Biochemical Effects of Storage Atmospheres on Grain and Grain Quality

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Abstract

Developments in grain storage technology have meant that insect damage may now be reduced to minimal levels by modifying the storage atmosphere. In these atmospheres, the commodity and its environment (storage atmosphere, temperature, and water activity) are the major factors determining the changes in quality that take place during storage. Recent work has shown that, given knowledge of temperature, water activity, atmosphere, and duration of storage, changes in the quality of both paddy and milled rice (as measured by change in kernel yellowness) can be predicted. This model of change in quality may also be useful in understanding some aspects of postharvest yellowing of paddy rice and other damp-harvested commodities prior to storage. Other research has shown that the model can be used to predict quality changes in wheat, and that similar models may be applicable to maize (corn), barley, and mung and soybeans. Storage temperature has the greatest effect on quality, with water activity also very important. Carbon dioxide has generally little effect on grain quality, whilst increases in oxygen concentration have a small deleterious effect. A quantitative appreciation of the effects of these factors will allow design of storage systems that will best retain grain quality.

NSECT resistance to pesticides and consumer version to pesticide residues have prompted onsiderable research into alternative pest ontrol techniques in the last decade.)evelopments in the technology of long-term torage of grain have meant that it is now ›ossible to store dry cereals for long periods ompletely free of insect infestation without the ıse of residual pesticides. The use of either ontrolled atmospheres (CA) or fumigants in ealed storages offers economically attractive lternatives to pest control procedures based on he use of residual pesticides. In both CA and umigation, an insecticidal atmosphere is naintained in a sealed storage enclosure for ufficient time to kill all insects present. The ;rain is subsequently maintained sealed in the ·nclosure, which provides a barrier to einfestation. High levels of carbon dioxide, low levels of oxygen, or the addition of phosphine can all be used as the insecticidal atmosphere.

When properly used, these techniques provide grain storage free from insects and residues. For example, the use of carbon dioxide sealed under plastic covers has been shown to be highly effective for milled rice and paddy rice (Annis et al. 1987). Long-term storage (greater than six months) using this technique has been implemented in Indonesia to provide buffer stocks and to help regulate domestic rice prices (Suharno 1986). The technique is being used with considerable success in Western Australia for the protection of wheat destined for export (Ripp 1984; Anon. 1987). In a properly constructed enclosure, no live insects can be found after storage, and grain held in this way seems to remain in good condition for long periods.

Until a timely review on the quantitative effects of controlled atmospheres (CA) on the

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quality of stored grain (Banks 1981), there was a notable lack of quantitative information on the interaction between grain quality and the storage environment. The need for better estimates of the effects of oxygen and carbon dioxide on grain quality, and their interactions with temperature and moisture content were highlighted (Banks 1981; Faure 1986). Since Banks' review, considerable progress has been made in quantifying the effect of storage on quality changes in wheat, rice, maize, and barley for atmospheres containing lowered concentrations of oxygen or increased concentrations of carbon dioxide. Large scale trials, and in some cases commercial development of CA storage have been carried out in Australia (Anon. 1987), China (FAO 1982; Wang and Tang 1986), Indonesia (Suharno 1986), Singapore (Annis, personal communication), U.S.A. (Jay and D'Orazio 1983), Malaysia, the Philippines, and Thailand (Annis 1990). The aim of this paper is to briefly summarise some of this progress in the maintenance of quality, and to outline a possible general approach to understanding the changes in quality which take place in storage in the absence of insects and moulds.

There are many potential advantages of developing a quantitative understanding of the effect of storage on quality. Some of the more important aspects are listed below.

1. Changes in the quality of grain in storage could be predicted from knowledge of the grain storage temperature, moisture, atmosphere, and initial grain quality. This is particularly relevant for sealed storage where monitoring quality changes during storage is impractical.

2. This would then provide a rational basis for manipulation of the commodity or storage environment to enhance the development of desirable quality factors or to retard the development of undesirable traits (Gras et al. 1989). For example, in some parts of the Philippines, slightly aged rice ('Laon') is said to display better organoleptic properties and commands a price premium in the marketplace. Careful commodity management could exploit this opportunity for 'adding value' to rice in storage.

