Session 6

Fumigants, Controlled Atmospheres, and Hermetic Storage

The significance of vapor pressure in quality preservation of stored commodities under gastight conditions

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Abstract

While investigating the preservation of the aroma of various spices we compared the effects of hermetic conditions, vacuum and carbon dioxide versus aerated storage. The quality of the tested spices stored under hermetic conditions was comparable to those stored in vacuum after 120 d of storage. At a given temperature, a substance with higher vapor pressure vaporizes more readily than a substance with a lower vapor pressure. Throughout the investigation on specialty coffee, the volatility was evaluated as particularly important because coffee taste and aroma are influenced by compounds that are volatile. We hypothesize that hermetic storage reduces the rate of the volatiles to spread to the atmosphere. Dry food commodities can be stored for extended periods, provided there is no insect infestation and their water activity is low enough to prevent microbial growth. However, in aerated storages quantitative and qualitative losses still occur. If the moisture content is maintained sufficiently low, insects and quality loss remain the main concern for the quality preservation of durable agricultural commodities. Although in hermetic storage, the major emphasis is placed on the control of insect pests, for quality preservation just maintaining the vapor pressure in the sealed structure is sufficient. Quality preservation under hermetic conditions remains an aspect that deserves more attention. This characteristic of hermetic storage is the tendency to maintain within the hermetic structure the substances that have the ability to vaporize.

Key words: Hermetic storage, vapor pressure, volatile substances, aroma, quality preservation, modified atmospheres, low oxygen, vacuum, stored-product insects, stored-product microflora.

Introduction

Hermetic storage is a type of modified atmosphere (MA) that can be applied for the protection of commodities. This method takes advantage of sufficiently sealed structures that enable insects and other aerobic organisms in the commodity or the commodity itself to generate the MA by depleting the O_2 and increasing the CO_2 concentrations through respiratory metabolism (Navarro, 2006).

Dry food commodities can be stored for extended periods, provided there is no insect infestation and their water activity is low enough to prevent microbial growth. However, in aerated storages quantitative and qualitative losses still occur. Qualitative losses, for example, may consist of changes in physical appearance, in color change, loss of flavor, in nutritional degradation due to oxidation and increase in free fatty acids, the presence of insects or their fragments, or contamination by mold or the presence of mycotoxins. If the moisture content is maintained sufficiently low, insects and quality loss remain the main concern for the quality preservation of durable agricultural commodities (Navarro and Donahaye, 2005). Although in hermetic storage, the major emphasis is placed on the control of insect pests, for quality preservation just maintaining the vapor pressure in the sealed structure is sufficient.

Vapor pressure is a less investigated characteristic of hermetic storage. It is the tendency to maintain within the hermetic structure the substances that have the ability to vaporize. Such volatility is directly related to a substance's vapor pressure.

In chemistry and physics, volatility is the tendency of a substance to vaporize. Volatility is directly related to a substance's vapor pressure. At a given temperature, a substance with higher vapor pressure vaporizes more readily than a substance with a lower vapor pressure.

According to Weast et al. (1987) "vapor pressure is the pressure exerted when a solid or a liquid is in equilibrium with its own vapor. The vapor pressure is a function of the substance and of the temperature".

Vapor pressure or equilibrium vapor pressure is "the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system" (Wikipedia Vapor pressure 2018). The equilibrium vapor pressure is an indication of a liquid's evaporation rate. It relates to the tendency of particles to escape from the liquid (or a solid). A substance with a high vapor pressure at normal temperatures is often referred to as volatile. The pressure exhibited by vapor present above a liquid surface is known as vapor pressure. As the temperature of a liquid increases, the kinetic energy of its molecules also increases. As the kinetic energy of the molecules increases, the number of molecules transitioning into a vapor also increases, thereby increasing the vapor pressure.

There are many examples for commodities with volatiles that make the aroma, the taste and the flavor special. For example, in spices and beverages like cocoa, coffee and spices, volatility is particularly important because taste and aroma are influenced by certain compounds that are relatively volatile. Retaining those volatiles during storage period of time has not been possible in aerated storage, but hermetic storage gave excellent results.

