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Research on the Influence of Carbon Dioxide Content, Exposure and Temperature on the Quality of Stored Paddy Rice with Different Moisture Contents*

Fu Pengcheng, Ye Zhenhong and Li Rongtao

Abstract: The determination of quality aspects of stored paddy rice was the subject of the presented study. After airing and drying in the sun and adjusting the moisture content of the rice at relative balance humidities of 60%, 70%, 80%, the rice was exposed into four different atmospheres at five different constant temperatures: 10℃, 15℃, 25℃, 35℃ and normal ambient temperature, which containing high contents of carbon dioxide. The atmospheres were applied by ventilation into the tested bulks of paddy after reduction of pressure and adjustment of the moisture. By periodic sampling, many performance indexes for quality were determined, such as viscosity, fatty acid value, germination rate, hydrogen peroxidase activity, taste panel scores, light transparency difference and alteration of microbes.

It was shown by experimental data that the quality of stored paddy was degraded as grain storage temperature and grain moisture content and storage period increased. The rate of degrading was correlating to the storage temperature and moisture content of the rice. At a storage temperature of 15℃, paddy with high moisture content kept excellent palatability. At 25℃, except for paddy with high moisture content, the quality of paddy with lower moisture contents did not change. At 35℃, except for paddy with low moisture content, the performance of paddy decreased significantly, and paddy with high moisture content loosing its dietary property completely. Based on the research on paddy performance, alteration rules were developed for different storage conditions, such as different temperature, humidity and content of CO_2 in the storage atmosphere, fatty acid value, taste panel scores and germination rate.

The CO_2 content influenced the quality performance of paddy, which had been stored for one year. However, it played obviously a role on grain storage pest control, and had a pronounced inhibition effect on the growth of grain microbes. When the volume content of CO_2 was beyond 15% and the temperature at 35℃, it had some inhibition effects on increase of the fatty acids for paddy with high moisture content above 15%. The further increase of the CO_2 content did not show a pronounced inhibition effect. When the moisture content was below 15% and the grain temperature below 15℃, the carbon dioxide inhibited excellently the growth of fungi, as well as with common paddy or paddy with lower performance. When the content of CO_2 increased above 35% and the grain storage temperature above 25℃, growth of fungi was inhibited in shortly stored paddy with high moisture content above 15% to some extent. Modified atmospheres (MA) with increased carbon dioxide content reduced significantly the mass growth of grain fungi but it could played no roles on the variety of fungi occurring in the stored rice. When the moisture content and the temperature of the stored paddy were high, it could not be stored for long time even under MA.

Key words: carbon dioxide, gas content, temperature, moisture, paddy, quality

Introduction

During the period of the seventh-five-year plan, the national emphasis science and technology brainstorm project of "research on application technologies in grain storage with MA" has been carried out in China. Mock-up tests have been carried out in granaries under different storage conditions[1]. The influence of different storage factors like temperature, moisture content of the stored paddy varieties and modification of the composition of the storage atmosphere by use of different amounts of carbon dioxide in air have been investigated with respect to pests control, mould inhibition and quality performance. Meanwhile, the limitations of use of such atmospheres especially under the aspect of safe storage period have been explored. It has been considered that modified atmospheres (MA) with increased amounts of carbon dioxide in air play a significant role to improve the storability of various grain varieties under otherwise bad conditions like high storage temperature and moisture.

Chengdu Grain Storage Research Institute, State Administration of Grain Reserves 601131

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The presented research results belong to special research projects for social public welfare businesses by the research institute and the academy in 2001. Based on researches achievements in the "seventh-five-year plan", elaborate choices to detect storage indexes have been made, for instance for viscosity, fatty acid value, germination rate, hydrogen peroxidase activity, taste panel scores. The light transparency difference has also been investigated.

In comparing with normal ambient atmosphere, modified atmospheres with three different contents of carbon dioxide of 15%, 35% and 60%, respectively, with rest air, have been investigated as storage atmospheres in granaries and in the laboratory. To implement the moisture content of paddy and the temperature as experimental factors, paddy rice was stored in balance with relative humidity at 60%, 70%, 80%, respectively, at different temperatures. Five different temperatures were adjusted. Some sensorial indexes, which have describe the quality of paddy rice were implemented into the investigation of the stored paddy.

Materials and Methods

Samples

The investigated paddy was harvested in former years in Gucheng Town, Pi count, Sichuan province.

