

# SUGAR SYRUPS FROM MAIZE

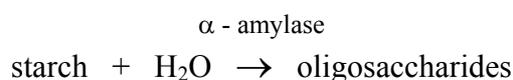
Starch is the substance that many plants use to store energy, and consists of large molecules made up of glucose units joined together. New Zealand Starch Products Ltd. break maize starch into glucose and maltose to form sugar syrups in a four step process.

## **Step 1 - Starch extraction**

Maize is steeped for 36 hours in a weak solution of sulfurous acid to soften the kernel before the protein, fibre and oil are separated from the starch by a series of grinding and screening steps. The raw starch is further refined by washing.

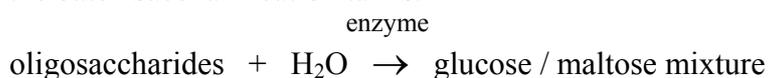
## **Step 2 - Liquefaction**

The starch paste is held at around 100°C for about 100 minutes while it is broken down to short chains of glucose molecules called oligosaccharides by an enzyme called alpha amylase:



## **Step 3 - Saccharification**

During saccharification a second dose of specialised enzyme is added to break the carbohydrate down into glucose and maltose molecules. The composition of the enzyme mixture is adjusted according to the specification of the product. Conversion can take up to 35 hours in the batch saccharification tanks.



## **Step 4 - Refining**

The syrup is filtered to remove any remaining proteins and fats and then bleached to give the final product.

## **Acid conversion**

An alternate process also used by New Zealand Starch Products Ltd. involves mixing a small amount of acid with the starch slurry after **Step 1** and allowing the acid to break down the starch. This is done instead of **Steps 2 and 3** and is easier and cheaper but more difficult to control.

Throughout the syrup manufacturing process the laboratory monitors the product composition. Most of this testing is done using high performance liquid chromatography.

## **INTRODUCTION**

New Zealand Starch Products Ltd, situated in Onehunga, Auckland, has been operating on its present site since 1958. Originally they simply purified starch paste, first from wheat and later from maize. In 1970 the company commissioned a glucose refinery to convert some of this starch to a sugar syrup to replace the imported syrups then used by the confectionery industry. In 1980 this operation was extended to include the manufacture of sugar syrups by enzyme hydrolysis - a process in which the manufacturer has much greater control over the composition of the end product.

At present, the equivalent of 35,000 tonnes of maize is converted annually to 24,000 tonnes

of starch. Approximately half of this starch is further processed into sugar syrups.

### Uses of starch and converted starch

Starch is produced for a highly diverse market ranging from the paper and adhesive industries to the food industry. Food starches are also modified to meet specific needs for meat and fruit pie fillings, UHT<sup>1</sup> dairy products, salad dressing and other related food products.

The sugar syrups are manufactured in a wide range of strengths, enabling them to be used in many different foods. The syrups produced include:

- a high-sugar fermentable syrup (96 DE<sup>2</sup>) that is used in alcohol production, brewing, vinegar manufacture and yeast manufacture,
- a high dextrose<sup>3</sup>/maltose syrup that is viscous but unlikely to crystallise and is used in fruit canning and ice-cream production,
- a high maltose syrup for the manufacture of high boiled confectionery,
- and a lower conversion syrup (17 DE) which has low sweetness and is of value as an extender and nutritional source in soups, beverages etc.

### Carbohydrate chemistry<sup>4</sup>

Before discussing starch processing, it is helpful to run over some basics of carbohydrate chemistry. Carbohydrates are generally classed into two groups, simple and complex. Simple sugars (monosaccharides) are carbohydrates that cannot be hydrolysed into smaller molecules. Glucose is an example of a simple carbohydrate. Complex carbohydrates are made of two or more simple sugar units. Maltose (a disaccharide made up of two glucose molecules) and starch (a polysaccharide made up of several thousand glucose molecules) are both complex carbohydrates. **Figure 1** gives the structure of a monosaccharide, a disaccharide and a trisaccharide. In aqueous solution glucose exists as an equilibrium mixture of  $\alpha$  and  $\beta$  epimers with small amounts of the open aldehyde.