3. Quantitative data on the rate of change of grain quality are necessary for benefit–cost analyses of the various pest control strategies, such as fumigation, pesticide treatment, and CA storage. Work to relate quality to price is under way in the Philippines (Umali and Duff 1988; Abansi and Duff 1988), but more research is required in this area. In practice, CA techniques involve higher capital outlay but can have lower maintenance costs and yield more grain of higher quality at the end of prolonged storage. Consequently, CA storage is usually considered a long-term storage option.

4. A quantitative description of the storage processes may provide a better understanding of the underlying chemical processes involved in grain quality change. This information will enable rational assessment of which strategies provide optimal management of grain in storage. This understanding may also be applicable to changes which take place during postharvest handling processes, such as during drying, handling while wet, or the delays before drying which are common in humid tropical regions. The model of the effects of drying processes on grain quality could be incorporated into models of grain drying processes to help optimise the design of grain drying systems.

Approaches to Quantifying Changes in Grain Quality

The objective of quantifying quality data is to enable characterisation of changes in quality over the possible range of storage parameters. In CA storage, these parameters include the grain and quality of interest, storage temperature, grain moisture content, atmospheric composition, and storage period. In order to assess the effects of each factor, it is necessary to vary one storage factor whilst holding the others constant. This implies taking measurements of quality at various times throughout storage under each set of storage conditions. Further, there is a need for replication given the usual inherent variation in grain quality data. Consequently, any serious attempt to quantify the effect of storage conditions on grain quality requires a large body of experimental work. The data are then fitted to a mathematical model, which allows the calculation of quality changes for situations within the range of conditions covered by the experimental work.

There are two general approaches to this type of modelling. The first is empirical model fitting where the best model that can be found is applied to the data. An example of this approach is the model used by Ellis and

Roberts (1980a) to describe declining germination in various grains (equation 1),

$$v = a - t/(10^{b - c.m - d.T}) \qquad (1)$$

where v is the probit of the percentage viability, t is storage time, m is moisture content (percent wet basis), T is temperature (°C), a is a constant dependent on the seed lot, and b,c,d are species dependent constants. Whilst this technique usually describes the data well, it provides no understanding of the underlying processes involved.

The second approach is the adoption of models with a theoretical basis. Recently, Gras et al. (1989) described yellowing in rice during storage using the model shown in equation (2),

$$k = ae^{b/T}(a_w)^c[O_2]^d \qquad (2)$$

where k is the rate of change (Hunterlab b units/day), T is absolute temperature (K), a_w is water activity, $[O_2]$ is the oxygen concentration in mole/m^3, and a,b,c,d are constants. This model is derived from simple chemical kinetics theory and is commonly used to describe the rate of a reaction in terms of the concentrations of reactants.

With either approach to modelling, the change in quality is quantified in terms of the storage conditions. The end result is an equation which can be used (subject to experimental limits and error estimates) to assess the effects of various storage conditions on changes in the quality factor of interest.

The methods of modelling represented by equations (1) and (2) incorporate the effects of water in different ways. The use of moisture content in equation (1) is attractive because moisture content is readily and commonly measured. The use of the water activity, as shown in equation (2), has the advantage that water activity reflects the actual availability of the water in the grain, both to microorganisms which might grow on the grain, and for chemical and biochemical processes within the grain. At water activities below 0.65, the growth of storage fungi is virtually eliminated, a very desirable state for grain that is to be stored for long periods of time.

The relation between moisture content and water activity is commodity dependent. This can be seen for such diverse crops as maize, flaxseed, milled rice, and white wheat, which have moisture contents of 12.9, 7.9, 13.4, and 11.8% respectively at 25°C and 60% equilibrium relative humidity (Hukill 1963). Commercially, the moisture content of cereals has particular value for the grain trade because it provides a guide to the amount of dry matter being bought and sold. For traders or agencies involved in the storage of grain, the water activity (a_w) or equilibrium relative humidity (ERH) of the grain is a more relevant quantity.