Temperature

Five temperatures, comprising 10℃, 15℃, 25℃, 35℃ and ordinary temperature, were investigated. The temperature of 10℃ was gained by freezing. The conditions of 15℃, 25℃ and 35℃ were adjusted by use of a constant temperature generator. Controlling of temperature was performed by installing a SWP – F803 – 01 digital temperature controller with relative accuracy of ±1℃. The ordinary temperature referred to was room temperature in the laboratory and varied from 6℃ to 34℃.

Moisture Content

According to the requirement of adjusting the grain moisture content at different temperatures, the grain was exposed in balance to air with different relative humidities of 60%, 70% and 80%, respectively, and the grain regarded accordingly as grain with low moisture content, safe moisture content and high moisture content, respectively (see table 1). After thorough mixing of the corresponding large samples, they were divided into samples of 10kg weight. The moisture content of the grain was adjusted by adding corresponding amounts of water or airing in the sun. Subsequently, the sub samples were introduced into glass bottles with twenty liter capacity. When the temperature reached about 15℃, they were transferred into the storage experiments at the respective temperature after balance time of 14 days.

Relative Humidity of the Atmosphere and Control of CO_2 Content

Carbon dioxide content and relative humidity of the atmosphere were controlled by the way of "gas split stream ways"[2]. After passing through oxygen gasometer, flow controller and flow meter in succession, the mixture of pressurized air from the cylinder and carbon dioxide from a liquefied source became a modified atmosphere with increased volume ratios of carbon dioxide, including 0%, 15%, 35%, 60%, respectively with the rest being air. The oxygen contents of the atmospheres were correspondingly about 20%, 17%, 13% and 8%, respectively. Subsequently, the atmospheres were adjusted to three different relative humidities of 60%, 70% and 80%, respectively. The gas was ventilated into rice samples with the corresponding moisture contents that were sealed by linking the sample outlet to a pot of water (gas washing vessel). From there the gas was ejected outside.

At the same temperature and gas content of the mixture, the flow rate of gas through each sample was 350mL/min. To keep the content of CO_2, it took one hour for ventilation every day, equal to about one volume exchange. By detection with CHX – 3010D infrared measuring device, the relative accuracy of CO_2 content was below 2%. The sampling for determination of the moisture content was carried out four times every year and showed that the adjustment of the relative humidity of the atmosphere fulfilled the requirement of the experimental design.

Table 1. Moisture content of paddy at different temperatures and humidities

Balance relative humidityin %	Moisture content	Temperature in℃		
		15	25	35
		Moisture content in %		
60	Low moisture	13.5	12.7	12.0
70	Safe moisture	15.0	14.2	13.5
80	High moisture	16.5	15.7	15.0

(Note: at 10℃, the paddy moisture content can be related to the result at 15℃ in the above table, the ordinary temperature was about℃)

Sampling and Quality Analysis

Sample

According to the storage condition and the paddy moisture content, paddy with safe or low moisture content was sampled every three month, four times in the whole year. Paddy with high moisture content stored at high and middle temperature was sampled already after the first month. At 10℃, samples were taken after half a year.

Samples for detection and determination of microbes: In the first two months, paddy with high moisture content was sampled one time every fifteen days and later on one time every month. Paddy with safe or low moisture content was sampled one time every three month.

Performance analysis method

Viscosity: refer to GB/T 5516 – 85

Fatty acid value: refer to GB/T 15684 – 1995

Germination ratio: refer to GB/T 5520 – 85

Hydrogen peroxidase activity: refer to GB/T 5522 – 85

Taste panel scores: refer to GB/T 15682 – 1995

Light transparency difference: There exists no recent national or professional criterion. Therefore, a method was used designed by the project group.

Detection for microbes:

Detection on outer mould of grain: refer to GB/T 4789.15 – 94

Detection on inner mould of grain: refer to GB/T 4789.16 – 94.

Results and Discussion

Rules on Performance Alteration Germination ratio

It was one of most important factors for the detection of fresh and good quality of rice. In the first one year depending on storage period, temperature, moisture content and storage period, germination ratio of paddy decreased slightly to different extents in the various samples (Fig. 1) (Please present the figure as it can be read with Latin letters in captions and explanations in English, otherwise it has to be omitted). At 35℃, germination ratio of paddy with safe and high moisture content decreased significantly. After storage for three months, germination ratio was above 90%. After six months of storage, the velocity of degradation was accelerating. Within a storage time of nine months, germination ratio decreased to zero. However, when the temperature was below 25℃, germination ratio after storage for one year remained above 80%. When the content of CO_2 was kept below 60%, the difference of carbon dioxide content did not play a significant role on germination ratio.