Starch is a naturally occurring energy source in seeds, roots and tubers. There are two sorts of starch: amylose and amylopectin. Amylose consists of approximately 2000 glucose units linked into linear chains by  $\alpha$ -1,4' linkages<sup>5</sup> and makes up 15 - 29% of the total weight of the starch. The remainder of the starch is amylopectin, a polymer of several hundred thousand

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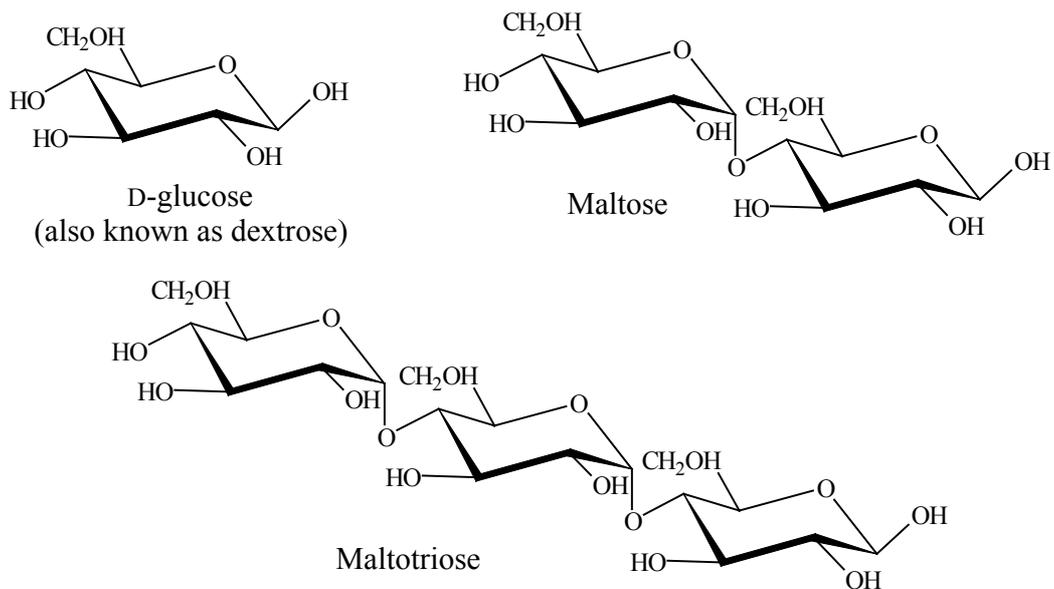
<sup>1</sup>Ultra heat treated.

<sup>2</sup>'DE' stands for 'dextrose equivalent' and is a standard measure of syrup strength. The dextrose equivalent is determined by establishing the concentration of reducing sugar (see sugar article) in a syrup, and from that working out the percentage of the solids in a syrup that would be dextrose if all the reducing sugar was dextrose. A rating of 96 DE means that 96% of the solids would be dextrose if all the sugar in the sample were dextrose.

<sup>3</sup>Note that dextrose is simply an older name for glucose.

<sup>4</sup>Further information about carbohydrates is given in the sugar article.

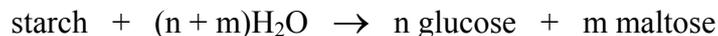
<sup>5</sup>The  $\alpha$  refers to the orientation of the bond, and the 1,4' indicates that the bond is between carbon one of one molecule and carbon four of another.