Effect of CA Storage on Quality in Rice

Germination

Viability of cereals during storage typically declines in a sigmoidal manner as a function of time. In most cases, this trend is well represented by the cumulative normal curve (Ellis and Roberts 1980b; Moore and Roos 1982). A commonly used measure of the rate of loss of germination is the reciprocal of the time for a 50% loss in viability ($1/t_{50}$), calculated using the probit transformation (Finney 1980).

Roberts (1961) stored rice at a range of temperatures and moisture contents, and hermetically sealed in air, nitrogen, oxygen, and carbon dioxide, and measured loss of viability as a function of time. The effects of the storage gases were not included in the mathematical model, but it was found that lowered oxygen levels were generally beneficial, whereas the effect of carbon dioxide was ambiguous. More recently, Bason et al. (1987) stored two cultivars of Australian paddy at a range of temperatures, one water activity (0.6), and a graded series of oxygen and carbon dioxide levels that were held constant throughout storage. Grain viability data were fitted to the equations

$$\ln(t_{50}) = a + b/T + c[O_2] \qquad (3)$$

and

$$\ln(t_{50}) = d + f/T + g[CO_2] \qquad (4)$$

where $[O_2]$ is the percent oxygen and $[CO_2]$ is the percent carbon dioxide in the storage atmosphere (dry basis), T is absolute temperature, and $a, b, c, d, f,$ and g are constants. It was found that low oxygen slightly increased the mean lifespan retention period, whereas atmospheres containing carbon dioxide were slightly deleterious to lifespan compared to those without. The magnitude of these effects was minimal compared with that of temperature, and unlikely to be of sufficient concern to either warrant the technically difficult maintenance of low oxygen atmospheres (<1% oxygen) or prohibit the use of carbon dioxide in large scale storage.

Further work (unpublished) has indicated that the rate of loss of germination (i.e., $k = 1/t_{50}$) can be fitted to a model in the form of equation (2), which also incorporates the effects of water activity. As before, the effects of temperature and water activity were large compared with that of gas concentration. This implies that strategies to maintain grain viability should focus on cooling and drying, whilst altered atmospheres may be used to maintain insect control.

Yellowness

Gras et al. (1989) stored two cultivars of milled rice under controlled conditions where the temperature range was 35°–60°C, water activity 0.4–0.8, oxygen concentrations 0.2 –100% (dry basis), and carbon dioxide 7.5–60% (dry basis). They demonstrated that yellowing, as measured by the Hunterlab b value, was well described by the rate equation (2). The kinetics of the yellowing were consistent with non-enzymic browning as the cause of the overall increase in yellowness. The coefficients indicated that, over the range of storage conditions used, temperature was the major determinant of the rate of yellowing, followed by water activity. Oxygen concentration had a minor effect, and carbon dioxide no significant effect. This has allayed previous concerns that carbon dioxide may induce yellowing in rice.

Recent work (Bason et al. unpublished) has indicated that yellowing rate in stored paddy c.v. Pelde is very similar to that of milled Pelde. Further, the model predicts rates of yellowing reasonably consistent with the limited data available in the literature. These results suggest that the model may be applied generally to other cultivars of rice, but further work is required to confirm this.

The model has several applications. For example, the common problem of 'stackburn' results from heating in paddy which has been allowed to stand in moist piles. The model indicates that temperature is the most important factor in yellowing of grain, so some method of cooling the grain bulk (for example, by increasing the surface area to volume ratio or by turning the grain piles) would reduce the incidence of the problem when drying is impossible. Alternatively, controlled heating could be used to accelerate the formation of 'aged' characteristics (such as reduced stickiness) which are preferred in countries such as the Philippines and Singapore. The problems of yellowing before drying are highlighted by the model, which predicts that significant yellowing can be expected in very wet rice held for as little as 24 hours at 45°C. This can be judged from Figure 1, where the calculated time to minimum discernible change in colour (0.3 b* units; Billmeyer 1962) is plotted against the storage temperature for selected storage water activities.