Viscosity

Because many factors play a role in judging quality, the viscosity change seemed not be a very clear factor (Fig. 2) (Fig. 2 can not be deciphered, may be omitted). With increasing storage time, viscosity began to rise to certain value and decreased again gradually. As paddy has a weak tolerance towards heat, the tendency of decreasing became more obvious at higher storage temperature.

Hydrogen peroxidase activity

H_2O_2 is produced during grain respiration. If hydrogen peroxidase activity decreases, H_2O_2 content is increased and the ageing of grain accelerated. With increasing storage time, hydrogen peroxidase activity dropped gradually. The speed of change was in accordance with temperature and time of grain storage (Fig. 3) (Fig. 3 can not de deciphered, present a readable version or omit it). Overall, it took about six month for the decrease from 63.5 mgH_2O_2/g to 32mgH_2O_2/g. If the grain would be stored for one year at ordinary temperature, hydrogen peroxidase activity would decrease to 80%.

Fatty acid value

Under all tested conditions in this study, all fatty acid values kept raising (In Fig. 4) (Fig. 4 can not be deciphered, present a readable version or omit it). With progressing storage time, the fatty acid value raised gradually. The speed of change correlated with storage temperature and moisture content of the rice in storage. At 25℃ and storage for one year, the fatty acid value was below 30 mgKOH/100g dry matter. At 35℃ and within nine month of storage, the fatty acid peak value of paddy with high moisture was obtained with 40 mgKOH/100g dry matter. When the content of carbon dioxide increased above 15% and the storage temperature was 35℃, the speed of change of the fatty acid value was reduced.

Light transparency difference

In recent years, light transparency has been investigated and brought forward as rice storage ageing index. Comparing with distilled water as reference, the light transparency ratio between rice and water and its iodine color has been determined by spectroscopy. The difference of the light transparency ratio between rice and water and its iodine color was regarded as the light transparency difference. As the starch content of paddy is generally about 60% – 80%, an alteration of this paddy performance would reflect changes in the starch structure. This change would lead to changes of the light transparency. Following the increase of the grain storage period and the increase of temperature and moisture, the tendency of change of the light transparency difference decreased (Fig 5) (Figure five needs to be presented in a readable form otherwise omit!). At 35℃ and 120 days of storage, the light transparency difference of the paddy with high moisture content decreased to 50%, from 8.2 to 4.0. The light transparency difference of paddy with low moisture always remained at about 70%. When the storage temperature was below 25℃, the light transparency difference of paddy with high moisture decreased to 60%. However, paddy with safe or low moisture content did not change its light transparency difference.

Taste panel scores

A taste panel determined directly the sensorial factors color, smell and flavor with samples of the stored and treated paddy. This determination was considered as easy and comprehensive index for the evaluation of the grain performance. When grain was stored for one year, the taste panel observed some changes (Fig 6) (A readablefigure 6 is neded, otherwise omit). With samples from a storage temperature of 10℃, the taste panel scored a slight decrease with low velocities of change. At storage temperatures of 15℃ to 25℃, the taste quality of paddy with safe moisture content did not change; all tested samples obtained about 80 scores. When the moisture content of the stored paddy was below the safe margin, the scores remained stable. So, under general storage condition s at about 25℃, the safe paddy could be stored safely for at least one year without loss in taste quality. High temperature played a significant role on scores. At a storage temperature of 35℃, paddy with safe moisture content could not be stored for one year without loss in taste quality, paddy with high moisture content not even 6 – 9 months.

Sensorial Indexes on Quality Changes

Sensorial indexes on quality changes were determined by variance analysis in this study. Variance analysis was carried out on every data set. The significance of a factor would be determinated by determining the "F" value and then indicated as of significant influence by one fold underlining (fiducial probability 95%). Special significant influence was indicated by double underlining (fiducial probability 99%). No-obvious influence was indicated by non-single underlining (fiducial probability 95% or 99%). The results of variance analysis are presented in table 2. When the sensorial index of quality was determined, and if there were at least one special significant factor and one significant factor among four factors, from the mathematical analysis standpoint it would be determined as primary sensorial index.

It is shown with results of variance analysis (Table 2) that five kinds of indexes, including the germination ratio, taste panel scores, fatty acid value, hydrogen peroxidase activity and light transparency difference have been regarded as sensorial index for the quality of paddy.

