ABSTRACT

Corn is used by wet millers as a raw material in a process that produces a solution of carbohydrates quite similar to the carbohydrate profile of the wort produced by brewers from barley.

This article reviews methods of manufacture of corn syrups with parallels drawn to the malting and brewing processes. It also briefly examines some global trends in the area of brewing syrups.

Keywords: Adjunct, Corn, Maltose, Syrup, Wet milling.

INTRODUCTION

According to Dr. Lie-Tien Chang at the South China University of Technology the first sweetener created from starch was a syrup produced in China at least about 1,000 B.C. by combining rice and malt. There are still many of these maltose plants in different locations in China using the traditional old method. It was not until the Napoleonic wars that commercial methods were developed for the manufacture of sweeteners from starch. The British naval blockade of France stopped all cane sugar imports. A reward was offered to anyone developing an alternative sweetener to sucrose in an attempt to satisfy the populace’s craving for sweets. In 1811, a Russian chemist by the name of Kirchoff overcooked a mixture of potato starch and sulphuric acid and ended up with a sweet syrupy substance. Kirchoff’s discovery launched the start of a new line of starch-based sweeteners.

Literature on brewing origins mentions dates such as 450 B.C. when Herodotus wrote in some detail about brewing methods. He referred back to 1960 B.C. to an Egyptian process used by Isis. Other reports put the start of brewing at about 5,000 years ago. In light of all this it would appear that corn syrups are still in their infancy.

The process of manufacturing corn syrup brewing adjuncts consists of four basic steps:

1) the acquisition of quality corn and corn steeping,
2) separation of the germ, fibre, gluten (protein) and starch,
3) conversion of starch to syrup,
4) refining of the syrup to a water white concentrate.

The key processes behind each of these steps respectively are:

1) biochemical and physiological response,
2) physical separation methods (i.e., density and filtration based methods),
3) enzymatic or chemical hydrolysis and,
4) carbon and/or ion exchange purification and evaporation.

CORN AND CORN STEEPING

All corn syrup brewing adjuncts have one thing in common and that is corn. Just as the maltster searches for barley with good viability, so the corn wet miller also tries to use corn with good viability.

Figure 1 shows a seed of germinating barley. Such terms as scutellum, aleurone cells, endosperm and husk are used to describe various of the seed’s components.
Figure 2 shows a diagram of a corn kernel with a cross section broken out. As one can see, the same terms are used. Both the corn wet miller and the malster are dependent on a seed to start their respective manufacturing processes and the seeds have quite a lot in common.

The function of any seed is to grow another plant. The purchased seed is hopefully mature, free of insect damage and mold as well as free of any damage from excessive heat during drying. The first stage in a corn wet mill and in the malthouse is called “steeping.” The corn wet miller does not want to have the corn germinate but rather hopes to initiate the biochemical processes that precede germination. The maltster on the other hand will proceed one step further to germination. The maltster pays close attention to the moisture content during steeping, whereas the wet miller does not want to lose valuable starch during this process through oversteeping. Palmer does a thorough examination of papers written on the subject of cellular enzyme sources involved in the breakdown of the endosperm in malting barley. To start the enzyme processes in corn, the seed must be activated by water and heat. As one can see in Figure 2, the water moves along an air path between the hull and the hyaline layer. The water enters the germ via the perforated cutin until the cementing barrier between the term and endosperm dissolves. At this point, the germ floats relatively free and water is now able to enter the endosperm from the germ. The protein-starch structure of the endosperm begins to break down. Since the corn is completely submerged in water, absorption continues until the kernel balloons slightly which separates the hull from the germ and endosperm.

All these processes are inherent in the seed and would proceed to germination if we wanted. If the corn had seen insect or mold damage (normally to the germ), heat damage (normally to the enzyme systems) or was immature, these natural processes would have been severely retarded or non-existent.

Separation of Corn Components

The milling process follows steeping. Table 1 shows the components of the corn kernel.

The objective of the milling process is to efficiently separate corn into the four major components of germ, fibre, starch and protein. This is done via physical separation methods. Figure 3 shows the sequential processing steps in the typical corn wet mill.

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**Table 1 Components of the Corn Kernel**

<table>
<thead>
<tr>
<th>Component</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>16</td>
</tr>
<tr>
<td>Starch</td>
<td>62</td>
</tr>
<tr>
<td>Protein</td>
<td>8</td>
</tr>
<tr>
<td>Fat</td>
<td>4</td>
</tr>
<tr>
<td>Fibre</td>
<td>8</td>
</tr>
<tr>
<td>Soluble Sugars</td>
<td>2</td>
</tr>
</tbody>
</table>

---

**Fig. 2. Cross section of corn kernel.**

**Fig. 3. Processing steps in a corn wet mill.**

The first stage is one wherein the swollen and softened corn is run through a series of coarse grind mills. These mills gently break the kernel open allowing the germ to float free. The freed germ is floated away from the rest of the slurry via a vortex generating device called a cyclone (Fig. 4).