Under the conditions of the studies described above, the growth of fungus could not have been a factor in the colour development. This is not to say that fungal infection does not play a part in the yellowing process. Indeed, fungal infection would be expected to lead to the accumulation of reducing sugars and amino groups as the result of the action of amylolytic and proteolytic enzymes released during the normal course of the growth of the fungus. The increased concentration of the reacting materials would be expected to lead to accelerated

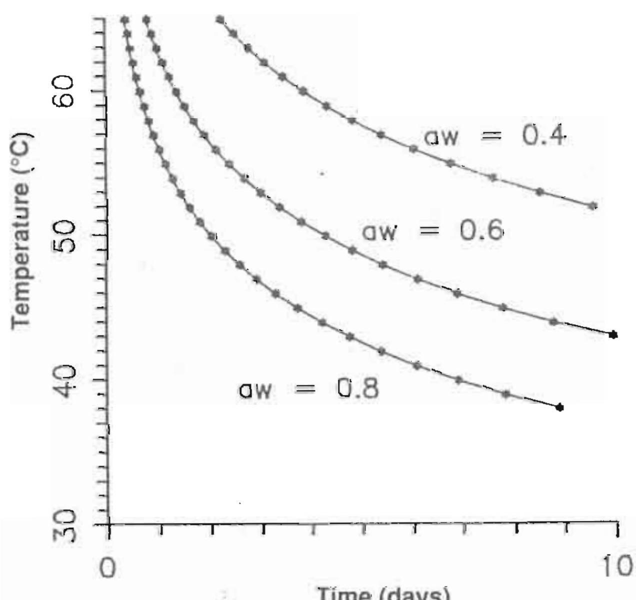

Fig. 1. Calculated time to minimum perceptible change in colour (0.3 Hunterlab 'b' units).

yellowing in the affected kernels. This is probably the basis of the successful 'Potential Yellows' test (Phillips et al. 1984, 1988), in which incubation at elevated temperature and water activity is used to predict the proportion of grains which might turn visibly yellow during extended storage.

Available Lysine Content

Lysine is the first limiting amino acid in rice (Juliano 1985). Widespread experience in the livestock industry has shown that not all the lysine in some cereals and feedstuffs is biologically available (Sauer and Ozimek 1986). Measurements of 'available lysine' provide an estimation of the lysine available for metabolism (Hurrell and Carpenter 1976; Walker 1979). Although controversial, such measurements are routinely made in the livestock industry. Measurements of available lysine in samples of milled rice with a range of yellowness resulting from varying periods of storage confirmed that changes in the yellowness of the rice (Minolta b* value) were closely correlated (r = – 0.77, 32 samples) with the levels of available lysine (Fig. 2). The loss of available lysine concurrent with the development of the yellow coloration provides support for non-enzymic browning as the mechanism of the yellowing reaction. This reaction is widely observed in many food products and consists of a complex series of reactions between protein or non-protein amino groups and reducing sugars. It requires some mobility of the reacting species, and

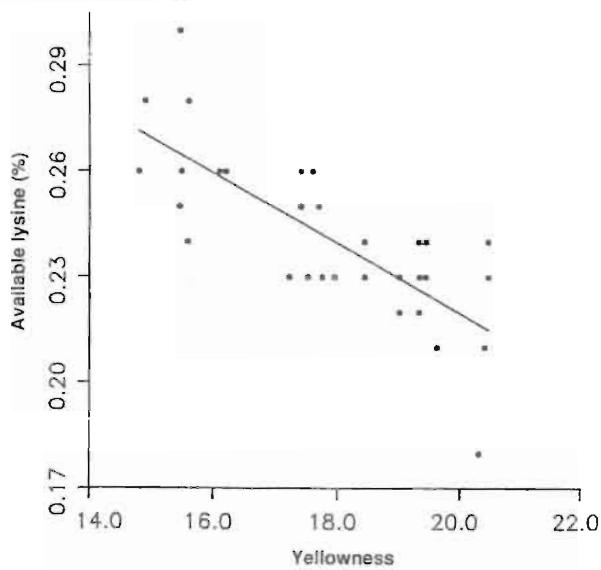

Fig. 2. Relation between available lysine and yellowness (Minolta 'b*' units) in milled rice stored under a range of controlled conditions.

would be assisted by elevated levels of reducing sugars and basic amino acids. These conditions exist even in sound grain, and are consistent with the kinetics observed.

The results also imply that there may be some loss in the nutritive value of rice which has yellowed extensively. This has public health implications, particularly for children on marginal diets, in areas where rice forms the major part of the diet.

