Conversion of Starch into Sugars

Vijay Singh
*Associate Professor*
Department of Agricultural & Biological Engineering
University of Illinois at Urbana-Champaign, Urbana, IL

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Carbohydrates and Fermentable Sugars

- Carbohydrates, or “hydrates of carbon,” are an important group of naturally occurring organic compounds.
- Commonly these are formed by green plants through photosynthesis.
- Carbohydrates are any of the various compounds comprised of carbon, hydrogen and oxygen, general formula \( C_n(H_2O)_m \).
- Carbohydrates are used to store energy until required by the organism.
  - Sugars, starches, cellulose, glycogen and related substances.
- Saccharides, the simplest form of carbohydrates, consist of single sugar units with five or six carbon atoms in ring form.
  - They are commonly called “sugars” or “sweeteners”.
Carbohydrates and Fermentable Sugars

• Starch and cellulosic compounds are polymeric molecules
  – Made up of basic unit called monomers
  – These monomers are joined together by a chemical bond called a glycosidic link
• Carbohydrates can be divided into four basic classes
  – Monosaccharides
  – Disaccharides
  – Oligosaccharides
  – Polysaccharides
  • Each of these comprises of successively more of the same basic unit or units

Carbohydrates and Fermentable Sugars

• Monosaccharides
  – Glucose and Fructose
  • Can be fermented to ethanol by yeast, only under anaerobic conditions
### Carbohydrates and Fermentable Sugars

- **Diac saccharides**
  - Sucrose and Maltose
  - Sucrose is fructose and glucose molecule linked together
  - Sucrose is obtained from sugar cane and sugar beets
  - Commonly known as table sugar
  - Maltose comprises of two molecules of glucose linked together
  - Both maltose and sucrose are fermentable to ethanol by yeast

- **Oligosaccharides**
  - Are saccharides with more than three but less than eight units
  - Oligosaccharides can not be fermented by yeast to produce ethanol
**Carbohydrates and Fermentable Sugars**

- **Polysaccharides**
  - Polymeric carbohydrates of many thousand of monomeric sugar units linked together through glycosidic linkages
  - Starch, glycogen or cellulose
  - Neither starch or cellulose can be directly fermented by yeast to produce ethanol
  - Must be hydrolyzed to fermentable sugars

**Degree of Polymerization (DP)**

- **Glucose** = DP1
- **Maltose** = DP2
- **Maltotriose** = DP3

- Four or more glucose molecules = DP4+

These can be fermented by yeast.
**Starch Structure**

- **Crystallinity**
  - Packing of amylose and amylopectin within starch granule is not random but is very organized
  - Prevents enzymes to breakdown starch granule
  - Can be disrupted by gelatinization of starch

![Hydrogen Bonding](image)

**Gelatinization of Starch**

- 67°C
- 75°C
- 85°C
**Solubilization of Starch Granules**

- Even at 95°C not all of the starch gets solubilized (pasted or gelatinized)
- Needs to be cooked for 5 minutes at 110°C to completely solubilize starch
- Pasting or gelatinization temperature starts at 60°C, but is not complete until > 105°C

**Dextrose Equivalent**

- Glucose is a reducing sugar
  - Free aldehyde group on carbon-1
Dextrose Equivalent

- In starch molecule

\[ \text{Dextrose Equivalent} \]

- With each hydrolytic cleavage of an alpha 1,4 or alpha 1,6 bonds, one reducing group on a glucose molecule is freed.
- Dextrose equivalent is measure of the percentages of glucosidic bonds that are hydrolyzed.
- DE is determined by measuring the amount of reducing sugars in a sample relative to the amount of dextrose.
- As starch is hydrolyzed, more and more dextrose is produced, and the amount of reducing sugars and DE increases.
**Dextrose Equivalent**

- The standard DE method involves treating a reducing sugar solution with a standard copper reagent and measuring the amount of cupric ion (Cu²⁺) remaining after reaction; the more Cu²⁺ that is reduced to Cu⁺, the higher the DE
- DE of dextrose is 100, representing 100% hydrolysis
- DE of malto-dextrins ranges from 5-20
- Dextrose syrups, which have DE>95 are often referred to as liquid dextrose

**Blue Iodine Color**

- When Iodine complexes with starch, it forms a color complex which is different for amylose and amylopectin
- The goal of the system and enzyme are to solubilize and lower all the starch in the grain—indicated by an amber to yellow iodine test color.
Iodine Color - Facts

- Different chain lengths = different colors
- All color changes occur between Dp\textsuperscript{12} & Dp\textsuperscript{45}
- Six glucose units are required per iodine
- Retrogradation occurs with Dp\textsuperscript{150} - Dp\textsuperscript{200} oligosaccharides

<table>
<thead>
<tr>
<th>Dp\textsuperscript{1-12} Yellow</th>
<th>Dp\textsuperscript{14-34} Orange</th>
<th>Red-Purple</th>
<th>Dp\textsuperscript{36-42} Purple</th>
<th>Dp\textsuperscript{45+} Blue</th>
<th>Blue-Green</th>
</tr>
</thead>
</table>

Enzymes

- Enzymes are a type of protein present in, and essential to, all living things
- Enzymes act as biological catalysts
  - They increase the rate of chemical reactions without undergoing any permanent change themselves
- Enzyme are not consumed in the reaction
  - Can continue to catalyze a reaction as long as the proper reactants are available
- The surface of each enzyme contains various chemical groups that can react with small molecules
  - High degree of specificity
Enzymes

- Comparison of enzymatic and nonenzymatic reaction kinetics

Liquefaction

- Liquefaction is the process of turning starches into smaller molecules called dextrins
  - Alpha amylase (AA) enzyme is needed for liquefaction
  - Granular structure of starch needs to be broken before AA can bring about hydrolysis of starch to dextrins
  - AA breaks randomly breaks alpha 1,4 glucosidic linkages but not alpha 1,6 linkages
Typical Alpha Amylase D.E. Development in Liquefaction

- The rate of D.E. is dependent on conditions mentioned above
- By increasing the dose 50%, the rate increases by 50%
- Mash iodine color should be purple to amber to be “starch negative”—blue color means raw starch is still present.

Saccharification

- New dry grind ethanol plants do Simultaneous Saccharification and Fermentation (SSF)
- Some plants still have separate saccharification process
Saccharification versus SSF

Different Enzyme Actions

- Glucoamylase
- alpha-amylase
- pullulanase
- Reducing End
- fungal amylase or beta-amylase