

low as 3.5. But the acidity is not responsible for the improving effect, since the latter is retained even after neutralization (Kulp *et al.*, 1985).

The resulting hypochloride is a strong oxidant, reacting with flour pigments and other components.

ClO₂ is a green gas that dissolves in water. It does not react with water, but with unsaturated chemical bonds and other reducing groups.

Chlorine and its derivatives affect pigments (bleaching), starch (partial breakdown of amylose and amylopectin that alters the pasting properties), proteins (improved solubility), fats (saturation) and pentosans (degradation, and hence reduced water absorption) (Kulp *et al.*, 1985).

Heat-treated flours have a certain similarity to chlorinated flour when combined with wheat starch, but chlorinated flour still achieves much better results (Seibel *et al.*, 1984).

18.3.9 Calcium Peroxide

Calcium peroxide is yet another commonly used oxidizing agent. Upon heating, CaO₂ releases oxygen that can be used in various oxidation reactions, for instance oxidation of ascorbic acid or water to hydrogen peroxide with the help of glucose oxidase. The effect of calcium peroxide is not very pronounced, but it is appreciated for its surface-drying property. For this reason it is always used in conjunction with more effective oxidizing agents. Calcium peroxide increases the pH of the dough. In certain limits this can be beneficial, particularly if the flour has high amylase activity. Larger amounts reduce the volume yield and cause excessive browning.

18.3.10 Other Oxidizing Agents

Tab. 86 summarizes the oxidizing agents that have been suggested for use in flour improvement. The "action in the dough" is based on the author's experience. For some of the substances, different information can be found in the literature. Some substances are rather risky, for instance acetone peroxide that tends to explode when exposed to even slight shock or friction. The substances not mentioned in the text above do not offer any considerable benefit as compared to the standard oxidizing agents.

Tab. 86: *Oxidizing agents suggested for flour treatment, and their typical reaction pattern*

Oxidizing agent	Action in dough	Remarks
Potassium bromate	Slow	
Potassium iodate	Fast	
Calcium bromate	Fast	
Calcium iodate	Fast	
Azodicarbonamide	Very fast	
Calcium peroxide	Slow	
Ammonium persulfate	Fast	
Potassium persulfate	Fast	
Acetone peroxide	Very fast	Highly explosive
Chlorine & chlorine dioxide		Reacts in flour
Hypochlorite		Reacts in flour
Benzoyl peroxide	Slow	Reacts in flour and dough
Ascorbic acid	Fast	Over-dosage: softening
Dehydroascorbic acid	Fast	
Cystine	Slow	Over-dosage: softening
Hydrogen peroxide	Fast	
Oxygen	Slow	

18.4 Reduction and Dough Softening

Gluten that is too short is difficult to process and results in a low volume yield, since the gas formed by the yeast is not able to expand the dough as it should. The problem can be solved by using substances with reducing properties that break down surplus disulphide bridges and thus give the protein molecules more room to move. Short gluten properties may result from the varieties used, but they are sometimes caused by the storage and processing of the grain (overheating) or the

use to which the flour is put (for instance, freezing shortens the gluten). Some applications, in particular biscuits and crackers, require extensive softening of the dough for optimum processing and product properties.

18.4.1 Cysteine

A suspected "opponent" of AA is cysteine, a simple amino acid that is a constituent of all proteins and produced either by hydrolysis of extremely cysteine-rich proteins such as those from feathers or hair and complex purification procedures, or by synthetic means.

As cysteine splits disulphide bridges like other reducing agents, one would expect it to counteract the effect of AA if used at the same time. Initially it was only discovered empirically that this is not the case (Kieffer *et al.*, 1990). In fact AA and cysteine complement each other. One makes the gluten firmer, while the other ensures adequate elasticity. This is possible – as was proved later – because the two substances act on different constituents of the gluten and attack it at different sites.

The use of these flour improvers, in frozen doughs especially, makes it necessary to add large doses of both substances, for on the one hand good fermentation stability it required

(AA) and on the other hand the deep-freezing process shortens the gluten, a problem that can be solved at least in part by cysteine. The amount of cysteine added is often two-thirds of the quantity of AA.

Cysteine is usually sold as L-cysteine *hydrochloride*, anhydrous or monohydrate, as it is more easily synthesized and has better water solubility in the latter form.

Sodium nitrocyanoferate/ammonium hydroxide can be used for detection, for instance on the wet pekar sample, but this is an unreliable method as the blue spots are sometimes difficult to see and fade quickly.