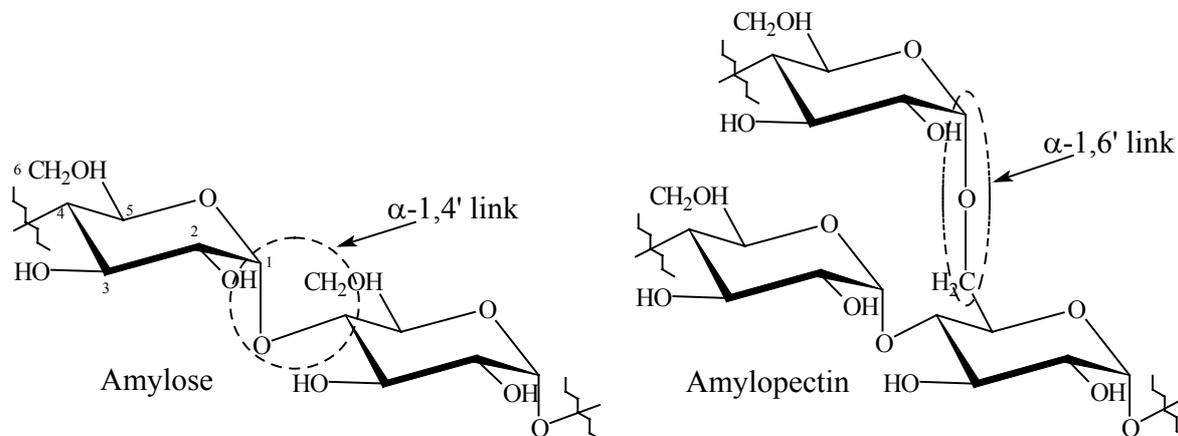
**Figure 1 - Some common sugars**

glucose units. Amylopectin includes some  $\alpha$ -1,6' linkages, linking some residues to three other residues and hence forming branched chains. These structural differences are shown in **Figure 2**.

When water is added, starch can be hydrolysed back to glucose, although either acid or an enzyme must be present for any significant degree of hydrolysis to take place. Normally the starch suspension is also heated before hydrolysis to cause the polymers to unwind, exposing reactive centres. The reaction occurring can be represented by:



Glucose and maltose (**Figure 1**) are the products of the reaction. Maltotriose, which is made up of three glucose units, is an intermediate formed during hydrolysis. The relative amount of the different products depends on reaction conditions such as reaction duration, temperature, pH and the presence of enzyme.



**Figure 2 - Structures of amylose and amylopectin**

## THE MANUFACTURING PROCESS

New Zealand Starch Products Ltd. use two processes to convert starch to glucose. The one more commonly used is enzyme hydrolysis. In this process starch is extracted from the maize grains and then hydrolysed by two different enzymes in two process steps. The syrup is then refined, packaged and sold.

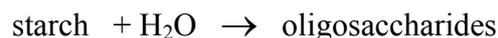
### Step 1 - Starch Extraction

The major components of the maize kernel (protein, germ oil, fibre and starch) are separated during starch extraction. The starch is further processed and the other components sold as by-products.

Starch extraction begins with steeping the maize grains in a weak solution of sulfurous acid to soften the kernel and help break the chemical bonds between the proteins and the starch. The soluble solids are leached from the grain, concentrated through evaporation and sold to feed compounders and fertiliser companies as a high protein concentrate. Next, oil is expelled from the germ to produce a crude maize oil which is sold for further refining before being used in the food industry. The starch and gluten are then separated from the fibre and from each other. The fibre is used in the animal feeds industry and the gluten is sold as cornflour. The starch is washed and concentrated to 40 % solids. About half of it is sold as either unmodified or chemically modified starch, and the remainder is converted to sugar syrups.

### Step 2 - Liquefaction

Liquefaction is the hydrolysis of the starch to oligosaccharides: glucose polymers of up to ten glucose residues. This is done by holding the starch slurry at 105°C for seven minutes at pH 6.0 - 6.5 in the presence of a heat stable alpha amylase enzyme. Small quantities (ca. 50 ppm) of a calcium salt are also added to the jet cooker to help stabilise the enzyme. During the seven minutes the starch hydrates and is broken down both by the shearing forces in the jet cooker and by the action of the enzyme:

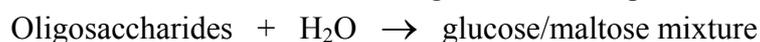


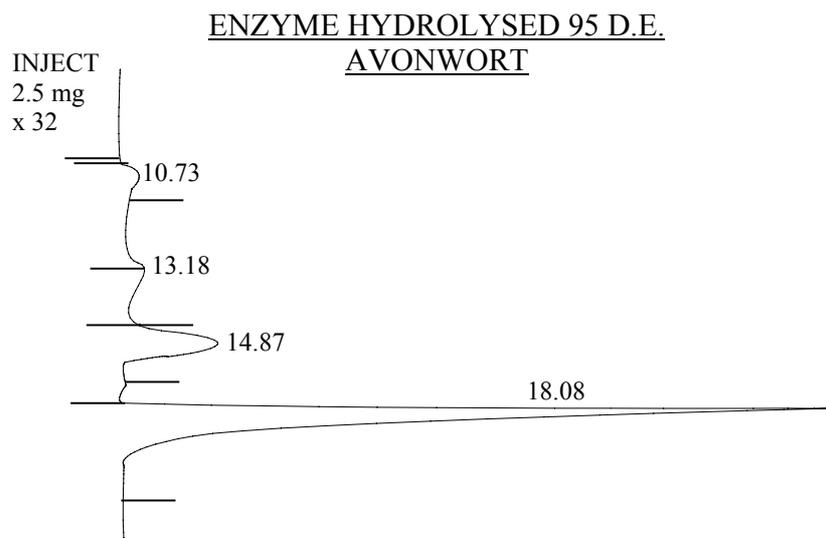
After this initial liquefaction the mixture is cooled to 97°C and transferred to a multichamber reactor, where the solution is held for 90 minutes to reach a dextrose equivalent of 10 - 12 units. As the name implies, liquefaction lowers the viscosity of the solution. By this means the more specialised reactions occurring in the next step can be more easily controlled.