**Fig. 4. Cyclone.**

By virtue of its high oil content the germ is lighter than the remaining fibre, starch and protein. When injected laterally into a confined vortex (i.e., the cyclone) the germ moves to the center and up whereas the other materials move to the outside and down. The germ is then washed and dried. The oil is later extracted from the germ using either a heated screw press or a solvent extraction method.

The process continues with use of a fine grind mill where the particulate material in the slurry is pulverized. This finely ground slurry is passed over screens where the fibre portion is filtered out. This fibre then has steep water (i.e., the protein rich liquid remaining after steeping) added to it and is dried and sold as 21% protein animal feed.

The two major components remaining now are starch and protein. Since the protein fraction is of lower density than that of the starch, one is able to separate and concentrate these over a series of centrifuges (Fig. 5).

Through use of centrifugal force one can:

a) remove excess water from the starch/protein slurry, then
b) separate the starch (which has a greater density) from the protein, then

c) dewater the protein component itself.

The protein carries forward through filtration to remove excess moisture before being dried and is sold as an animal feed containing 60% protein. The starch is further washed through another set of small cyclones and stored in slurry form.

For the reader interested in a more in-depth description of the corn wet milling process, the reference by May is recommended reading.\(^{(14)}\)

Because starch is a polymer of the basic carbohydrate dextrose it can be depolymerized to various degrees resulting in a host of mixtures of an infinite range of compositions. From the paper industry to the fireworks industry one finds examples of starch use in addition to its great versatility in the food industry. These processes might be interesting to a number of readers but digress from the central topic of this article. Readers so interested can pursue the subject by reading a number of texts by Hebeda and Schenck, Knight, Radley, Watson, and Whistler which provide descriptions of the processes used.\(^{(2,10,13,30,31)}\)

For the purposes of this article the starch is ready to be converted to sugars. The conversion of starch to sugars by the corn syrup refiner has several similarities to the mashing process used by the brewher.\(^{(33)}\) Both processes use heat to gelatinize the starch. Subsequently, acid or enzymes are used to convert the starch to sugars. The brewher uses the mixed amylases naturally present in the malted barley. Since this is a mixed enzyme system the brewher has to depend on timed temperature ramps to convert the starch first via the alpha amylases and then by the beta amylases. The corn wet miller will use commercially available amylases, or a combination of these with hydrochloric acid to produce fermentable syrups. These are purified enzymes and thus the wet miller can adroitly add them at the desired step at the desired temperature and pH with less of the difficulties associated with the mixed enzyme system inherent with malted barley. Just as the brewher is developing methods to predict yeast performance\(^{(29)}\) so the enzymologist works to develop mathematical models to predict the performance of the purified enzymes that the corn wet miller uses.\(^{(28)}\)

**CONVERSION OF STARCH TO SYRUP**

We now have the substrate for performing a myriad of reactions. The uses of starch for industrial and food uses are many.
The first step in the conversion of starch to syrup is called liquefaction. The objective here is to convert the starch slurry, which is a mixture of starch particles in water, into a true solution of carbohydrate molecules.

Depending on whether the corn refiner is running an acid or enzyme hydrolysis system, a mixture of starch slurry and acid or starch slurry and enzyme is prepared. This is pumped through a venturi-type jet system into which steam is injected as shown in Figure 7.

![Fig. 7. Steam Jet Cooker.](image)

If an enzyme is used here, it is typically a heat stable alpha amylase sourced from either Bacillus licheniformis or Bacillus stearothermophilus. The "jet cooker" subjects the mixture to a shearing action that ruptures the starch granule. The mix is held at a temperature of about 105 degrees C for about five minutes. The temperature is then reduced to 95 degrees C and held for about one hour. During this holding time, the alpha amylase is breaking down the long chain polysaccharides. At this point, the starch slurry has been converted to a solution of about 10 DE.

DE stands for dextrose equivalent and simply put is a measure of the reducing power (or the average molecular weight size) of the solution. Theoretically, a solution of 100% dextrose would have a DE of 100. A slurry of starch in water would have a DE of 0. Consequently, DE can be thought of as representing the degree of depolymerization of starch.