18.4.2 Reducing Yeast Preparations

Yeast also produces reducing substances, but these are only released when the cells die. There are now preparations made of inactivated, killed yeast on the market that have a softening effect similar to that of cysteine (Fig. 114). But as the dose required is about 100 times higher (100 - 1,000 g to 100 kg of flour), even the lower price (about 1/10 or even less) cannot make up for it. This is true even of so-called glutathione yeast, a variant with a very high reductive potential. So one might say that the main advantages of inactivated yeast are in the field of labelling.

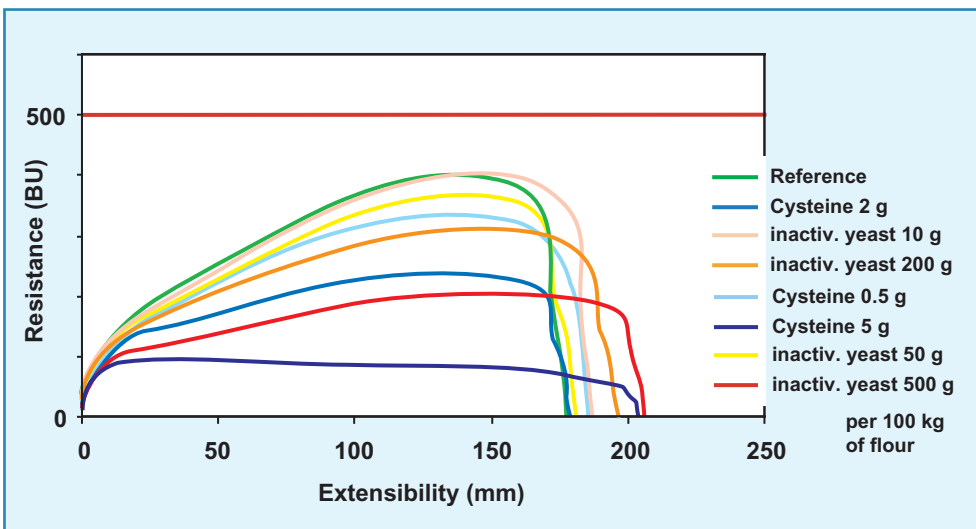


Fig. 114: The effect of reducing agents (L-cysteine or inactivated, glutathione-rich yeast) on the Extensogram (45 min)

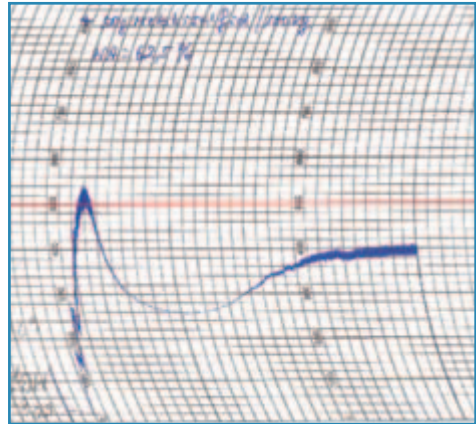
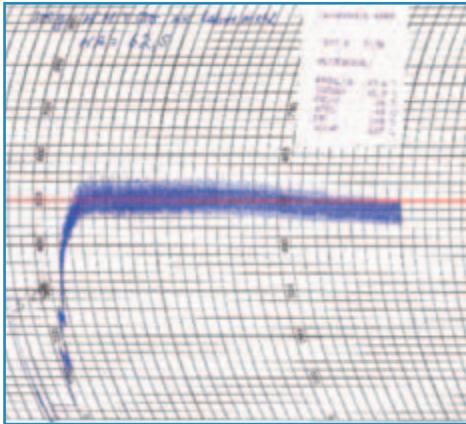


Fig. 115: Farinographs of German soft wheat flour without (left) and with 500 ppm SMB (right)

18.4.3 Sodium Metabisulphite and Sulphur Dioxide

These powerful reducing agents are especially good at breaking down the gluten fast and reliably (Fig. 115), which greatly simplifies the production of biscuits, crackers and wafers. But as these substances are known to destroy vitamin B₁ (thiamine) and to cause health problems in sensitive persons, their use should be avoided. They also impart a sulphur taste which can only be tolerated as long as no comparison to products without sodium metabisulphite (SMB) can be drawn. The dosage of SMB varies from 10 ppm to more than 1,000 ppm. Whereas 10 ppm are hardly effective, concentrations above 100 ppm are detectable sensorily, and concentrations larger than 500 ppm even cause a clear off flavour. Alternatives based on enzymes are now available; they achieve the same results but react rather more slowly and often require some process adjustment and hence knowledge on the part of the user. On the other hand, certain enzyme preparations based on proteases and amylases permit the reduction or omission of expensive ingredients, e.g. sugar, milk or whey powder, and therefore offer economic advantages.

