CHANGES IN RHEOLOGICAL AND CHEMICAL PROPERTIES OF A CANADIAN WESTERN HARD RED SPRING WHEAT CULTIVAR NEEPAWA DURING STORAGE

A thesis
Submitted to the Faculty
of
Graduate Studies
The University of Manitoba
by
Basil Al-Farisi

In Partial Fulfillment of the
Requirements for the Degree

of

Master of Science
Department of Plant Science
October, 1982

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ACKNOWLEDGEMENTS

Upon ending this academic program, I would like to express my thanks and gratitude to Dr. B.L. Dronzek, my advisor, and wish to acknowledge his direction of the project and his guidance in the preparation of this thesis.

I am grateful to the Government of Iraq for granting me a study leave and for supporting me financially.

I also express my heart-felt thanks to Mr. R. Zillman and Miss M. Rourke for their technical support and suggestions during the experimental stage of this project. My thanks to Mr. R. Batenchuk for the amino acid analyses. I thank Mrs. Dianne Lapsley for typing of the manuscript.

Finally, I express deep gratitude to my wife, Manal, for her encouragement, moral support and dedication to our family.

ABSTRACT

Al-Farisi, Basil A. Aziz, M.Sc., The University of Manitoba, October, 1982. Changes in the Rheological and Chemical Properties of a Canadian Western Hard Red Spring Wheat Cultivar Neepawa During Storage. Major Professor; B.L. Dronzek.

The rheological and chemical properties of stored Canadian western hard red spring wheat (Neepawa) from the 1979 and 1980 crops (freshly harvested) at 12, 16 and 18% moisture contents, stored at different temperatures (30, 40 and 50° C) for various periods (10, 20 and 30 days) were investigated. In order to control the storage conditions of the wheat samples, sealed containers were used to control the moisture level while a controlled environment cabinet and an air oven were used to control the temperatures.

The samples at high moisture levels stored at high temperatures for long periods of time developed fungal infestations, which resulted in changes in the organoleptic properties such as color and odor. Storage at three temperatures, as well as storage times, had little effect on the percentage of recovered flour, bran and shorts for the wheat stored at the three moisture levels. The proximate compositions of stored wheat flour samples were directly related to the storage conditions. Ash content, starch damage and free amino acid composition showed marked changes compared to the control, especially in the samples at high moisture levels and high temperatures stored for a long period of time. On the other hand, protein content and amino acid composition were unaffected by the storage conditions. The storage conditions adversely affected the rheological behavior of stored wheat dough as measured by the farinograph, extensigraph and amylograph; the effects were pronounced when the storage conditions such as temperature, moisture and storage period increased. The samples stored at high moisture levels and high temperatures for long periods of time showed a marked decrease in sedimentation value, percent of wet gluten, as well as a significant decrease in loaf volume.

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I. INTRODUCTION

Man has been storing grain and its products since the Stone Age period. Over the years, man has learned by trial and error that grain can be stored for long periods of time without damage or deterioration.

Grain storage conditions are very important in order to avoid deterioration of the grain and its products. Parpia (1976) reported that the Food and Agriculture Organization estimated that 5% of all food grain harvested are lost prior to consumption. Post-harvest losses of up to 50% of the total production have been observed quite often in countries like India, where inadequate storage facilities have existed.

Storage aims to preserve grain with minimal loss in weight and quality of grain. Losses in quantity and quality of stored grain are caused principally by fungi, insects and rodents. In this study, attention will be focused on the physical and chemical changes which occur during post-harvest storage and the effect of these changes on the quality on the stored grain crop.

Studies on the changes which occurred during storage have, in many cases, produced somewhat conflicting results. McCalla et al. (1939) in tests at room temperature and Cuendet et al. (1954) in tests at slightly higher temperatures have reported flour deterioration occurring within 3 months or less of storage. On the other hand, Saunders et al. (1921) reported minor deterioration in quality of flour which had been stored for up to 14 years. Greer et al. (1954) reported that canned flour was still in a good condition after 27 years of storage at 10 to 20° C.

All grain and milled products undergo a variety of changes throughout post-harvest storage regardless of how they are stored. These changes can be beneficial when storage conditions are favourable. However, some deterioration in quality can occur under adverse storage conditions (Bushuk and Lee 1978).

This thesis was initiated to study the effect of different storage conditions on the Canadian Western hard red spring wheat cultivar, Neepawa (Triticum aestivum s. sp. vulgare) for two different crop years. The wheat was stored at three moisture levels, 12, 16 and 18%, at three different temperatures, 30, 40 and 50° C and for various periods of time (10, 20 and 30 days). The objectives of this thesis were to examine the changes in rheological and chemical properties of the stored wheat as affected by different storage conditions.