Quality preservation under hermetic conditions remains an aspect that deserves more attention. In the present paper, this aspect of hermetic storage in the quality preservation capacity of volatile substances that are emitted from the products is emphasized. The objective of this presentation was to explore the significance of vapor pressure in quality preservation of stored commodities under gastight conditions.

Materials and methods

A- Laboratory trials

Source of spices:

The spices were freshly imported from Bangladesh from a spices company interested in exploring the effects of vacuum and other storage methods on quality preservation of spices. The selected spices for test were: cumin seeds (Vijayanand et al., 2001), chili pods (Duman, 2010), coriander seeds (Bandoni et al., 1998) and turmeric rhizomes (Goyal and Korla, 1993).

Samples of spices:

Prior to tests, five samples from each spice were taken. Samples sizes were: 100 g of cumin seeds, 100 g of turmeric rhizomes, 100 g of coriander seeds, and 50 g of chili pods. The experimental samples were kept in a room at 27±2ºC and 65±5% relative humidity (r.h.) for 120 d.

Relative Humidity:

The equilibrium relative humidity (ERH) of the spices was checked using Defensor® Novasina model ms1, Switzerland, with box sensor enMBRK-3. The equilibrium r.h. values expressed in this paper as percentages are equivalent to the decimal values in terms of water activity (a_w) which is the ratio of the water vapor pressure in the agricultural commodity to the water vapor pressure of pure water at the same temperature. Tests were carried out at 26.0-26.3ºC. The ERH of the cumin seeds was 52.2%, chili pepper pods was 43.3%; coriander seeds was 44.5% and turmeric rhizomes was 75.4%.

Storage conditions of spices: The spices were stored under the following conditions:

a- *Control under continuous airflow:* burlap sack was filled with a sample of the tested spice. Each sack was then inserted into a separate 500 mL glass container (for the chili pods we used 1,000 mL glass container). A plastic tube was then inserted from the top of the container and placed at the bottom below the burlap sack. The plastic tube was then connected to a small aquarium air pump allowing the air to flow through the sack at in airflow of 350 mL/min. The glass container remained open at the top for the entire duration of the test .

b- *Hermetic storage:* Each of the tested spices was sealed in a separate 1,000 mL glass jar. The jars were hermetically sealed for the entire duration of the test.

c- *High CO_2 (90% to 100%) atmosphere*: Each of the tested spices was sealed in a separate 750 mL glass jar. The jars were saturated with 100% CO_2 inserted through a rubber sealer at the jar lead. The CO_2 concentrations were examined periodically (once a week) and corrected when needed to adjust to CO_2 concentrations higher than 90%.

d- Vacuum: Each of the tested spices was sealed in a 500 mL vacuum glass container. The pressure in the container was initially reduced to 6.5 mmHg absolute pressure. The pressure was examined periodically (once a week) and maintained below 25 mmHg. In some samples higher pressures than 25 mm were recorded due to the difficulty in maintaining the low pressure. Those pressures were immediately rectified to the target pressure.

e- Burlap sack without aeration (also used as control): Each sack was filled with the tested spice. All burlap sacks were placed on shelve, exposed the room temperature and humidity.

Quality test: After 120 days of storage, all treated spices were removed from their experimental containers and placed in a container covered with a plastic Petri dish. The treatments were given a score from 1-5 for aroma and color 1 (dark color or other defects) represent the poorest and 5 best aroma and the best color (bright red color with no defects).. For these tests 15 individuals (6 women and 9 men) from the Department of Stored Products of the Israel Agricultural Research Organization were asked to score the sensory evaluation. Only chili pods were scored for color change and their pungency by smelling. Comparisons for all pairs were analysed using Tukey-Kramer HSD (honest significant difference) test method (SAS, 2014)

B- Field trials

The following two field trials were conducted by commercial companies that market chili pepper. Test results reported to the authors were not complete, but they were supported by available data description of the tests and pictures taken during and at the end of the trials.

