Enzymes - benefits and opportunities
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41st Autumn Conference - 7th/8th October 1996

To examine the opportunities and benefits that enzymes offer us in the baking industry it would be useful to first remind ourselves what an enzyme Is and which types are both useful to us and permitted by legislation.

Enzymes are biological catalysts which under certain conditions of pH, temperature and hydration are able to 'digest' the food, or substrate, upon which they find themselves. In general terms, for the breadmaking process, enzymes either modify and make better use of their substrate or are used to remove those which may be detrimental. The substrates in the case of breadmaking are all contained in wheat flour.

Before examining the substrates in detail let us look at the legislation which has regulated the use of enzymes in bread in the UK over the last 25 years.

Prior to 1984 'enzyme active preparations' were permitted but between 1984 and 1996 a restriction to alpha amylases and proteinases was imposed. During this period however there was increasing interest in the use of and need for the use of hemicellulases. This was particularly brought about by the loss of the use of potassium bromate and the increasing use of European wheats. Our industry, working through BATA and UKBICC, established a case for need for hemicellulases which resulted in their being permitted in the UK from January this year. Additional representations to MAFF resulted in a further relaxation being brought about in July by the total deregulation of enzymes used in the baking industry.

The composition for wheat flour shown in the diagram details the substrates available. In outline the enzymes in use are amylases, which interact with starch; hemicellulases, which modify the pentosan or hemicellulosic fraction; proteases and glucose oxidase, which modify protein structure, and lipase and lipoxygenase, with their influence on crumb colour and endogenous lipids.

This paper will concentrate on what I believe to be the two most important areas, which will involve first the pentosan or hemicellulose fractions and then starch.

Wheat flour for breadmaking consists primarily of the ground endosperm of the wheat kernel. The cells of the endosperm have cell walls largely composed of hemicellulose (mainly arabinoxylan and arabinogalactan) and comprises about 2.5% of flour. There is a predominance of pentose sugars in this hemicellulose and hence it is convenient to refer to it as pentosan.

The pentosans present in wheat flour may be classified into two groups: approximately half are soluble and these are mainly arabinoxylans and arabinose. The other half are insoluble; these are also arabinoxylans but are more highly branched with inter-chain covalent linkages.

It was noted in the past that fungal alpha amylases of nominally identical strengths would perform differently in bread doughs and this was eventually attributed to differing side activities in the commercially purchased enzyme cocktail. Eventually hemicellulases were identified as side activities and linked directly with the differences in performance of the commercial alpha amylases.

The term hemicellulase refers to those enzymes which specifically degrade hemicellulose. They may act via an exomechanism, whereby hemicellulose is degraded by successive removal of terminal sugar residues but more commonly they are of the endo- type whereby the polymer is cleaved at random.

The approximate distribution of water in bread dough is 50% through starch, 27% through protein and 23% through pentosans. Therefore the pentosans take approximately 10 times their own weight of water and must have a major effect on the water distribution and viscosity of a dough.

The soluble pentosans have a beneficial effect which has been attributed to their contribution to gas retention of the dough. Yeast in a dough produces carbon dioxide which dissolves in the aqueous phase and then diffuses into gas cells formed by the gluten structure.

Soluble pentosans, in the presence of mild oxidising agents, possibly even air, interact with the gluten proteins to give a macromolecular complex which inhibits carbon dioxide diffusion out of the dough which would result in the collapse of proof volume.

When we examine how the gluten structure is formed in dough we should note that:

- S-H groups must come close to one another for the formation of disulphide bonds
- we should have good hydration of the protein (gluten)
- the protein should form a continuous gas-tight film around each carbon dioxide bubble.

Insoluble pentosans are detrimental to bread quality. Due to their high water absorption properties they swell, form large agglomerates and so disrupt the continuity of the complex gluten films which surround gas cells.

It is known that enzymically modified insoluble pentosans are beneficial to bread quality. It is postulated therefore that when a hemicellulase enzyme complex is added to a dough the insoluble pentosans are de-polymerised, rendering them more soluble. In doing so therefore, we have decreased the detrimental insoluble pentosan effect and increased the beneficial soluble effect. Overall this increases the gas retention properties of the dough, making better use of the gluten protein and hence this will improve the characteristics of the final bread product.

In the latter stages of baking, as the loaf structure starts to set, the beneficial hemicellulose gel is believed to break down, thus releasing water to enable swelling of the starch.

Let us now examine the amylases which act on the major component of wheat flour, starch.

Alpha amylases are categorised into their fungal, cereal or bacterial origins and in that order are of increasing thermal stability. They are endo-cleaving, attacking mid-chain, whereas amyloglucosidase and maltogenic amylase are exo-acting, progressively cleaving single units from the end of starch chains.

It is a maltogenic amylase which is of benefit to us in the retardation of staling but to obtain some insight into its action we must look more closely at the baking process.

Beyond 65°C we start to get the deactivation of fungal amylase which up to this time has helped to keep the dough mobile and capable of further expansion or oven lift, and at the same time has aided the production of sugars on which the yeast feeds.

Starch gelatinisation starts to take place and as it does so it swells with water and exudes amylose. The starch granules and amylose then form a 3D matrix and the loaf volume is set.

The staling of bread is due partly to the crystallisation of starch as each granule loses water. Additions of emulsifiers such as GMS can inhibit this process and give short term prevention of staling. The other part of the staling mechanism is the cross-linking of the exuded amylose fibrils with protein creating a more rigid structure.

The exo-acting maltogenic amylase has the ability to reduce the length of the amylase fibrils, thus reducing their potential to cross-link with protein and therefore significantly reducing the staling of bread.

In summary, enzymes offer the baker the benefit of modifying the components of flour such that they perform better and give the baker, miller and dough conditioner manufacturer, working together as a team, the opportunity to use flours previously thought unsuitable for breadmaking.