### Step 3: Saccharification

After liquefaction the pH is lowered to between 4 and 5 and the liquid is cooled to around 60°C. This inactivates the liquefaction enzyme and creates conditions suitable for the saccharification enzymes.

A specialised enzyme or enzymes are then added. The enzymes added depend on the type of syrup that is to be produced, i.e. how much of the free sugar should be glucose, how much should be maltose etc. For example, if a high glucose syrup is required then an amyloglucosidase is added, but if a high maltose syrup is preferred then a fungal alpha amylase could be added. If a high sugar syrup including both these sugars is required then both enzymes will be added. The reaction occurring follows the equation below:





DATE: July 15 1995      PRESSURE: 600.0  
 COLUMN: Ion exchange      FLOW: 0.70 mL / min  
 MOBILE PHASE: Water      CHART SPEED: 0.50 cm / min  
 TEMPERATURE: 80°C

EXTERNAL STANDARD QUANTITATION: % Area

PEAK #	AMOUNT	RT	%	
1	17.28390	10.73	0.89	Dextrins
2	18.48330	13.18	0.96	Maltotriose
3	134.49900	14.87	6.98	Maltose
4	1754.91000	18.08	91.15	Glucose
TOTAL	1925.18000		99.99	

**Figure 3 - Chromatogram of 95 DE enzyme hydrolysed syrup for fermentation<sup>6</sup>**

Conversion to the desired sugar chromatogram can take up to 35 hours.

#### Step 4 - Refining

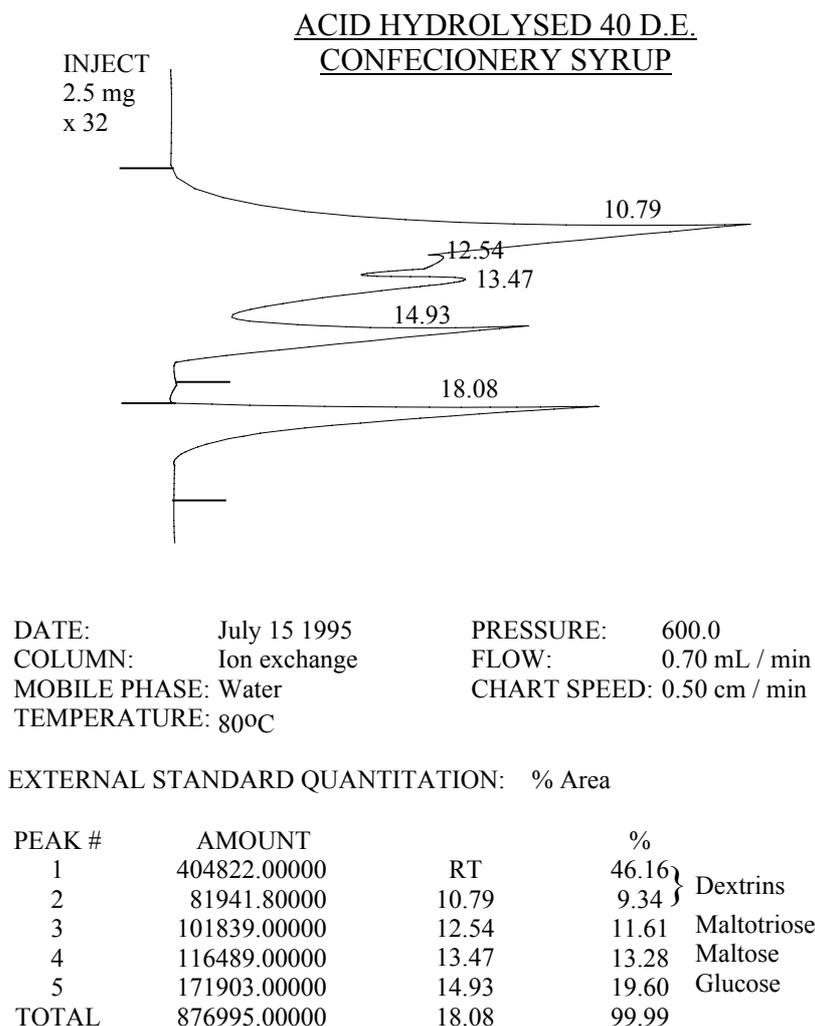
The raw sugar syrup requires refining to remove impurities such as residual proteins and fats. This is done by passing the solution through a rotating vacuum filter coated with diatomaceous earth then decolourising it with activated carbon. The product is then concentrated to the desired solids level (typically 75 - 85 % solids) and packaged for sale.

