. Various streams are blended to produce the commercial 55% fructose product. End products are clarified and filtered before delivery. High fructose corn syrup (HFCS) is the primary

sweetening agent used in soft drinks and other foods and beverages.

pH Measurements

pH measurements are made throughout the milling process to optimize the product yield. The bulk of the water used for rinsing and washing usually needs pH adjustment to prevent altering the nominally acidic pH present during the various steps. Rinse waters are generally recycled upstream, but must be eventually treated (and neutralized) before disposal.

Specific pH applications include the following:

1. The pH in the steeping tank is used to control the addition of the sulfur dioxide (or other acid) that begins to release the starch from the corn. Too much acid may release the starch prematurely and causes corrosion of stainless steel process lines. Not adding enough will not prepare the corn kernels adequately.
2. Starch modification is used to lower the viscosity of the starch product. This process must be conducted under controlled pH to meet product specifications.
3. Dextrin roasters also use pH control to catalyze the process. Dextrins have lower viscosity and dissolve in water (most starches are insoluble), making them ideal for use in adhesives.
4. The enzymes used in starch conversion are expensive and function best at well defined pH levels (typically in the 3-5 range depending on the enzyme used). pH levels higher than normal will not utilize the enzymes efficiently, while operation at lower pH may allow the reaction to proceed too far

and cause plugging of downstream filters. High pH values cause the product to set into a viscous gel that is difficult to process.

5. pH is also controlled during the filtration of the corn syrup to prevent crystallization of sugar in the syrup. Solid crystals will be filtered out and will lower yield from this step.
6. Corn syrup end users require that the pH of the product they use have specific pH values, normally in the range of 3.5 to 5.5. Final quality control of pH is used to ensure that soft drink bottlers, wineries, and breweries can confidently use the corn syrup without affecting their final products.

Several other pH measurements may also be useful throughout the process.

INSTRUMENTATION

pH measurement in corn syrup and starch is strongly affected by the high concentration of non-conductive sugars and starch present. On-line pH sensors must continue to measure pH accurately without allowing sugars to contaminate the inside of the sensor. The InPro[®] 4200 Solid Polymer pH Electrode in conjunction with the InTrac[®] 777-SL has proven reliable in these kinds of applications. Ideal instruments to use with the InPro 4200 pH sensor include the Model 2100 pH analyzer.

Although corn products typically have high enough conductivity that pH can be measured with an on-line pH sensor, some corn syrups are purified by ion exchange and have very low conductivities. Such products cannot be measured with standard on-line pH equipment and may be better characterized by electrical conductivity or wet analysis.

PRODUCTS

2100 pH Analyzer

- Detachable front panel and plug-in terminals for ease of installation
- All functions accessible through the keypad for increased ease of use
- Continuous sensor and transmitter diagnostics to monitor performance
- FM certification for Class I, Div 1 & 2 Environments and CSA General Purpose Approval
- 3 year warranty

InPro[®] 4200 Solid Polymer pH Electrode

- Patented Xerolyt[®] solid polymer reference system maintains a stable potential for accurate and repeatable pH measurement and low maintenance
- Open junction eliminates reference clogging and extends sensor life
- High pressure resistance eliminates requirement for pressurizable housing
- Integral RTD for higher measurement accuracy
- Rugged IP67 rated quick connect VarioPin connector

InTrac[®] 777-SL Retractable Housing

- Rugged 316L SS or PVDF construction for maximum chemical resistance
- Flushing chamber for automatic cleaning and calibration reduces overall system downtime
- Patented immersion tube design isolates the sensor on retraction and guarantees complete separation of the process from the outside environment.
- Safety interlocks prevent sensor removal from housing while in measuring position
- Manual or pneumatic operation for maximum use