Table 2. Variance analysis on influence of temperature, moisture, gas composition and storage period on paddy storage quality

Resource	Free degree	Germination ratio		Viscosity		Hydrogen peroxidase activity		Fatty acid value		Light transparency difference		Taste panel scores	
		Average variance analysis	F value	Average variance analysis	F value	Average variance analysis	F Value	Average variance analysis	F value	Average variance analysis	F value	Average variance analysis	F value
T(℃) (A)	2	29099.1	30.09	1354.36	78.24	1317.31	3.42	53.54	4.92	938.38	12.77	49.72	1.02
Moisture (%)(B)	2	6328.78	4.39	31.50	0.70	380.24	0.94	5.82	0.49	68.31	0.75	435.13	10.74
CO_2(%) (C)	3	13.43	0.01	59.20	1.36	43.50	0.11	2.04	0.17	31.87	0.35	2.25	0.05
T(h) (D)	3	5044.48	3.56	14.71	0.33	11216.9	181.74	116.36	13.92	1512.74	33.04	782.19	31.11

Note: Among five different levels of temperature in table 2, sample capability at 10℃ and ordinary temperature were 6 and 12 respectively, all others three levels of sample capabilities were 48. All sample capabilities in three different levels of moisture content were 48. Among five different levels of storage period, sample capability of one month was 12, others were 48. They remained the same as the explanation in "t" inspection table.

Influential Factors on Change of Quality and Analysis on its Significance

(Since Table 3 can not be deciphered is has to be presented again in a readable version or the whole has to be discarded.)

Table 4 "t" inspection on paddy Hydrogen peroxidase activity and Fatty acid value

From table 3 it can de deduced, that at 35℃ the average germination ratio of paddy equaled to 55%. It was obviously lower than the germination ratio at the other four temperatures. The storage of paddy with low moisture content showed, that the germination ratio of paddy remained higher than from samples that were stored with safe and high moisture content. During the first three months, the germination ratio of paddy showed generally no variance. In the period of 3 – 6 months, the tendency of decreasing became obvious, and till 6 – 12 months, the tendency was very stable.

It is shown in table 4 that hydrogen peroxidase activity at a storage temperature of 10℃ remained higher in paddy than at other temperatures. Hydrogen peroxidase activity at 35℃ was lower than at other temperatures. After storage for three months, hydrogen peroxidase activity decreased significantly, especially after 6 months. The tendency increased until after one year of storage the activity dropped to almost zero.

The fatty acid value at 35℃ remained obviously higher than the values of paddy storage at the other temperatures. At 25℃ it was higher than at 10℃, 15℃. During the first nine months of storage, it appeared to raise.

Table 5: Inspection on paddy light transparency difference and taste panel scores

It can be derived from table 5 (Table 5 need s new presentation in a readable version!! Or discard!) that light transparency differences of paddy decreased as storage period increased and temperature raised.

The scores of the taste panel for paddy with high moisture content level were lower than for those samples with safe and low moisture content. As the storage period expanded, the taste panel scores of paddy samples with longer storage period decreased within the first half of the year. Temperature played a significant role on taste panel scores of paddy. At storage temperature of 35℃, it was lower than at other temperatures; at 25℃ it was lower than at 10℃ and 15℃.

Insect Pests

It is one of the keys of grain storage technologies to identify appropriate storage conditions for pest control. For the grain storage experiment for one year, pest development in paddy is described in Table 6.

Table 6. Pests, mould growth and sensorial quality determination of stored paddy

Relative humidity (%)	Temperature In℃	CO_2 content in air in %			
		0	15	35	60
Low (60)	15			Normal quality	
	25	*		Normal quality	
	35	* *	*	Normal quality	
Middle (70)	15			Normal quality	
	25	* *	*	Normal quality	
	35	* *	*	Normal quality	
High (80)	15			Normal quality	
	25	* *	*	Normal quality	
	35	* * *	*	Normal quality	

*: Low pest density, **: Middle pest density, ***: High pest density, temperature at about at 25℃

It is shown in Table 6 that pest growth in grain within one year of storage occurred in close relation with grain moisture, storage temperature and CO_2 content of the storage atmosphere. When the temperature ranged between 25℃ and 35℃ and the amount of carbon dioxide was zero, paddy with high moisture content suffers from serious damage by growth of pests and mould and looses its value completely. Slight increase of carbon dioxide content to 15% results in reduced pest growth. When the CO_2 content is increased to 35% or more, pest growth is completely inhibited, color and luster of paddy are kept fresh. So, when the storage temperature is kept at 15℃ or CO_2 content above 35%, all grain can safely be stored without the risk of pest growth.

Succession Rules on Microflora

Experimental data indicated as follows:

(1) In the combination of all kinds of storage temperatures with content of carbon dioxide in the storage atmosphere, growth of fungi in stored paddy can be inhibited in grain with low moisture content.