II. LITERATURE REVIEW

A. Physical Properties of the Stored Grain

1. Moisture

Air which moves from a high temperature region to a low temperature region gives up moisture to maintain its relative humidity. In extreme cases, the air which comes into contact with a cold surface may be cooled below the dew-point. The result is water condensing onto the wall of the storage bin or on the surface of the grain. This water causes the relative humidity in the region to rise and hence increases the risk of grain deterioration. In addition, when grain which contains a high moisture level is exposed to the air, the moisture moves from the grain to the air until there is an equilibrium between the grain moisture and the atmosphere (Hall 1970, Burrell 1974, Bushuk and Lee 1978).

Moisture is the key to safe storage of grain and their products. Grain at low moisture content in equilibrium with 70% relative humidity can be stored for a long period of time with little deterioration (Hunt and Pixton 1974). When the moisture content exceeds this critical level, storage fungi begin to grow. This results in an increased rate of respiration in the stored grain which may cause excessive heating. Sinha and Wallace (1965) termed this excessive heating damp grain heating. Hall (1970) and Hunt and Pixton (1974) reported that different types of grain in storage had a specific critical moisture level which influenced the growth of the storage fungi which in turn influenced the chemical deterioration of the grain. The safe moisture content for storage is grain in equilibrium with 70% relative humidity. Above 75% relative humidity fungi develop rapidly, cause heating of stored grain, followed by subsequent deterioration of the grain and loss in quality.

Smith (1969) cited that 40% of the total volume between the stored grain was air space. The grain was also characterized by a low thermal conductivity with an ability to exchange moisture with the air within the grains and with the air around the grain.

Absorbed water, due to the moisture levels and relative humidity of the storage grain, may be held loosely in the grain by capillary forces and could play an important role in storage. Another type of water is adsorbed water which is held firmly by molecular attraction and is not as important in stored grain (Smith 1969, Trisvyatskii 1969, Hunt and Pixton 1974).

2. Temperature

Grain is an excellent insulator. Therefore, grain temperature changes very slowly. Smith (1969) and Burrell (1974) reported that the thermal insulation characteristics of the grain were five to 10 times better than a similar bulk of concrete. If cold grain is stored in bins in winter, the grain remains cold throughout most of the summer and its temperature will rise only a few degrees. Due to the low thermal conductivity of grain, the temperature effects on the outside of the grain mass in storage are slowly transmitted to the centre. On the other hand, the temperature of the grain at the centre of the bulk may rise due to the presence of insect, microorganism and dockage.

During the various stages of insect life cycles, insects require and consume food and oxygen producing carbon dioxide, water and heat. The heat produced by the insect cause a localized increase in temperature which is called "hot spot". This can also lead to migration of moisture to the cooler upper grain surface resulting in a condensation near the cool surface. This in turn promotes grain sprouting and mold growth.

3. Flow Property

In addition to the factors which cause "hot spot" during storage, there is in grain a flow property factor. This property depends on the natural segregation of the grain during the movement and handling, which in turn depends on the gravity, the specific weight and the heterogeneity of the grain. The flow property factor can create undesirable storage conditions such as spontaneous heating and caking.

Trisvyatskii (1969) explained this phenomenon and reported that when grain is loaded into an elevator, the sound and heavy grains having a high specific weight, falls vertically and rapidly towards the bottom of the bin. On the other hand, the small, shrivelled grain, insects and spores having a low specific weight fall slower and are thrown by air currents against the bin walls.

As a result of natural segregation, therefore, sectors of grain are formed in the bin which differ from each other to some extent in composition. Shrivelled grains, dust, micro-organisms and insects accumulate mainly along the bin walls where the moisture level and temperature are normally above the mean of the whole batch. This condition facilitates micro-organism and insect growth (Bushuk and Lee 1978).

Trisvyatskii (1969) reported that when grains of different specific weights are discharged from a bin by gravity, the grains with a high specific weight moved out from the central part of the bin first. This grain is replaced by grain with a lower specific weight, micro-organisms and insects which were previously found along the bin walls.

