Ethanol 101

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This presentation is intended to provide an overview of how ethanol is produced in a dry-mill corn ethanol plant by walking through each of the process components.

The Corn Kernel

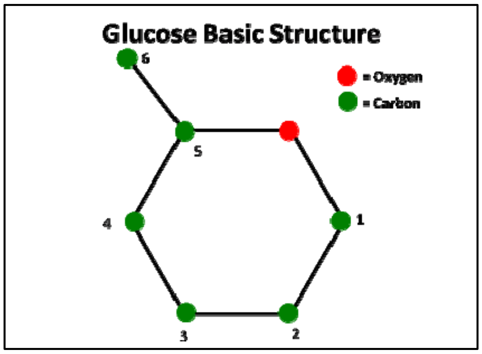
A corn kernel can be divided into 4 main parts. The endosperm, or the yellow part of the kernel is made up primarily of starch (60%) and gluten (20%, mostly protein). The pericarp is the outer covering of the kernel and is mostly fiber (cellulose). The germ is the white, rubbery center of the corn kernel. It contains the genetic information, enzymes, vitamins and minerals, but mostly oil (4%). Finally, the tip cap is where the kernel attaches to the corn cob. It is the only portion of the corn kernel that is not covered by the pericarp. The rest of the corn kernel is composed of water (16%). These percentages are rough, but they represent the general corn kernel composition by weight. There are some genetically modified (GM) corn products that vary these percentages, but for the purposes of this presentation, these percentages will suffice.

Carbohydrates

For ethanol production, the carbohydrates are the key. There are two main types of carbohydrate, starch and cellulose. Cellulose provides structural support for plants while starch is primarily an energy storage molecule. Since most of the ethanol plants today are not producing cellulosic ethanol, this presentation will focus on how starch is utilized within a dry-mill corn ethanol plant.

Glucose and Starch

Let's begin with a discussion of how starch is constructed. To do this we must begin with the basic building block for both cellulose and starch, the glucose molecule. The figure below shows the basic structure of the glucose molecule which includes 6 carbon atoms and 1 oxygen atom. The carbon atoms are numbered as shown in the figure. This will become more important as we continue our discussion.



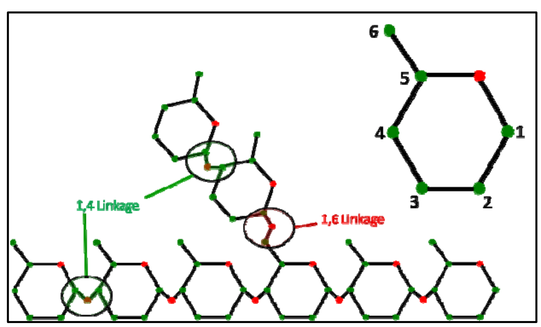
Glucose is also known as "dextrose", "sugar", or "fermentable sugar". It is used by most biological systems as a food source. When we are talking about carbohydrates, glucose is a monomer. Monomer means "one" or "single". When we put many monomers together we get a polymer, which means "many". Since starch is made up of many glucose molecules linked together we say that starch is a polymer of the monomer, glucose. Cellulose is also a polymer of glucose, but has a very different construction than starch. There are two different types of starch, amylose and amylopectin. Amylose is simply a straight chain of glucose molecules and amylopectin is branched, like a tree branch. Both types of starch are present in corn kernels and we will discuss the significance of this are we progress.

Dry-Mill vs. Wet-Mill Ethanol Plants
Now that we have a basic understanding of how glucose and starch are related, we will begin walking through a dry-mill corn ethanol plant. There are dry-mill and wet-mill corn ethanol plants. The basic difference between the two is that in a dry-mill plant, the entire corn kernel ends up in the fermenter. This includes not only the starch/fermentable sugars, but also the protein, fiber and oil. In a wet-mill ethanol plant, the starch is separated from the rest of the kernel prior to fermentation and only fermentable sugars are added to the fermenter. Again, this presentation will focus on the dry-mill corn ethanol plant since most of the plants in operation today are dry-mill.

The Hammer mill
The process begins with milling or grinding the corn. Most ethanol plants today use hammer mills as opposed to rollermills. Hammer mills use a series of rotating hammers that "hammer" the grain into smaller particles. A retention screen "retains" larger particles in the mill until they have been ground to the proper size. This process is critical to the plant operation since too course of a grind will not result in efficient use of the starch and a grind that is too small can cause the grain to "ball up" in the cooking tanks.

The Cooking Process
After the corn is ground, water is added and the cooking process begins. The mixture of ground grain with water is now called a "mash". The primary purpose of the cooking process is to breakdown the starch (long, straight and branched chains of glucose) into shorter chains of glucose. There are two phases to the cooking process, the gelatinization phase and the liquefaction phase. The gelatinization phase combines heat and agitation to causes granules of starch to swell and break apart. It is called the gelatinization phase because the mash can become very thick or viscous during this phase. The second cooking phase, liquefaction, uses enzymes to begin chopping up the starch into shorter glucose chains.

