

# LECTURE 5: ENZYMATIC DEGRADATION OF POLYSACCHARIDES – STARCH PRODUCTION OF DEXTRINS AND MALTODEXTRINS

## 1 Introduction

Starch is the commonest storage carbohydrate in plants. It is used by the plants themselves, by microbes and by higher organisms so there is a great diversity of enzymes able to catalyse its hydrolysis. Starch from all plant sources occurs in the form of granules which differ markedly in size and physical characteristics from species to species. Chemical differences are less marked. The major difference is the ratio of amylose to amylopectin; e.g. corn starch from waxy maize contains only 2% amylose but that from amylo maize is about 80% amylose. Acid hydrolysis of starch had widespread use in the past. It is now largely replaced by enzymatic processes. Acid hydrolysis requires the use of corrosion resistant materials which gives rise to high colour, salt and ash content (after neutralisation), needs more energy for heating and is relatively difficult to control.

## 2 Amylases

Enzymes involved in degradation of starch belong to hydrolases (Glycosidases). Amylases are the most important starch degrading enzymes. They hydrolyze the starch to oligosaccharides and simple sugars. Of the two components of starch, amylopectin presents the great challenge to hydrolytic enzyme systems. This is due to the residues involved in  $\alpha$ -1,6-glycosidic branch points which constitute about 4 - 6% of the glucose present. Most hydrolytic enzymes are specific for  $\alpha$ -1,4-glycosidic links yet the  $\alpha$ -1,6-glycosidic links must also be cleaved for complete hydrolysis of amylopectin to glucose. The following are the most important enzymes.

### 2.1 $\alpha$ -amylase

$\alpha$ -amylase is an endoenzyme. It hydrolyzes the  $\alpha$ -1,4 glycosidic bonds randomly along the chain. Amylopectin is hydrolyzed to oligosaccharides that contain two to six glucose units. The branch points are over jumped. A mixture of amylose and amylopectin is hydrolyzed into a mixture of dextrans, maltose and glucose. Amylose is completely hydrolyzed to maltose. Calcium ions are required for its activation.  $\alpha$ -amylase cleaves both amylose and amylopectin molecules producing oligosaccharides. Oligosaccharides of 6-7 glucose units are released from amylose.  $\alpha$ -amylase activity leads to a rapid decrease in viscosity of starch solution. Enzymatic hydrolysis is increased by the gelatinization of starch.  $\alpha$ -amylase hydrolyzes the  $\alpha$ -1,4-bonds of amylose and amylopectin in a random manner, liberating small units with free non-reducing end groups. Low molecular weight dextrans are formed.

### 2.2 $\beta$ -amylase

$\beta$ -amylase also hydrolyzes the  $\alpha$ -1,4-bonds of amylose and amylopectin, removing maltose units from the non-reducing end of starch in an orderly fashion. The  $\alpha$ -amylase and  $\beta$ -amylase do not cleave the  $\alpha$ -1,6-linkages in amylopectin.

### 2.3 Glucoamylase

Glucoamylase is used in combination with an  $\alpha$ -amylase to produce D-glucose syrups and crystalline D-glucose. The enzyme acts upon fully gelatinized starch sequentially releasing single D-glucosyl units from the nonreducing ends of amylose and amylopectin molecules.

## 2.4 Pullulanase

Pullulanase hydrolyzes  $\alpha$ -1,6 glucosidic bonds in polysaccharides, e.g. in amylopectin, glycogen, and pullulan. Linear amylose fragments are formed from amylopectin.

## 3 Production of Dextrins and Maltodextrins

**Dextrins:** Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of starch. Dextrins are mixtures of polymers of D-glucose units linked by  $\alpha$ -(1 $\rightarrow$ 4) or  $\alpha$ -(1 $\rightarrow$ 6) glycosidic bonds. They are less complex than starch.

Dextrins can be produced from starch using enzymes like amylases or by applying dry heat under acidic conditions. The latter process is used industrially, and also occurs on the surface of bread during the baking process, contributing to flavour, colour, and crispness. Dextrins are produced by heating starch with hydrochloric acid or phosphoric acid at levels of 0.15 to 0.17 % to attain desired degree of polymerization. Dextrins produced by heat are also known as pyrodextrins. During the hydrolysis of starch to maltose by amylases, starch is broken down to dextrins of decreasing molecular weight before all the starch is converted into maltose.

Dextrins have adhesive and film forming properties. They are used as binders, fillers, encapsulating agents and carriers of flavour. Dextrins are used as a crispness enhancer for food processing, in food batters, coatings, and glazes.

**Maltodextrins:** Maltodextrins are polysaccharides that are used as a food additive. They are produced from starch by partial hydrolysis and are usually found as a creamy-white hygroscopic spray dried powder. Maltodextrins consist of D-glucose units connected in chains of variable length. The glucose units are primarily linked with  $\alpha$ -(1 $\rightarrow$ 4) glycosidic bonds.

Maltodextrins are typically composed of a mixture of chains that vary from three to seventeen glucose units long. Maltodextrins are classified by DE (dextrose equivalent) and have a DE between 3 to 20. The higher the DE value, the shorter the glucose chains, the higher the sweetness, the higher the solubility and the lower heat resistant. Above DE 20 it is glucose syrup. DE of a product of hydrolysis is its reducing power as a percentage of the reducing power of pure dextrose. Maltodextrins of lowest DE are non hygroscopic, while those of highest DE tend to absorb moisture.

Maltodextrins are easily digestible, being absorbed as rapidly as glucose, and might be either moderately sweet or almost flavourless. Maltodextrins provide bulk to food systems. They are commonly used for the production of sodas and candy. It can also be found as an ingredient in a variety of other processed foods. Maltodextrins are a common adjunct to beer brewing to increase the specific gravity of the final beer product.