Field Trial 1: One set of trial was conducted by the company HAJISONS at Kunri of District Umar Kot in the Province of Sindh area of Pakistan during the period of 7 months between December 3 - 9, 2016 and July 5, 2017. The area has foggy winter (Nov –Feb) with few western disturbances causing rain; pleasant spring (Feb –April); summer (April – June) with dust, rain storms and heat wave periods and rainy monsoon (July – August). The hottest month is June, where average highs routinely exceed 40°C. Coldest month is January with average high 19.8ºC. Dry chili was stored in jute bags that served as control and compared with GrainPro hermetic bags indoors.

Field Trial 2: The second set of demonstration trial was conducted within the facilities of Olam Agro India Limited at District Guntur, Andhra Pradesh, India. The trial lasted for 6 months. The climate in Guntur is tropical. The average temperature is warm to hot year-round. The average annual temperature is 28.5ºC. The trials were conducted by Mr. Madhu Nagaraj and Mr. Hari Babu of the Olam Agro India Limited. The practice was storing the whole dried RCPs (red chili pepper). However, this method requires a lot of space in a storage facility or during transport. It was recommended to test storing dried RCPs in powdered form to maximize capacity for storage and transport. Various parameters were measured every month for 6 months of storage including weights, moisture, colour, pungency and aflatoxins.

Results

Results of Laboratory Trials:

Results of blind test are shown in Table 1 which indicates that the control with airflow and in burlap sack gave the poorest results with scores below 2. For aroma tests best results obtained after 120 d under hermetic storage and vacuum. Although high CO_2 provided better preservation compared to controls, it was still inferior to hermetic and vacuum. The purpose of providing an active airflow in the control was to demonstrate that aerating to remove the aromatic volatiles would be more effective than the static control without aeration in burlap sack. The fact that airflow provided better results than the burlap sack may indicate that the jars where airflow of 350 mL/min were exposed was not sufficiently aerated compared to the volatiles that were evaporated from the burlap sacks.

Statistic test of comparisons for all pairs using Tukey-Kramer HSD showed that there was no significant difference for all spices stored under vacuum or hermetic storage. The storage under high CO_2 showed also no significant difference from stored under vacuum or hermetic storage excluding turmeric rhizomes. In both, storage in burlap sack or airflow showed the poorest performance compared with the other treatments. Vacuum storage gave best results followed by hermetic storage and high CO_2.

Table 1- Blind tests (Mean ± SE) for aroma of spices stored for 120 d at 27°C and 65% r.h.

Treatment	Cumin seeds	Chili pods*	Coriander seeds	Turmeric rhizomes
Airflow (control)	1.9 ± 0.31	1.5 ± 0.31	1.5 ± 0.40	1.4 ± 0.22
Hermetic storage	4.2 ± 0.36	3.7 ± 0.49	3.9 ± 0.36	4.1 ± 0.54
High CO_2	3.6 ± 0.40	4.0 ± 0.49	3.5 ± 0.31	2.7 ± 0.56
Vacuum	4.1 ± 0.36	4.1 ± 0.45	4.4 ± 0.45	4.6 ± 0.27
Burlap sack (control)	1.1 ± 0.13	1.2 ± 0.36	1.5 ± 0.40	1.3 ± 0.22

The Standard d Error of all means was 0.2

*For chili pods pungency tests served as criteria instead of aroma.

Table 2 shows results obtained using blind test for color difference of chili pods. Statistic test of comparisons for all pairs using Tukey-Kramer HSD showed that there was no significant difference for the color of the chili pods stored under vacuum or hermetic storage. This in spite of the fact that vacuum has better results. Storage under high CO_2 showed no significant difference from stored under hermetic storage, but was significant difference for those stored under vacuum.

In both, storage in burlap sack or airflow showed the poorest performance compared with other treatments. vacuum storage gave best results followed by hermetic storage and high CO_2.

Table 2- Blind tests (Mean ± SE) for color and pungency of chili pods stored for 120 d at 27°C and 65% r.h.