#### Acid Conversion

Although the enzyme hydrolysis of starch allows the composition of the syrup produced to be carefully controlled it is a time-consuming and expensive process. For this reason, some syrups are still made using the more traditional acid hydrolysis method. Here small quantities of hydrochloric acid are added to a 40 % starch slurry. Under controlled conditions of acidity, temperature, pressure and time the starch partially hydrolysed into a mixture of glucose polymer fragments. The extent of conversion depends on the reaction conditions, but a typical acid converted syrup would have a dextrose equivalent of 40. Acid converted syrups find a ready market in the pharmaceutical and confectionery industries for

<sup>6</sup>Note that RT refers to retention time in minutes, and the pressure is given in psi.

applications where the exact composition of the sugar syrup is unimportant.



**Figure 4 - Chromatogram of 40 DE acid hydrolysed syrup for confectionery**

The differences of specificity between acid converted syrups and enzyme converted syrups are shown in **Figures 3** and **4**. As can be seen in **Figure 4**, the relative concentrations of the different sugars cannot be controlled, and a random distribution of mono, di, tri and higher saccharides results<sup>7</sup>. In contrast, **Figure 3** shows an enzyme hydrolysed syrup that has been designed to have consistently high glucose levels.

## THE ROLE OF THE LABORATORY

The laboratory is involved with product analysis throughout the process to ensure strict quality control. The main technique used in high performance liquid chromatography, a technique which is explained in detail below.

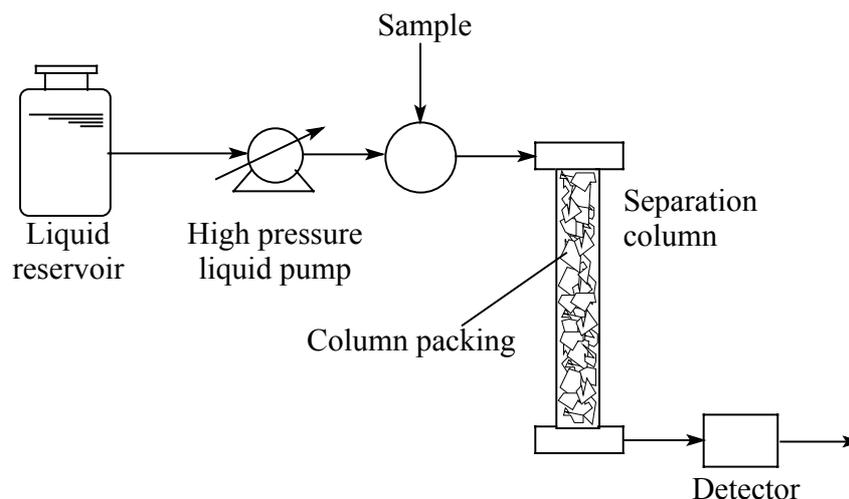
### The theory behind high performance liquid chromatography

An essential tool in sugar syrup process design and quality control has been **High**

<sup>7</sup>Note that dextrins are polymers of between four and ten glucose residues.

**Performance Liquid Chromatography (HPLC).** This technique has allowed the manufacturer to monitor the exact sugar composition from batch to batch, ensuring product consistency from the start.