Sensory Evaluation

The acceptability of the product to the consumer is the ultimate quality test of any product. Recently, sensory evaluation has been carried out using rice consumers in the Philippines to assess the effects of storage under a range of temperatures, water activities, and concentrations of oxygen and carbon dioxide on rice acceptability (Gras et al., 1990). Preliminary analyses of the results suggest that panel ranked preference data can be fitted to the same form of model as equation (2). In this case, no significant effect of either oxygen or carbon dioxide could be detected, but well over 90% of the variation in ranked preference scores was explained by the temperature and water activity components. Yanai et al. (1979) have reported slightly superior retention of the organoleptic properties of rice when stored in nitrogen or carbon dioxide rather than in air, which is consistent with the results given here.

In both of the above studies, altered atmospheres did not lower the perceived quality of stored rice. On the results so far obtained, the increasing use of carbon dioxide as a storage atmosphere for rice seems well justified.

Other Quality Parameters

Other quality parameters of rice include milling yield, proportion of broken grains, cooking parameters (water uptake, volume expansion, cooking time, hardness, stickiness, etc.), gelatinisation temperature, gel consistency, amylose content, and fat acidity. The quantitative effect of altered atmospheres on these properties is under investigation. The few data in the literature suggest that the effect is minimal (Iwasaki and Tani 1967; Yanai et al. 1979; Ory et al. 1980), but further work is required.

Effect of CA Storage on Quality in Maize

Germination

Bason et al. (1987) stored white dent maize at a range of temperatures (35°–60°C) and one water activity (0.6) under a graded series of carbon dioxide levels (7.5–60%) which were held constant throughout storage. The data were fitted to equation (4). It was found that carbon dioxide had no significant effect on the mean lifespan retention period. Recent results (unpublished) have indicated that lowered oxygen levels generally extend lifespan in this cultivar. However, under some conditions the lowest oxygen level used (0.2%) gave lower than expected lifespans, presumably because there was insufficient oxygen to support respiration.

Physical Properties

There is still a lack of information on the effect of controlled atmospheres on the physical properties of maize. In large scale experiments in the Philippines, stacks of bagged white flint maize stored under carbon dioxide showed an average percentage weight loss of 0.1% compared to 2.0% for similar storage under air (Esteves et al. 1988). This was due to effective insect control under carbon dioxide but not in the control stacks stored in air. Other associated physical changes included a significantly larger amount of yellowing and increase in redness for grain stored in air compared with that stored in carbon dioxide.

In tropical regions, maize is often milled into grits and consumed much like rice. The yield of grits is an important physical quality parameter, since it reflects the amount of edible material that can be recovered from the maize. Laboratory studies (unpublished) have indicated that the yield of edible grits increases with storage time. The effect of altered atmospheres on yield of maize grits is under investigation, but as yet is not established.

Chemical Properties

Sowumni et al. (1982) stored yellow maize under nitrogen in small airtight silos and in air for three months. By comparison with storage in air, storage under nitrogen retarded changes in proximate constituents, carbohydrate fractions, and lipids. However, the moisture content increased in the samples stored in air but not in nitrogen, and therefore the changes may have been due to a greater water activity rather than a lower oxygen content. Esteves et al. (1988) found a significantly lower increase in fat acidity of white maize stored in carbon dioxide compared with air.

Further work is required under more tightly controlled conditions to quantify the effect of CA storage on all aspects of maize quality. It would appear likely, however, that storage under either low oxygen or high carbon dioxide levels is not worse than storage under air, and therefore is an acceptable storage option for this grain in terms of quality preservation.

Effect of CA Storage on Quality in Wheat

Germination

In accelerated aging experiments, Banks and Gras (1982) exposed three cultivars of wheat to a range of oxygen concentrations (0.2%–100%) and to one atmosphere containing 60% carbon dioxide. The effect of each gas mixture was determined at three water activities (0.4, 0.6, 0.8) at 60°C. Average lifespan generally increased with decreasing oxygen concentration at all three water activities. A model was developed which satisfactorily quantified the effects of oxygen and water activity on viability. There was a linear relation between viability and the logarithm of the oxygen concentration, and between the viability and the logarithm of the water activity, which is consistent with the results for rice and maize germination. Storage under carbon dioxide was slightly detrimental to retention of viability, but the quantitative effect could not be determined from the single atmosphere used. Data from a more extensive range of CA storage experiments are currently being compiled.