Treatment	Chili pods
Airflow (control)	1.0 ± 0.0
Hermetic storage	4.2 ± 1.2
High CO_2	3.5 ± 0.5
Vacuum	5.0 ± 0.0
Burlap sack (control)	1.5 ± 0.8

Results of Field trials

Field trial 1:

Test results of the are shown in Table 3 which gave a good indication of quality preservation capacity of dry chili peppers after 7 months of storage. In this case the quality parameters of color preservation, pungency, freshness, moisture preservation and fruit weight were well preserved in hermetic storage compared to lower quality observed in chili peppers stored in jute bags.

The weights of both whole and powdered chili peppers (RCP) remained constant throughout the 6-months storage period. For RCPs stored in Cocoon Indoor, the moisture content for whole RCP remained stable at 7.15%, while for powdered RCP, no change in moisture content was observed. For whole RCPs stored in SuperGrainBags (SGB), fluctuating moisture was observed taking into consideration the moisture analyzer that was utilized and the non-uniform moisture content of RCP lots that were stored. Cocoon Indoor and SGBs are designed to prevent moisture ingress during storage, maintaining moisture of the stored commodity. It is a must that properly dried agricultural commodity are dried and stored in safe moisture to inhibit mold growth thus preventing aflatoxin or mycotoxin production. In the case of RCPs, a final moisture content of about 8% is ideal, as moisture content above 11% allows mold growth and below 4% causes excessive color loss.

Table 3- Results recorded at the end of storage period of dry chili peppers in GrainPro hermetic bags and jute bags at Haji Sons, Pakistan after 7 months.

	Hermetic	Jute bag
Color	No discoloration, shined red	Discolored, dull
Pungency	Same as fresh/high	Diluted
Freshness	High	Low
Moisture	No change	Increased
50 fruit weight (g)	36	24

Field trial 2:

The initial pungency of both whole and powdered RCPs measured in heat units were comparable to the heat units taken from RCPs stored for 6 months. Pungency of the spices is caused by several compounds, such as capsaicin for RCPs, which are volatiles. In a gastight system such as SGBs and Cocoon Indoor, these volatiles create equilibrium within the storage, trapping these compounds thus preserving pungency of RCPs.

Colour of whole and powdered RCPs were observed to decline during the storage period. The coloring pigment of chilies is carotenoid which is sensitive to light. Carotenoid pigments degrade when exposed to light, thus storing RCPs in the cold storage or dark room have low rate of color loss. During the trial at Olam, the set-up was placed outdoor since there was not enough space indoor. Even though RCPs were placed in woven polypropylene bags along with SGBs and Cocoon Indoor, light could still penetrate the stack leading to change in color of RCPs.

Light and oxygen contributed to the rate of colour loss. Color degradation of whole RCPs were more evident compared to powdered RCPs since it is less compact allowing more light to enter the stack.

The aflatoxins of RCPs were observed to be 0.5 ppm initially up to 6 months, except on 2nd month for powdered RCPs and 3rd month for whole RCPs in SGBs. These fluctuations in reading might be brought by limitations of the method of analysis for aflatoxin. SGBs and Cocoon Indoor were effective in preventing aflatoxin production during storage. In the previous discussion, moisture ingress is prevented when using SGBs and Cocoon Indoor thus inhibiting molds by maintaining safe moisture for dried RCPs during storage. When molds are inhibited, production of mycotoxins, including aflatoxins is also prevented.

During the trial, whole and powdered dried RCPs were stored. The capacity of SGBs was maximized when storing powdered RCPs (i.e. 40 kg/SGB) compared to storing whole RCPs (i.e. 8 kg/SGB). Several parameters were tested including moisture, colour, pungency, weight and aflatoxin. For 6 months of storage, these parameters measured from powdered and whole RCPs were comparable. Moreover, the colour was observed to be better when storing powdered RCPs compared to whole RCPs.

Discussion

Ambient humidity is an abiotic factor of the air surrounding the commodity. Within the confined storage space, the moisture of the commodities, tend to reach equilibrium with the humidity of the intergranular air. Its greatest influence is on molds, which begin to develop at intergranular air humidities above 65% (Navarro and Donahaye, 2005).