Furthermore, sulphites are often not permitted, or they are restricted to low dosages or have to be declared in the labelling. Enzymes, on the other hand – natural proteins classified

as processing aids – are not subject to restrictions and do not have to be declared in most countries.

18.4.4 Other Substances with Reductive Potential

Tab. 87 lists substances commonly used in bread production which have a certain potential for reducing disulphide bonds to thiol groups. Even malt flour has been found to have a softening effect through its reductive potential (Tab. 88). Ascorbic acid acts as a reducing agent at elevated levels which cannot be completely oxidized by ascorbate oxidase because of limited oxygen in the dough. The threshold depends largely on the processing conditions.

Tab. 87: Reducing substances used in baking applications

Reducing agent	Dosage (g/100 kg flour)
L-cysteine	0.5 - 4
Glutathione	1 - 8
Inactivated yeast	50 - 500
Sodium metabisulphite	1 - 50
Ascorbic acid	> 25
Malt flour	50 - 200
Sorbic acid	5 - 50

Tab. 88: Reducing potential of malt flour ^a

Product		Diastatic power (DP)	SH concentration ^b (μM/g)	SH conc. as Cys-HCl ^c (ppm)
Wheat flour	(0.55% ash)	< 1	2.0	32
Wheat malt	(high diastase)	19.8	15.1	240
Wheat malt		10.6	5.6	90
Rye malt		10.2	8.4	130

^a Modified from Lösche, 2002 ^b Sulfhydryl (thiol) concentration

^c Sulfhydryl (thiol) concentration as cysteine hydrochloride equivalents.

Pure cysteine hydrochloride (anhydrous) equals 1,000,000 ppm Cys-HCl.

18.5 Enzymes

Enzymes have been in common use in the food industry for years. In contrast to most other applications in which enzymes find their way into foods, the enzymes in this case do not react at the place where they are added, namely in the mill; they do not take effect until the baker adds water.

This difference in time and place is a great

challenge to the flour treatment sector in general, but in the case of enzymes it is an especially complex matter. On the other hand enzymes are highly specific; that is, if they are pure enough they act on selected targets and only have to be added in small quantities. Moreover, they are entirely natural as they can only be obtained from micro-organisms by way of fermentation or from vegetable or animal tissue and fluids by means of extraction (Fig. 116).

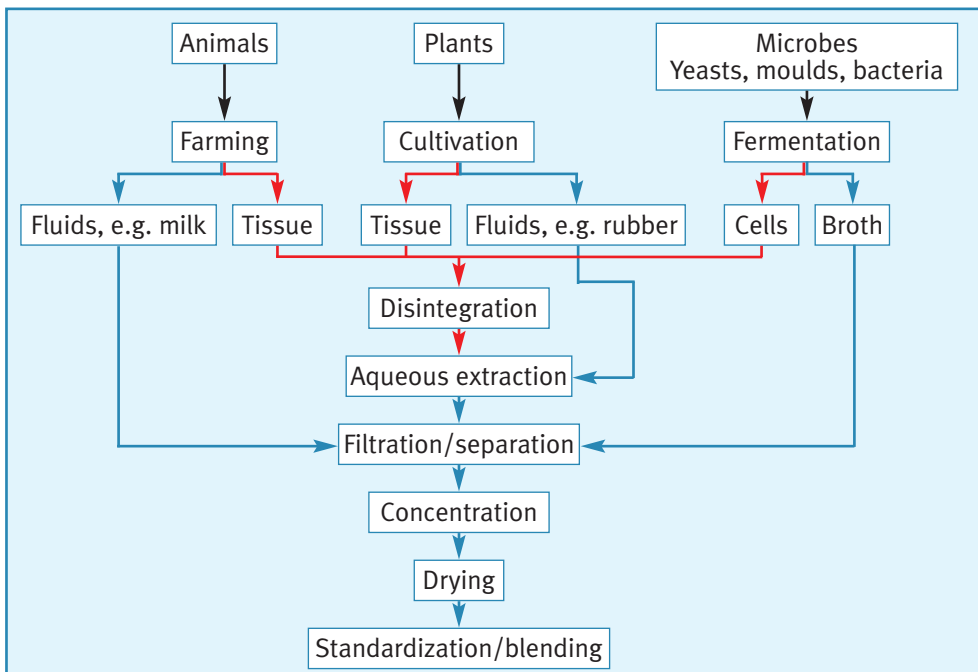


Fig. 116: Diagram showing the principle of enzyme production