4. Respiration

During storage, grain respires and produces moisture (water) and carbon dioxide. Hummel *et al*. (1954) and Trisvyatskii (1969) observed that there are two kinds of respirations: aerobic and anaerobic. In aerobic respiration the sugars (hexoses) are completely oxidized to form carbon dioxide, water and energy. This respiration predominates in normal grain storage where there is an excess of air. Aerobic respiration is shown by the following formula:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\,CO_2 + 6\,H_2O + \text{energy}$$

In anaerobic respiration, grain is stored under unfavourable conditions and a lack of oxygen. During respiration, the sugars are decomposed to form the oxidized organic product, such as ethyl alcohol, as shown by the following formula:

$$C_6H_{12}O_6 \rightarrow 2\,CO_2 + 2C_2H_5OH + \text{energy}$$

Trisvyatskii (1969) reported that most of the energy produced during respiration is liberated. This energy produces heat which is released into the surrounding space. The heat, formed by the stored grain, may as a result of poor thermal conductivity be retained. Consequently, this heat may be one of the causes of spontaneous heating (a hot spot) in stored grain.

B. Rheological Properties

It is generally accepted that the rheological properties of dough are very important for the baking performance of a product and its final quality. Charm (1962) defined rheology as the branch of physics dealing with forces and deformations, their relationship and interrelationships with time. Proteins play a very important role in determining the rheological properties of the dough. About 85% of the proteins in wheat flour consist of the gluten components, gliadin and glutenin (Bushuk 1977). These fractions differ markedly in their physical properties. Gliadin is extensible and inelastic, whereas glutenin is elastic but relatively inextensible. The gluten of a good breadmaking flour contains gliadin and glutenin in approximately equal amounts. Gluten is the insoluble protein material remaining after the water solubles and starch are washed out of dough in a stream of water. Gluten content in flour is a measure of breadmaking potential (Bushuk 1977).

Flour strength refers to wheat protein or flour protein and encompasses both protein quality and quantity. On the basis of flour strength, wheats can be classified into two major types, namely hard (strong) and soft (weak) types of wheat (Pyler 1967). Hard wheat flours have relatively high protein content, high water absorption and forms an elastic gluten with good gas retaining properties. Soft wheat flours, on the other hand, have a lower protein content and yield a gluten which is less elastic. This type of flour is generally better suited for baked goods such as biscuits and cakes (Wheat Flour Institute 1971).

Protein quality criteria are related primarily to the gluten protein. Quality is appraised largely by subjecting the flour to several physical testing devices which measure various rheological properties. The tests are performed usually on flour water doughs and are widely employed in quality measurements. These tests characterize the gluten protein of the protein by measuring such factors as extensibility and resistance to extension of dough at rest, hydration time, maximum development time and tolerance or resistance to breakdown at a predetermined consistency during mechanical mixing (Pratt Jr. 1971).

Larmour *et al*. (1961) stored flour and farina (coarse flour) for 5 years in a variety of packaging material and storage conditions. Dried flour (8% moisture content) showed a minimum change in farinograph properties during storage, while the normal flour (14.5% moisture content) showed marked changes in farinograph properties after 3 and 5 years of storage. On the other hand, the extensigraph indices for the dried sample stored in standard packs showed some evidence of an accelerated, apparently irregular, rate of change in dough properties. The increase in resistance to extension accompanying storage was slightly more rapid for the dried samples rather than for the normal moisture flour and farina.

Yonegama *et al*. (1970a, b) measured the SH content of freshly milled flour stored for 90 days at 30° C in air and in nitrogen. The flour stored in air showed a marked decrease in SH content, while the flour stored under nitrogen showed a much smaller decrease in SH content. This, in turn, seemed to directly affect the changes in rheological properties of the dough and hence the breadmaking quality.

Westermarck-Rosendahl and Ylimaki (1978) and Westermarck-Rosendahl (1978) stored for 5 and 7 days, winter and spring wheat, which was harvested at moisture contents between 18.6 and 38.0%. Under such storage conditions, spontaneous heating developed. The farinograph tests on these samples showed a very short dough development time for the winter wheat stored at 37.5% moisture content for 2 days. On the other hand, the spring wheat stored at 37.5% moisture content showed a marked decrease in development time following 2 days of storage. The extensigraph properties declined in the winter wheat following 3 days of storage while in the spring wheat the extensigraph properties declined following 1 day of storage.

Bell _et al_. (1979) found that there were no detectable changes in rheological or baking properties of flours milled from English ('Weak'), Canadian ('Strong') and mixed English and Canadian wheat ('Medium') held at -20° C for 66 months' storage with the exception that the free lipid acidity increased slightly. However, at ambient temperature, the deterioration in baking quality of the stored flours was highly dependent on the nature of the baking test used.