Micro-organisms are the biotic factor composed of molds, yeasts and bacteria. They are universally present on the grain, but are inactive when the equilibrium relative humidity is below 65% .

When discussing microflora activity and preservation of grain quality, it is more meaningful to consider the moisture content of the intergranular environment or the equilibrium relative humidity (ERH) corresponding to a particular commodity moisture content. This is because various grain types may have different moisture contents at the same ERH. The microfloral activity and susceptibility of grain to deterioration is correlated to the ERH. An additional term frequently used in food microbiology is "water activity". Water activity (a_w) and ERH are numerically equivalent, but ERH is expressed as a percentage and aw as a decimal of ERH, thus a_w 0.8 = 80% ERH (Lacey et al. 1980).

Favorable conditions occur when the moisture content of the grain or the relative humidity of the intergranular atmosphere rises above a certain threshold. This threshold is generally considered to be around 75% RH (termed the critical relative humidity) or the corresponding equilibrium moisture content of the grain (e.g. for wheat it is about 14%) - often termed its critical moisture content. Beyond this threshold, microflora become activated, and starts to grow, accompanied by active respiration, liberation of metabolic heat and water. At humidity or moisture conditions above this level, deterioration increases at an exponential rate .

The availability of water in the food medium is a vital factor determining both the types of bacteria or fungi capable of growth, and the rate at which they can grow. It is usually measured in term of water activity, and is a function of the moisture content of the food.

Bacteria grow best at water activities near to unity, and will not grow at a water activity less than about 0.95. Yeasts occupy an intermediate range, and they will grow at water activities as low as 0.85. Fungi are more resistant to the effect of dry conditions, although the vast majority are inhibited by water activities lower then 0.70, a very few species will show some growth at a water activity as low as 0.65 (Lacey et al. 1980).

Tests were carried out in various climate conditions to observe product preservation under hermetic conditions. Among other quality parameters such as insect infestation, milling recovery, head rice, yellow kernels, germination, and weight loss, changes in moisture content of hermetic and non-hermetic storage of paddy was reported (Navarro et al,1997). Accordingly they report paddy stacks of capacities ranging from 13.4 to 31.9 tonnes that were stored outdoors in flexible enclosures for 78 to 183 days. The quality of the paddy was compared with that of three control stacks (5.3–5.6 tonnes capacity) held under tarpaulins in the open for 78–117 days. The trials were conducted at the NAPHIRE compound, Nueva Ecija, the Philippines (Navarro et al., 1997). There was a real trend towards an increase in moisture content in the two control stacks during the wet season and toward a decrease in moisture content in the control stack stored during the dry season. No significant changes were noted, in the eight hermetic stacks and two silos. These field trials indicated that the changes in moisture content and weight of the grain changed only very slightly within the stacks and the silos due to hermetic storage.

Lane and Woloshuk (2017) studied small hermetic bags (50 and 100 kg capacities) used by smallholder farmers in several African countries as a low-cost solution for preventing storage losses due to insects. In their study they compared the effects of environmental temperature and relative humidity at two locations (Indiana and Arkansas) on dry maize (14% moisture content) in woven polypropylene bags and Purdue Improved Crop Storage (PICS) hermetic bags. The results indicated that the PICS bags prevented moisture penetration over the three-month storage period. In contrast, maize in the woven bags increased in moisture content. The work of Lane and Woloshuk (2017) is an additional indication that hermetic storage enables maintaining the water vapor as expressed as humidity in their work. They concluded that the PICS hermetic bags are effective at blocking the effects of external humidity fluctuations as well as the spread of fungi to non-infected kernels.

The more volatile the compound is the faster it will vaporize. This is why the coffee brewing temperature is so important; it allows proper and fast extraction of nonvolatile components, while preserving the volatile ones. Espresso extraction is a few degrees lower than drip coffee. Pressure helps extract more total dissolved solids (TDS) at a lower temperature, while preserving volatile components. TDS is a measure of the combined content of all inorganic and organic substances contained in a liquid in molecular, ionized or micro-granular suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a filter with two-micrometer (nominal size, or smaller) pores (Wikipedia, TDS, 2018).