All forms of liquid chromatography are differential migration processes, where sample components are selectively retained by a stationary phase. Components can be separated by means of different solubility, polarity etc. by the selection of suitable column packing (stationary phase) and eluent (mobile phase). Stationary and mobile phases are chosen so that different components of the sample have different affinities for the stationary phase and hence travel at different rates enabling the composition of a sample to be found by measuring the retention time of components. A diagram of an HPLC system is given in **Figure 5**.

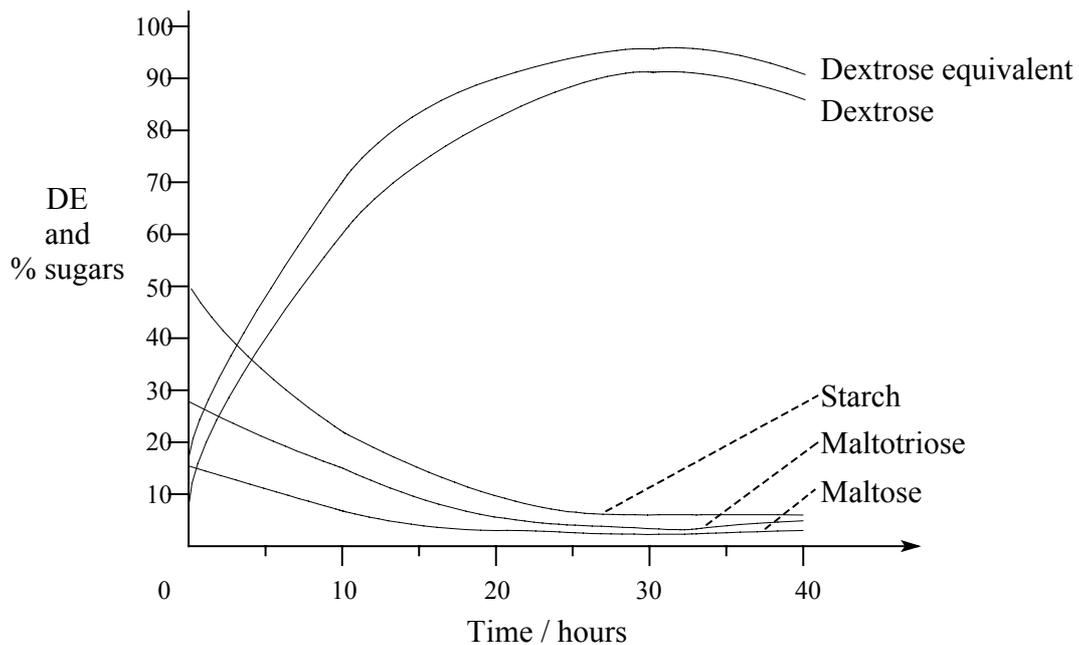


**Figure 5 - Simplified diagram of an HPLC system**

Unlike traditional liquid chromatography, which is slow and generally insensitive, modern HPLC is comparable to other analytical techniques. In early liquid chromatography, the mobile phase moved through the column under the force of gravity and flow rates typically were a few tenths of a millilitre per minute. To achieve even these flow rates, relatively large packing particles were used, which, in turn, limited column efficiency. This problem was overcome by designing system to operate at pressures of up to 2500psi (ca. 300atm). At these high pressures, adequate flow rates are obtained even with packing particles as small as 2 to 3  $\mu\text{m}$  in diameter. Liquid chromatography using high efficiency columns at high pressure has come to be known as HPLC. HPLC is used extensively in the pharmaceutical, fine chemical production and food industries.

### **HPLC in sugar syrup analysis**

The primary use of HPLC measurements is in quality control, to ensure that the syrups have the composition stated on their labels. However, these measurements are also useful for developing new processes for manufacturing other syrups. By taking measurements throughout the saccharification step, graphs such as **Figure 6** can be constructed and the optimum conversion time calculated. For example, in Avonwort (a high dextrose syrup) the dextrose content peaks after 32 hours (**Figure 6**) and then certain side reactions reduce both the DE and the dextrose content of the syrup. This graph thus shows that Avonwort should be left in the saccharification tanks for 32 hours for maximum conversion.



**Figure 6 - Graph of Avonwort Saccharification**

Written by J. W. Beishizen (NZ Starch Products Ltd.) and revised by F. K. Clarke (NZ Starch Products Ltd.).

Edited by David Yuen and Heather Wansbrough with reference to:

- Hargis, L.; *Analytical Chemistry*; Prentice-Hall; 1988.