Dough Reduction Chemistry

Cysteine is unique among the protein amino acids because it has a sulphhydryl group at the end of the molecule. Cysteine is important to dough reduction chemistry because it occurs in the gluten protein from flour, in the tripeptide glutathione from yeast, and in free amino acid form as a synthetic reducing agent.

O               O
||              ||
HSC'H2CHCOH     NH2
L-cysteine

O               O
||              ||
HSC'H2C—NHCH2COH

O                   NH
||               |
HOCCHH2CH2C      NH2
     O
Glutathione

The significance of cysteine's sulphhydryl group is that two of them from different proteins can be oxidized to one molecule of cystine, with the creation of a disulfide bond between them. When gluten molecules become linked (oxidized) during breadmaking, the dough strength increases but its extensibility decreases. During mixing, these linkages are broken mechanically to provide the extensibility needed for moulding. The process is reversible, and the gluten matrix reforms during the later stages of proofing and baking.

SH   SH

The disulfide bonds in gluten that are broken mechanically during mixing can also be broken chemically by a series of reactions with cysteine or glutathione.

A Guide to Reducing Agents

Reducing agents (like L-cysteine) are a type of dough conditioner used to reduce mix time and improve extensibility. They are used in bread to increase bakery throughput and to adjust for flour variation and in a number of other yeast and chemically leavened applications.

FUNCTIONALITY

During mixing, the gluten in the flour is stretched and pulled apart so that it can be reformed during proofing and baking to provide the needed strength and structure. Reducing agents act like mixing to reversibly break down gluten so that once they have been used up the gluten reforms. This mechanism is the opposite of oxidizing agents, which build up gluten.

Reducing and oxidizing agents can be used separately, or a reducing agent can be used with a slow oxidizing agent (like potassium bromate) to increase gluten breakdown early in the process and gluten reformation later in the process. When reducing agents are used with fast oxidizing agents (like iodate or azodicarbonamide), they counteract each other.

Bread dough requires a combination of strength, extensibility, and tolerance that depends mostly on flour quality, water absorption, and mixing conditions. Reducing agents are used especially with high-strength flour and high-speed processes to reduce mix time, lower energy input, improve machinability, and improve loaf volume. Frozen bread dough is a special case where short mix time is especially important because it helps improve yeast stability.

Extensibility is important in other yeast and chemically leavened applications including pizza, tortillas, cookies, saltines, and other crackers. Reducing agents decrease the elasticity that can cause shrinkage or curling after these products are formed.

CHARACTERISTICS

Protein-based reducing agents include cysteine, glutathione, and yeast. Cysteine is the most commonly used reducing agent in bread. It is an amino acid that is usually produced synthetically as L-cysteine hydrochloride, is usually added at the mixer, and acts quickly. Glutathione is a peptide that contains cysteine but is not generally available in its pure form. It functions similarly to L-cysteine but is potentially more effective because it can react more times. Yeast is a natural source of glutathione. Special nonleavening yeasts are used as reducing agents in the same applications as L-cysteine.

Sulfites are commonly used reducing agents in cookies and crackers. Their active ingredient is the bisulfite ion that is obtained from sulfur dioxide or from one of its salts, such as sodium bisulfite. Sulfites

REDUCING AGENTS AND MIX-TIME REDUCERS

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>USE LEVEL</th>
<th>CONSIDERATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-cysteine</td>
<td>10–90 ppm</td>
<td>Most-common reducing agent</td>
</tr>
<tr>
<td>Glutathione</td>
<td></td>
<td>Not commercially available</td>
</tr>
<tr>
<td>Nonleavening yeast</td>
<td>0.05–1.0%</td>
<td>Natural source of glutathione</td>
</tr>
<tr>
<td>Bisulfite</td>
<td>20–100 ppm</td>
<td>May require finished product labeling</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>100–200 ppm</td>
<td>For closed system continuous mix</td>
</tr>
<tr>
<td>Sorbic and fumaric acids</td>
<td>10–90 ppm</td>
<td>Limited use as reducing agent</td>
</tr>
<tr>
<td>Protease</td>
<td></td>
<td>Not a true reducing agent</td>
</tr>
</tbody>
</table>
Dough Reduction Chemistry (Continued)

known as disulfide interchange. The reactions are shown here, with R and R’ representing the two gluten molecules and with cysteine as the reducing agent:

\[R-S-S-R' + cysteine \rightarrow R-S-S-cysteine + R'-SH\]
\[R-S-S-cysteine + cysteine \rightarrow cysteine + R-S-S-cysteine + SH\]