Ribeiro, et al. (2011) evaluated the physical, chemical, and sensory qualities of green coffee beans (*Coffea arabica* L.) during storage in different types of packaging. Coffee was stored in a warehouse in Brazil. The treatments consisted of two types of packaging (hermetic big bags with the injection of up to 60% CO_2 in a controlled atmosphere; similar bags but without the injection of CO_2 in a modified atmosphere). The storage of green coffee beans under these conditions was viable over a 12-month period. The coffee packed in big bags maintained its quality and exhibited an intensification of the green coloration of the grains during storage. Sensory analysis of coffee beans stored in a controlled atmosphere showed that the medium sampling position yielded the best ratings. The results of Ribeiro, et al. (2011) analysis demonstrated that the tested storage technique can potentially increase the effectiveness in preserving the sensory quality of coffee beans.

In another study Borém et al,. (2013) commercially validated the effects of an artificial atmosphere on the color, flavor and aroma of green coffee beans stored after 12 months. The coffees were evaluated by a sensory panel composed of 13 tasters who were judges certified by the Specialty Coffee Association of America and who operate commercially in various coffee-producing regions of Brazil. The evaluation consisted of hermetic big-bags with and without CO_2 injection. Two additional treatments served as controls: jute sacks and GrainPro sacks. The beans were qualitatively evaluated for their color and for their beverage quality attributes including their fragrance, sweetness, acidity, flavor, body and aftertaste. The beans packaged in hermetic big-bags with a CO_2 injection maintained a specialty coffee classification. Impermeable packaging preserved the initial color of the coffee beans. Coffee storage in hermetic packaging preserved the desirable aromas of the coffee. In these studies Borém et al,(2013) showed that undesirable flavors and aromas predominated in the coffees packaged in jute sacks. In all these studies with coffee it is most possible that the quality preservation under sealed conditions, weather under vacuum, hermetic storage or CO_2 assisted modified atmospheres, the packages were maintained sealed that most possible the escape of the volatiles from the coffee to maintain its organoleptic qualities.

We do not have a current method to assess the vapor pressure of the volatiles in the commodities. However, all these studies are in line with the basic understanding that hermetically sealed storages maintain the vapor pressure of the volatiles enabling the commodities better quality preservation. Whereas in all tested aerated storages loss of the volatiles dues to their vapor pressure that should have maintained, was accompanied with loss of quality. Therefore, the conclusions from these studies lead to the understanding for the preservation of the quality of spices and beverages the preferred method of storage should be hermetic sealed storage. Additional supporting research should be carried out on quality preservation of the hermetic storage as an added benefit to the control of insects.

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Hermetic storage technology for handling of dry agricultural commodities: Practice, challenges, opportunities, research, and prospects in Zimbabwe

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Abstract

Storage pest management practices have relied on synthetic pesticides comprising: dust powders, liquid formulations and fumigants. Reduced efficacy against targeted species, negative health-related issues and increase in consumer awareness on potentially detrimental effects of synthetic pesticides have led to a shift towards safer and environmentally-benign alternatives. Hermetic technology is a pesticide-free storage alternative currently being used in Zimbabwe and other African countries. In the current paper, we review forms and characteristics of the hermetic technology available, organisations driving the technology, research and development (R&D) initiatives, and access and uptake trends in the country. The review draws out future prospects in terms of: stakeholder partnerships and roles, up-scaling/adoption options, R&D gaps, capacity building, and funding mechanisms for effective and sustainable uptake. Critical areas identified in the review include: the need for increasing the number of hermetic plastic liner brands available to enhance access and competitive pricing, improved distribution mechanisms for hermetic storage containers for easy access in remote areas, and generation of evidence-based efficacy data on the various hermetic storage containers in preserving quality of commercial, parent and foundation seed. Future opportunities include use of hermetic containers in the disinfestation of organic horticultural products using carbon dioxide gas hermetic fumigation. However, supporting policies are necessary to ensure sustainable adoption of the hermetic technology at subsistence and commercial scales.

Keywords: synthetic pesticides, pesticide-free storage, gas hermetic fumigation, hermetic technology adoption