Shuey and Tipples (1980) cited that Lange (unpublished data) found a direct relationship between storage time at different temperatures and the loss in malt activity. After 11 weeks' storage at 22.7° C the loss in malt activity was estimated at 36%. Also, they reported that as the storage temperature increased, the rate of loss in malt activity increased, i.e. at 23.9° C storage temperature, a 2% per week loss in malt activity occurred; at 35° C a 11% loss per week and at 46° C a 25% loss per week in malt activity.

C. Chemical Changes During the Storage

1. Protein and Amino Acid Changes During Storage

Very few authors have studied the changes that occur in grain proteins during storage. At present, the information concerning these changes in grain protein during storage remains unclear.

Jones and Gersdorff (1941) studied the effect of storage under different conditions at various intervals over a 2 year period upon the protein of white flour, whole flour and wheat kernels. The results showed that three different types of changes occurred: (i) a decrease in the solubility of the proteins, (ii) a partial breakdown of the proteins indicated by a decrease in protein content and a decrease in the amount of nitrogen precipitable by trichloroacetic acid and by an increase in amino nitrogen and (iii) a decrease in digestibility. The extent of these changes depended on the temperature, the type of container, the duration of storage and the moisture of the material stored.

Pixton et al. (1964), Pixton and Hill (1967), Pixton et al. (1975) and Pixton (1980) reported that wheat, when stored for 6, 8, 16 and 18 years in cooled bins at -15° C at moisture levels less than 14%, showed a slight decrease in the salt soluble proteins during the first 2 years of storage and remained constant thereafter. Crude protein, however, remained unchanged during the 6, 8, 16 and 18 years of storage. Similar results were reported by Fifield and Robertson (1959), Westermarck-Rosendahl (1978) and Westermarck-Rosendahl and Ylimaki (1978).

Daftary et al. (1970a, b) investigated the effect of temperature on the chemical composition of two hard red spring wheat flours stored at about 18% moisture content for 16 weeks at 23, 30 and 37° C. The study found a slight change in the protein content of the stored wheat samples with the mold-damaged sampled having a slightly higher protein content than the corresponding sound flours. The relative increase, on a percentage basis, could be explained by the respiratory losses of carbohydrates. However, the gluten from the damaged flours was difficult to wash out and had impaired rheological properties. In damaged flour, the yield of gluten was reduced and that of the starch fraction was increased with the starch fraction rich in protein. Starch-gel electrophoretic patterns of the gluten showed a decrease in glutenin and an increase in gliadin-like components; the water-soluble fraction contained an unusual component migrating to the anode and essentially no fast-moving component. Baking studies of reconstituted wheat doughs indicated damage to lipids, gluten and water-soluble proteins; no damage to the starch was demonstrated

Shearer et al. (1975) reported that no changes had occurred in wheat flour gliadin and glutenin proteins extracted from flour stored at 25, 12 and -20° C for 18 months. Sodium dodecyl sulfate-polyacrylamide gel electrophoresis showed minor changes in the molecular weight distribution of the gluten protein on storage.

Patey et al. (1977) found that prolonged storage of wheat for several years resulted in a progressive decline in the amount of acetic acid soluble protein, whereas the protein solubility remains unchanged. Westermarck-Rosendahl and Ylimaki (1978) and Westermarck-Rosendahl (1978) studied the effect of spontaneous heating on the protein properties of stored wheat at high moisture content. The reports found that the gluten content and the sedimentation value of wheat flours decreased when spontaneous heating occurred.

Devay (1952) reported that 18 free amino acids and an unknown ninhydrin-reacting substance were found in sound and moldy wheat. In addition, gamma-amino butyric acid was identified only in moldy wheat stored at relatively high moisture contents. Visual comparisons of chromatograms of sound and moldy wheat indicated changes in the concentrations of certain free amino acid. Alanine, gamma-amino butyric acid, proline, serine and lysine increased while histidine decreased in concentration in moldy wheat relative to the concentrations of the other amino acids in sound wheat.

Yoneyama et al. (1970a, b) found that the soluble SH content decreased markedly during the first 10 days of storage when the flour was stored at 30° C. For the flour stored at -30 and 0° C, soluble SH content decreased slowly but continually during 90 days of storage. These results indicated that the oxidation of the soluble SH groups in air depends to a large extent on the storage temperature of the flour.

Ferrel et al. (1970) stored samples of highly fortified wheat (by adding lysine HCl) at 9, 11 and 13% moisture contents at 32.2 to 37.7° C. The study indicated that lysine HCl added to the wheat under reasonable conditions of storage is stable for at least 1 year.