These reactions reduce the number of cross-links between the gluten subunits proportional to the number of cysteine or glutathione molecules added and are reversible so that the degree of relaxation can be controlled. The reaction is similar with either cysteine or glutathione, except that with glutathione less is required. This is because an enzyme present in flour converts glutathione disulfide into two glutathiones with free SH groups that can participate in further disulfide reactions. Because no analogous enzyme exists for cysteine sulfide, each cysteine SH can be used only once.

International Perspective:
FRENCH BREAD AND MODERN FLOUR

Parts of the French baking industry have modernized rapidly since the 1970s, with increased production of pan bread and frozen dough on high-speed lines with short processes. In response, French wheat growers and flour millers have selected wheat varieties for increased strength. But the increase in strength has come at the expense of extensibility and has made optimum mixing and moulding more difficult to achieve.

The problem of decreased extensibility is worsened by traditional product types and legal restrictions. Baguettes must be long and regular in shape with well-defined top cuts. Croissants and brioches require thin dough laminations without tearing. For these and other products, French regulations prohibit most reducing agents, including L-cysteine, sulfites, and sorbic acid. Techniques such as decreased dough temperature and reduced proofing time help somewhat by slowing oxidation reactions but create other problems.

Since 1990, French bakers have begun using increasing amounts of nonleavening yeast as a dough conditioner for high-strength/low-extensibility flour. The products have a high glutathione content so that they act as reducing agents and are permitted under French regulations as “deactivated fermentative agents.” Versions are available for artisanal and industrial applications and for a range of products including bread, pastry, puff pastry, and retarded dough. The same products are used in other European countries with similar flour/product/regulatory requirements and in the U.S. and Canada for bromate replacement and other applications.

Fermaid® Dough Relaxers

FERMAID® DOUGH RELAXERS are nonleavening yeast products that reduce mix time and improve dough extensibility. They are natural replacements for L-cysteine hydrochloride, sulfites, and other chemical reducing agents in breads, rolls, pizza, pretzels, tortillas, and crackers. Fermaid® dough relaxers are processed to maximize available glutathione—a naturally occurring yeast peptide that acts as a reducing agent. They function similarly to L-cysteine but with the added benefit of being label-friendly.

For breads and rolls, Fermaid® dough relaxers can be used to reduce the mix time required for high-strength flour or high water absorption. They give a dough that is smoother and easier to handle at the moulder, with good flow in the pan. Finished volume is high and uniform, with a fine, uniform internal structure. Using Fermaid® dough relaxers to optimize mix time minimizes the effect of flour changes, improves machinability, and avoids both “bucky,” undermixed doughs and sticky, overmixed doughs.

Fermaid® dough relaxers are available in versions for a range of products and applications. Those with lower glutathione levels are used at higher doses so that they also contribute flavor and crust color. Those with higher glutathione levels are used at lower doses to provide dough relaxation without contributing taste or flavor. Formulations with other dough conditioner ingredients are optimized for specific applications including pizza, pies, crackers, tortillas, and wraps.

A Guide to Reducing Agents (Continued)

destroy the vitamin thiamine, are inhibitory to yeast, cause sensitivity reactions in some people, and require special label declarations if used in the U.S. at levels in the finished product above 10 parts per million.

Ascorbic acid (vitamin C) is used as a reducing agent only in certain closed continuous mix applications. In the presence of oxygen it functions as an oxidizing agent, but in the absence of oxygen, as a reducing agent. It can be used in coated form for increased stability as a component of bread improvers and dough conditioners.

Other acids that have been suggested as reducing agents, but are not commonly used, include sorbic acid and fumaric acid. They are part of a group of “activated double-bond compounds” and are more commonly used as preservatives. These acids are inhibitory to yeast and less economical than other synthetic reducing agents.

Proteases are used to decrease mix time and increase elasticity but are not reducing agents. They are natural enzymes that break down gluten irreversibly and must be used with careful attention to dose, time, and temperature to avoid overconversion.

Baking Update

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