In the acid system hydrochloric acid is normally used. The pH of the slurry is reduced to about 1.8 and the mixture is again pumped through a "jet cooker." In this case the temperature is taken to 140 degrees C and after starch granule rupture the mixture is held for about ten minutes. Dependent on pH, temperature and residence time, DEs anywhere from 20 to 50 can be obtained. For a brewing syrup this would be the first conversion step and the DE would range anywhere from 20 to 40. Syrups converted by acid alone are very minimally used in the brewing industry. Note that "hydrolysates produced by acid conversion alone are insufficiently fermentable for normal brewing applications being typically in the range of 40-45% fermentable."(33) The extremely harsh reaction conditions of low pH and high temperature combined contribute to the production of furan products such as 5-hydroxymethylfurfural (HMF) and levulinic acid which are produced from actual fission of the glucopyranose rings.(10) Consequently, an acid converted syrup having a DE greater than about 50 to 55 has a bitter taste, placing a limitation on the practical degree of conversion to fermentables attainable by the corn wet miller.

Whether an acid or enzyme liquefaction system is used, it is followed by a second enzyme conversion system. Because the long chain polysaccharides present at this stage are likely to retrograde or bond with each other the second enzyme must be added speedily often by in-line mixing. At this point in the process, a number of possibilities are available to the manufacturer. If one wants a high maltose low dextrose syrup, one would liquefy the starch using an enzyme as outlined above and then choose either a fungal alpha amylase from Aspergillus oryzae or a beta amylase from a plant source for the second stage of conversion.(9) The α,β glycosidic bond in the polysaccharide is not hydrolyzed by these enzymes hence a pullulanase can be used should one desire higher levels of maltose and fermentables.(10) If a high dextrose syrup is required, a glucoamylase from Aspergillus niger is used. For a syrup in the 60-65 DE area, a mixture of fungal alpha amylase and glucoamylase would be used. A low DE maltodextrin which Wilson suggests would be of use in providing mouthfeel in a low alcohol beer would be converted via enzyme at the point of liquefaction.(33) A wide range of carbohydrate profiles are possible dependent on the settings on the jet cooker and the selection of post liquefying enzyme as shown in Table 2.

![Table 2](image)

<table>
<thead>
<tr>
<th>Liquefaction</th>
<th>DE</th>
<th>10</th>
<th>10</th>
<th>20</th>
<th>42</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
<td>Enzyme</td>
<td>Enzyme</td>
<td>Acid</td>
<td>Acid</td>
<td>Enzyme</td>
<td></td>
</tr>
<tr>
<td>Saccharification</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sacch. Enz. #1</td>
<td>Fungyl-Alpha</td>
<td>Beta-Amylase</td>
<td>Fungyl-Alpha</td>
<td>Gluco amylase</td>
<td>Gluco amylase</td>
<td></td>
</tr>
<tr>
<td>Sacch. Enz. #2</td>
<td></td>
<td>Pullulanase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbohydrate Profile</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP1</td>
<td>8</td>
<td>1</td>
<td>8</td>
<td>35</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>DP2</td>
<td>56</td>
<td>71</td>
<td>42</td>
<td>30</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>DP3</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>13</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>DP4</td>
<td>20</td>
<td>10</td>
<td>34</td>
<td>22</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Table 2
Conversion Methods and Resultant Carbohydrate Profile
Though there is a wide choice of carbohydrate combinations available to the brewer, much recent work seems to be suggesting that a high maltose (approximately 55%) low dextrose type of syrup is gaining preference. The phenomenon of "glucose repression" or "catabolite repression" has been investigated by several researchers. The ready acceptance of glucose by the yeast seems to lead to a consequent lag phase in the fermentation of other sugars when there is a high initial level of glucose. Maltotriose, on the other hand, is the last sugar to be removed. This can be done either by carbon or ion exchange resins or both combined. Carbon leaves a water white solution, 50-60% maltose and 15-20% maltotriose. Consequently, it is not surprising that a 55% maltose type syrup adjunct does perform well.

**REFINING OF SYRUP**

Once the brewer has converted the melted barley starch to sugars, the mix carries forward to the kettle and then fermentation. Once the corn wet miller has converted the corn starch, the fourth and last stage of the process starts - that is refining.

The pH of the syrup is first adjusted to the isoelectric point that maximizes the insolubility of any residual proteins present. For an acid converted syrup, this pH would be in the 4.8 to 5.2 range. For an enzyme converted syrup, it would be near 4.5 pH. The proteins precipitate and help coagulate any remaining corn oil and fibre. These solids are filtered out.

The second main refining process is soluble compound removal. This can be done either by carbon or ion exchange resins or both combined. Carbon leaves a water white syrup which still has all the salt components in solution. Salts present would be predominantly sodium chloride but also a host of other elements are present including sulfites which have come under intense scrutiny by regulatory agencies in recent years. Ion exchange resins, however, not only yield a water white solution but also remove all salts except for trace concentrations. Table 3 shows the differences in concentration of a number of selected compounds and elements between a carbon refined syrup and an ion exchanged syrup.