2. Carbohydrate

Grain taken from an ancient Egyptian tomb, more than 3,000 years old, was reported to contain dextrins and considerable amounts of reducing sugars. This indicated that the amylase activity appeared to continue in the stored grain even after respiration could no longer take place (Geddes 1935, Pomeranz 1974).

Loney and Meredith (1974) showed that peak amylograph viscosity increase with aging time, both for active and inactive enzyme states. The data indicated that the aging effect is not attributable to a decline of amylase activity but involved changes in other components such as starch. Storage at -25° C held the pasting ability relatively constant

Pixton et al. (1964), Pixton and Hill (1967), Pixton et al. (1975) and Pixton (1980) recorded that the non-reducing sugar of a Manitoba hard wheat and a soft English variety declined very quickly in the period between 6 and 8 years of commercial storage. Wheat at 12% moisture content stored between 8 and 16 years in the same storage conditions showed no marked effect on the proportions of reducing and non-reducing sugars. Again during the storage period from 16 to 18 years the reducing and non-reducing sugars decreased for both types of wheat in all bins.

Glass et al. (1959) stored grain under aerobic and anaerobic (nitrogen) conditions at different moisture levels (13 to 18%). Samples were removed at intervals of 2 to 4 weeks and tested for mold counts, viability and reducing and non-reducing sugars. An increase in reducing sugars at all moisture contents was observed. This change was more pronounced at the higher moisture contents and in particular with those samples stored in nitrogen. At 18% moisture content there was a 285% increase in reducing sugars in the nitrogen stored sample as compared to 120% in the air-stored sample. Non-reducing sugars decreased in all samples above 13% moisture. This change was somewhat greater at the higher moisture contents, although the samples stored in air showed a greater decrease in non-reducing sugars than those stored in nitrogen.

Lynch _et_ _al_. (1962) carried out additional work on the changes that occurred in the wheat sugars during storage, in presence or absence of mold. Sound wheat was stored in atmospheres of air, nitrogen or carbon dioxide for 8 weeks at 30^{o} C and 20% moisture content. By most of the criteria used, the samples stored under anaerobic conditions, and hence without mold growth, deteriorated almost as rapidly as did a sample stored in aerobic conditions. All stored samples had undergone extensive changes in sugar content and gave flour of extremely poor baking quality after 8 weeks. In air, the sucrose content of wheat decreased markedly, whereas minor changes occurred in glucose, fructose, galactose or maltose content. In carbon dioxide and nitrogen, the sucrose content decreased concomitant with a large increase in glucose, fructose and galactose.

3. Lipids

Sound grains contain fairly active antioxidants so the fats are effectively protected against the effects of oxygen during storage. Milled products in storage pose a serious problem, particularly whole grain milled products. Whole wheat flour can be kept for only a short time because it readily becomes rancid, regardless of its moisture content and storage temperature (Zeleny 1954). When the moisture content and temperature are high, fats in grain are broken down by lipases into free fatty acid and glycerol during storage. Mold growth also increases this type of change because of the high lipolytic activity of the mold. Fat hydrolysis takes place much more rapidly than protein or carbohydrate hydrolysis in stored grains (Pomeranz 1974). Two types of reactions, oxidation and hydrolysis, can occur in grain lipids during storage. The reactions produce a variety of products which contribute to the development of a rancid taste and odor. Hydrolytic degradation of grain lipids during storage is catalyzed by exogenous (fungal) and to some extent, by exogenous lipases, resulting in the production of free fatty acids and glycerol (Pomeranz 1974, Bushuk and Lee 1978).

Zeleny and Coleman (1938), Hummel et al. (1954), Glass et al. (1959), Larmour et al. (1961), Yoneyama et al. (1970a) and Westermarck-Rosendahl and Ylimaki (1979) have reported that the acids produced by the lipases include free fatty acids, acid phosphates and amino acids. The levels of fat acidity increase most rapidly during the early stages of deterioration. The fatty acid content of grain has often been suggested as an indicator of grain deterioration.

Daftary and Pomeranz (1965) stored hard and soft winter wheat for about 6 months after harvest at 4° C. The original moisture of the wheat samples was 12.8 and 13.4%, respectively and each was moistened to 18 to 22%. The study found that titratable acidity was about 7% higher in benzene extracts than in petroleum ether extracts of wheat. Benzene extracts of moistened wheat contained more free fatty acids than did extracts of wheat redried to 11 to 12% moisture contents. Changes in