(2) There is much alteration of fungi quantities in stored paddy with high moisture content in different storage conditions. When the temperature is kept at 15℃ or below and the carbon dioxide content at 60%, paddy can be stored safely without fungal problems at least 140 days. When the carbon dioxide content is between 15% and 35%, fungi quantities begin to increase 20 – 50 times within storage for 80 days, CO_2 does not inhibit growth of fungi under these conditions. When the storage temperature is above 25℃ and the content of carbon dioxide higher than 59%, CO_2 inhibits the growth of fungi in stored paddy to certain extent, fungi quantities would remain stable within a storage period up to 140 days. However, the sensorial qualities of the grain would slightly decrease, such as color and luster of grain kernel would become dark and some harmful smell would appear. When the content of CO_2 is below 35%, it would cause weak inhibition effects on growth of fungi, fungi quantities would increase 20 – 100 times, there could develop mildew stains on grain kernels, color and luster of grain kernel could become dark and some smell after mould growth could appear.

(3) At all tested temperatures and CO_2 contents, development of different species of fungi in low moisture paddy were as follows: the occurrence of agricultural field fungi, mainly *Fusarium* and *Alternaria* decreased slowly. However, storage fungi, represented by *Aspergillus flavus*, *Aspergillus candidus*, *Aspergillus glaucus* and *Aspergillus niger* developed gradually as dominating fungi. CO_2 inhibited weakly the growth of storage fungi growth in paddy with low moisture content.

(4) In all kinds of temperature and CO_2 contents, development of fungi species in safe moisture paddy was as follows: the detection rate of agricultural field fungi, mainly of *Fusarium* and *Alternaria* was generally stable. However, storage fungi, represented by *Aspergillus flavus*, *Aspergillus candidus*, *Aspergillus glaucus* G. and *Aspergillus niger* increasing and developed gradually as dominating fungi. CO_2 caused weak inhibition effects on growth of storage fungi in paddy with safe moisture content.

(5) In all kinds of temperature and CO_2 contents, development of fungi species in high moisture paddy was as follows: In the first period of grain storage, occurrence of storage fungi, represented by *Aspergillus flavus*, *Aspergillus candidus*, *Aspergillus glaucus* and *Aspergillus niger*, increased rapidly, even reached 100% during the whole storage period with constantly high detection rate. Also, the occurrence of agricultural field fungi remained generally stable. At high temperature, carbon dioxide caused weak inhibition effects on growth of storage and field fungi in paddy with high moisture content.

Conclusion

Sensitive Indexes on Qualities

According to comprehensive analysis above, taste panel scores, fatty acid value and germination ratio (paddy not dried in oven) have been regarded as sensitive index of paddy qualities.

Influence of MA on Fungi in Grain Storage

Carbon dioxide inhibited very effectively the growth of grain fungi, which grew on bad qualities paddy or paddy with low moisture (below 15%) or at low storage temperature (below 15℃).

Contents of carbon dioxide in the storage atmosphere of more than 35% inhibited to a certain extent and for a short time growth of fungi, which grew on paddy with high moisture content of more than 15% or high storage temperature of more than 25℃. However, as storage time increased, damaging effects of fungi became worse, especially the storage fungi were not inhibited.

Modified atmospheres with increased content of carbon dioxide caused inhibition of mass growth of grain fungi not so much on the reduction of species of fungi. The carbon dioxide rich atmospheres did not ensure safe storage of paddy with high moisture content at high temperatures for a long period.

Conditions for Safe Grain Storage

According to comprehensive paddy quality analysis on various sensorial indexes as pests growth, color and luster, smell and mould grow, conditions for safe grain storage for one year can be determined as follows (Table 7):

Table 7. Conditions for safe grain storage for one year

Moisture content of stored paddy (relative humidity in balance in %)	temperature in℃	CO_2 content in air in the storage atmosphere in %			
		0	15	35	60
Low(60)	15	Safe	Safe	Safe	Safe
	25	/	Safe	Safe	Safe
	35	/	/	Safe	Safe
Middle(70)	15	Safe	Safe	Safe	Safe
	25	/	/	Safe	Safe
	35	/	/	Safe	Safe
High(80)	15	Safe	Safe	Safe	Safe
	25	/	/	Safe	Safe
	35	/	/	/	/

Note: "/" means unsafe.

It can be derived from the results presented in Table 7 that several factors influenced the safety of grain storage, such as grain moisture content, storage temperature and content of carbon dioxide in the storage atmosphere. So, grain could be stored safely by decreasing the temperature, lowering the moisture content or relative humidity and increase the amount of carbon dioxide in the atmosphere of the store.