**Table 3**

<table>
<thead>
<tr>
<th>Attributes</th>
<th>Carbon Refined</th>
<th>Ion Exchanged</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>1.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Heat Color</td>
<td>3.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Conductivity</td>
<td>1111</td>
<td>7</td>
</tr>
<tr>
<td>Ash, %</td>
<td>0.4</td>
<td>0.01</td>
</tr>
<tr>
<td>Protein, ppm</td>
<td>51</td>
<td>ND</td>
</tr>
<tr>
<td>Chlorides, ppm</td>
<td>1100</td>
<td>2</td>
</tr>
<tr>
<td>Sulfites, ppm</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Sodium, ppm</td>
<td>950</td>
<td>4</td>
</tr>
<tr>
<td>Phosphorous, ppm</td>
<td>60</td>
<td>ND</td>
</tr>
<tr>
<td>Potassium, ppm</td>
<td>20</td>
<td>ND</td>
</tr>
<tr>
<td>Calcium, ppm</td>
<td>90</td>
<td>ND</td>
</tr>
<tr>
<td>Iron, ppm</td>
<td>1</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND = non-detectable

**GLOBAL TRENDS**

Casting our eyes globally, we will see some syrup usage patterns that really are not surprising when one considers the local farm economies. Table 4 lists various regions of the world and the corresponding adjunct types used.

In Australia and New Zealand, sucrose from cane sugar is used at an 8% to 15% level with the remainder up to a 40% adjunct level coming from a high maltose or high DE syrup. The starch source can be either corn or wheat.

In South America, 50/50 blends of rice/55% maltose syrup up to a 45% adjunct level are used in Argentina. In Brazil, syrup adjunct is used at a 15% to 40% level with the syrup being a 55% maltose from an acid-enzyme conversion process. In Central America, 63 DE corn syrup is used at a 40% adjunct level. Surprisingly, this syrup is produced from a straight acid conversion process.

In Asia, syrup adjunct is not common. Adjunct used in Japan is all compacted corn starch. Malaysian and Chinese brewers use rice.

In Africa, starch is used in Kenya. Nigeria, which has no foreign exchange, uses sorghum. South Africa uses a 55% high maltose treated with amyloglucosidase to reduce non-fermentables to a 25% level. Dextrine is also used.

The adjunct in Europe is predominantly an enzyme/enzyme converted 70% maltose syrup at 20-30% levels. The exception here is Germany where adjunct is used only in exported beer.

In North America, the favored adjuncts are a 62 DE high conversion corn syrup at up to 40-50% adjunct levels and dextrin in light beers in the United States. Canada uses, in the vast majority of cases, an enzyme/enzyme converted 55% high maltose syrup at 20-40% levels.
### Table 4
Regions vs. Adjunct Types(32)

<table>
<thead>
<tr>
<th>Region</th>
<th>Adjunct Type</th>
<th>Adjunct Level (%)</th>
<th>Plant Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia &amp; New Zealand</td>
<td>sucrose &amp; 62DE or 55% maltose</td>
<td>to 15 to 30</td>
<td>cane sugar wheat/corn</td>
</tr>
<tr>
<td>Argentina</td>
<td>rice &amp; 55% maltose</td>
<td>to 22 to 22</td>
<td>corn</td>
</tr>
<tr>
<td>Brazil</td>
<td>55% maltose</td>
<td>15-40</td>
<td>corn</td>
</tr>
<tr>
<td>Central America</td>
<td>63 DE syrup</td>
<td>to 40</td>
<td>corn</td>
</tr>
<tr>
<td>Japan</td>
<td>compacted corn starch</td>
<td></td>
<td>corn</td>
</tr>
<tr>
<td>Kenya</td>
<td>starch</td>
<td></td>
<td>corn</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Sorghum</td>
<td></td>
<td>corn</td>
</tr>
<tr>
<td>South Africa</td>
<td>55% maltose Dextrose</td>
<td>25</td>
<td>corn</td>
</tr>
<tr>
<td>Europe</td>
<td>70% maltose</td>
<td>20-30</td>
<td>corn/wheat</td>
</tr>
<tr>
<td>U.S.A.</td>
<td>62 DE syrup Dextrose</td>
<td>to 40</td>
<td>corn</td>
</tr>
<tr>
<td>Canada</td>
<td>55% maltose</td>
<td>to 40</td>
<td>corn</td>
</tr>
</tbody>
</table>

As one can see, there are a great number of types and uses of brewers syrups. The human race has, over the years since 4,000 B.C., come a long way in its ability to manipulate biotechnology to suit its purposes. Work goes on investigating different types of sugars as adjuncts and new concepts to design breweries.(5,22,23) In another 100 years, it might be commonplace to see plants with a photosynthesis unit at one end generating carbohydrates, a synthesis unit producing polymers and flavor compounds, a fixed bed, immobilized cell, ethanol generating station in the middle, and a plethora of pleasant elixirs being packaged up at the end.

**ACKNOWLEDGEMENTS**

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