Dough and Baking Quality

Subsequent work by Gras (unpublished data) has demonstrated that there is a correlation between germination and various dough and baking properties in wheat. Storage under conditions that were detrimental to germination also led to a longer time to peak dough development and lower peak resistance in mixograph tests, and reduced loaf volume in microbaking tests. Quantification of the relative contributions of storage time, temperature, water activity, and gaseous environment is in progress, but it appears that the storage gas composition has only a minor effect on wheat quality.

Effect of CA Storage on Quality in Barley

Germination

Barley needs to be at least 95% viable to be classified as malting grade. The effect of storage on germination is therefore critical to the value of the product. Shejbal and Di Maggio (1976) reported longer retention of viability in barley stored in nitrogen than when stored in air. Duff et al. (1986) stored three cultivars of barley under a range of oxygen concentrations (0.2%–100%) and one atmosphere containing 60% carbon dioxide in air, and at three water activities (0.4, 0.6, 0.8) at 47°C. All varieties indicated an inverse relation between lifespan and oxygen concentration, consistent with results for the other cereals mentioned previously. In similar experiments over an extended range of temperatures (35°–60°C), Konik and Gras (1988) reported a temperature dependence in the effect of carbon dioxide in that it may be deleterious at higher storage temperatures but not at 35°C. Whilst lowered oxygen generally increased lifespan, it was noted that grain viability was often retained for less time in 0.2% than in 2.0% oxygen, similar to observations for maize. There is a need for further research to determine minimum oxygen requirements in barley. It is worth noting that the effect of the gaseous atmosphere was much smaller than that of storage temperature and water activity.

Malting Properties

Storey et al. (1977) and Storey (1980) reported storing barley under reduced oxygen conditions and in air at 27°C and 50% RH for up to 6 months. Results were somewhat inconsistent, but overall the reduced oxygen environment appeared neither beneficial nor detrimental to malt quality. Gras et al. (1988) reported that the malting quality of barley stored in carbon dioxide under normal storage temperatures (up to 35°C) and water activities (up to 0.6) was at least as good as that of barley stored under similar conditions in air. Therefore, storage of barley under carbon dioxide appears to be an acceptable option under normal conditions.

Alternative Insecticidal Atmospheres

There are various fumigants available that provide effective insect control within a sealed enclosure. The advantages of low oxygen or carbon dioxide enriched atmospheres are that their effect on quality is minimal and they leave no toxic residues on the grain. Recently phosphine has been used in place of conventional CA gases. There has, as yet, been no systematic study of the effects of phosphine (or other fumigants for that matter) on grain quality: this is urgently required.

Conclusions

Quantification of the changes in grain quality have been particularly useful in the study of yellowing of rice in storage. These studies suggest that the mechanism of the yellowing may be non-enzymic browning, and that this process may be independant of direct yellowing resulting from the growth of fungi. It is quite possible that residual enzymes, small peptides, and simple sugars resulting from fungal invasion may thus potentiate the yellowing process. It is equally clear that sound rice will become yellowed given sufficient time under normal tropical storage conditions. The quantitative model of the yellowing of rice may also be useful for the prediction of quality changes to be expected from drying, and also for predicting the consequences of poor postharvest handling.

Quantification of the effects of storing cereals under controlled atmospheres has provided valuable information on the utility of these atmospheres for maintaining grain quality. Practical storage atmospheres with low levels of oxygen or high levels of carbon dioxide have only minimal effects on the quality of rice, maize, wheat, and barley. In general, storage under atmospheres containing reduced concentrations of oxygen provides slightly improved retention of quality, whereas carbon dioxide can reduce viability in some cases, most importantly in barley at high temperatures and water activities. The effects are not sufficiently large, however, to be of commercial concern in most cases. Thus, from the quality perspective, the increasing use of these atmospheres as an alternative insect control technique is quite acceptable. The effects of other insecticidal atmospheres such as phosphine on stored grain quality requires further research.

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