Proteins and Enzymes
Before we continue, a brief discussion of proteins and enzymes is necessary in order to fully understand what is happening in the liquefaction phase. Proteins are critical components of biological cells. They are structural proteins and active or catalytic proteins (enzymes). In the same way starch is a polymer of glucose molecules, proteins are polymers of amino acids. The main difference is that once amino acids are linked together, they fold up into very distinct three dimensional shapes. It is this shape that defines its function either as a structural protein, or as an enzyme. An enzyme is simply a protein that speeds up or causes a chemical reaction to occur. But it is not used up in the reaction. Because of its distinct shape, each enzyme can cause very specific reactions to occur. Starch is composed of two different types of linkages that require two different enzymes to break those linkages (see figure at right). A "1,4 linkage" in starch is where the #1 carbon on a glucose molecule is linked to the #4 carbon on another glucose molecule. A "1,6 linkage" is where the #1 carbon on a glucose molecule is linked to the #6 carbon on another glucose molecule. Notice that 1,4 linkages occur



when there is a straight chain of glucose molecules and 1,6 linkages occur where there is a branch.

The Cooking Process (continued)
Let's now return to the second phase of the cooking process, liquefaction. During this phase, the enzyme α-amylase (pronounced alpha-amylase) is added to the mash. The active site for α-amylase is the 1,4 glucose linkages. As a result, the long chains of glucose in the starch molecules get broken down into short glucose chains called dextrins. The term liquefaction comes from what happens during the liquefaction phase. The viscous mash becomes more liquefied or less viscous as the enzymes breakdown the starch.

Saccharification/Fermentation
Once liquefaction is complete, the starch has been broken down into dextrins or short glucose chains. Additional reduction to individual glucose molecules is still required before yeast can use it as a food source. The step that does this is called saccharification and it is accomplished with an enzyme called glucoamylase. Like α-amylase, glucoamylase is active on 1,4 linkage sites, but only on terminal linkages (linkages at the end of a chain). Unlike α-amylase, glucoamylase is also active on 1,6 linkages. As a result, glucoamylase accomplishes the final goal of breaking down the dextrins (short chains) into individual glucose molecules that the yeast can use for food.

Although saccharification is listed as a part of the cooking process, it actually takes place in the fermenter in a process called simultaneous saccharification/fermentation (SSF). In an SSF plant (which most ethanol plants are) the glucoamylase, mash, and yeast are added to the fermenter at the same time. The glucoamylase converts the dextrins to glucose. The yeast eats the glucose and makes ethanol and carbon dioxide. Fermentation continues for approximately 50 hrs at which time the distillation process begins.

Distillation
Distillation is the process used to separate the ethanol from everything else that was in the fermenter. The basic principle of distillation is that different substances boil at different temperatures. A general description of what goes on inside a distillation column is as follows. The liquid and solids from the fermenter are heated. Since ethanol has a lower boiling point than water, the ethanol vaporizes first and moves to the top of the distillation column. The vapor at the top of the column is then condensed back into a liquid. If all is going well, this should be nearly pure ethanol. In reality, it is impossible to get pure (100% ethanol) using distillation alone due to a physical limitation called an azeotrope. The azeotrope for a water ethanol mixture is the point at which the concentration of ethanol and water in the vapor are equal. At this point it is no longer possible to separate the two liquids using distillation. For an ethanol water mixture this is around 95%. Therefore it is impossible to purify ethanol in a water mixture to greater than 95%. The next step uses molecular sieves to remove the remaining 5% water from the ethanol.

Molecular Sieves
Molecular sieves are composed of columns filled with a material called zeolite. This material can be manufactured to very exact pore sizes. The size of the pores is measured in Angstroms (Å). Since one molecule of water is about 2.8 Å and one molecule of ethanol is 4.4 Å, then a

molecular sieve with a pore size of 3-4 Å would be able to absorb the water, but not the ethanol. As the 95% ethanol/water mixture passes over the molecular sieve material, the water is absorbed and the ethanol passes through resulting in 100% ethanol. The ethanol then must be denatured (so it cannot be sold as a beverage) by adding 5% gasoline. It is then ready for blending and resale.

The Stillage

Let's return now to the distillation column. Once the ethanol has been extracted, the water and solids that remain in the distillation column are called the stillage. This would include oils, protein, water, soluble nutrients, and fiber. The stillage is then processed into a number of different livestock feeds including Distiller's Dried Solubles (DDS), Distiller's Dried Grains (DDG), Condensed Distiller's Solubles (CDS), Distiller's Wet Grains (DWG), and Distiller's Dried Grains with Solubles (DDGS).