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CO_2 DYNAMICS AND QUALITY OF CORN GRAINS STORED IN HERMETIC AND NON-HERMETIC ENVIRONMENTS

Author: Geraldo Acácio Mabasso
Supervisor: Professor Dr. Osvaldo Resende
Cosupervisor: Dr. Diene Gonçalves Souza

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July – 2025

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DEDICATORY

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Geraldo Acácio Mabasso, son of Acácio Mupoza Mabasso and Artimiza Aurélio Macamo, was born on August 25, 1984, in the neighborhood of “Xipamanine”, in the municipal district of “Kalhamanculo”, in Maputo city, Mozambique. He currently lives in the Vila Nova neighborhood, in Chimoio city, Manica province, Mozambique. Geraldo Mabasso is married with Marcela Fernando, with whom he has three children, Gercelo, Géssica and Enzo Christian.

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He has published several technical and scientific papers, including manuscripts, book chapters, posters and abstracts presented at events and journals with an impact factor in the field of Agricultural Sciences, especially in the post-harvest of vegetable products. He also contributes as a reviewer of scientific manuscripts in specialized journals.

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LIST OF SYMBOLS, ACRONYMS, ABBREVIATIONS AND UNITS

CO_2	Carbon dioxide
%	Percentage
[CO_2]	Concentration of carbon dioxide
a*	Green/red coordinate
AI	Acidity index
ANOVA	Analysis of variance
AOAC	Official Association of Official Analytical Chemists
a_w	Water activity
b*	Blue/yellow coordinate
BD	Bulk density
BROK	Percentage of broken grains
C*	Chroma
CF	Crude fiber
CHO	Carbohydrate
CONAB	Companhia Nacional de Abastecimento
CUR	*Curvularia spp.*
CV	Coefficient of variation
DBO	Biochemical Oxygen Demand
dm	Dry base
DML	Dry matter loss
EC	Electrical conductivity
EE	Ether extract
EMC	Equilibrium moisture content
FAO	Food and Agriculture Organization
FERM	Percentage of fermented grains

FLA	*Aspergillus flavus*
FUS	*Fusarium spp.*
g mL^{-1}	Gram per milliliter
g 100 g^{-1} dm	Gram per hundred grams, dry base
GM	Germination
H	Hermetic
H*	Hue angle
ID	Insect damage
IDL	Insect damage loss
II	Iodine index
IMAT	Percentage of immature grains
IMC	Initial moisture content
IMP	Percentage of impurity
kg	Kilograms per cubic meter
kg m^{-3}	Kilogram per meter
L*	Black/white coordinate
MAPA	Ministério da Agricultura, Pecuária e Abastecimento
MC	Moisture content
MOLD	Percentage of moldy grains
NDIR	Non-dispersive infrared
NH	Non-hermetic
NIG	*Aspergillus niger*
NIR	Near infrared
ºC	Celsius degree
PCA	Principal component analysis
PI	Peroxide index
POR	Porosity
ppm	Parts per million
RH	Relative humidity
SC	Storage condition
SEM	Scanning electron microscope
SFA	Saturated fatty acids
SHRI	Percentage of shriveled grains

ST	Storage time
T	Temperature
t	Time
TD	True density
TDG	Percentage of total defect grains
TGM	Thousand grain mass
UFA	Unsaturated fatty acids
wb	Water base
WDG	Percentage of weevil-damaged grains
ΔE	Color difference
ε	Porosity
ρ_{ap}	Bulk density
ρ_u	True density

GENERAL ABSTRACT

Brazil has been one of the countries with the highest corn production and productivity rates. Developments in the production sector are putting pressure on post-harvest care, in terms of storage capacity and product conservation conditions. Currently, the storage capacity does not meet the needs and alternative forms of storage in bag silos have been adopted by storage units. Bag silos are hermetic infrastructures which, apart from their cost, offer advantages in terms of losses due to biotic factors, guaranteeing greater availability and quality when good management practices are adopted. Thermometry has been used as the main mechanism for managing stored grains, but usually by the time the hot spots are detected, the damage has already occurred, and efficiency depends on the distribution of the cables in the storage structure. The use of CO_2 sensors has been reported as a complementary and effective measure in the early detection of deterioration signs, allowing for good accuracy in decision-making. In view of this, the aim of this work was to evaluate the quality of grains stored with different initial moisture contents, both hermetically and non-hermetically, as well as their relationship with the dynamics of CO_2 levels, temperature and relative humidity in the grain mass. An experiment was carried out in a completely randomized design, with a 2 × 3 × 6 factorial scheme, corresponding to two storage conditions (hermetic and non-hermetic), three initial moisture contents (14, 16 and 18% wb), six storage times (0, 30, 60, 90 and 120 days) and three replications. Throughout storage, CO_2 concentrations, temperature and relative humidity in the grain mass and in the external environment were monitored using CO_2 sensors. The physical properties, color, proximal composition, dry matter loss, water activity, grain integrity using X-ray images and scanning electron microscopy, insect and fungal damage, as well as the quality of the oil extracted over the 120 days of storage were also assessed. The data was evaluated using regression models, t-test, correlation and multivariate analysis, using RStudio 4.3.2® software package. It was concluded that the temperature, relative humidity and CO_2 concentrations were influenced by the storage conditions, with the values increasing with the increase in initial moisture content and storage time; the condition of higher moisture content was generally more detrimental to the grain quality, as well as the extracted oil, with greater intensity for the grains stored hermetically. With regard to the classification of the grains, for a moisture content of 14% wb, storage can be carried out up to 120 or 90 days for hermetic or non-hermetic conditions, with 30 days being the maximum tolerable for conditions with a moisture content of 16 and 18% wb.

Keywords: *Zea mays* L.; dry matter loss; CO_2 sensor; proximal composition; hermetic storage

RESUMO GERAL

O Brasil tem se destacado entre os países com maiores índices de produção e produtividade milho. A evolução no setor produtivo gera pressão nos cuidados pós-colheita, quanto a capacidade estática e as condições de conservação do produto. Atualmente, a capacidade estática não satisfaz as necessidades e a adoção de formas alternativas de armazenamento em silos bolsa tem sido adotado pelas unidades armazenadoras. Os silos bolsa são infraestruturas herméticas, que além do custo oferecem vantagens em termos de perdas derivadas de fatores bióticos, garantindo maior disponibilidade e qualidade, quando são adotadas boas práticas de manejo. A termometria tem sido usada como principal mecanismo de manejo de grãos armazenados, porém, geralmente quando detectam os focos de aquecimento o dano já ocorreu e a eficiência depende muito da distribuição dos cabos na estrutura de armazenamento. O uso de sensores de CO_2 tem sido reportado como uma medida complementar e eficaz na detecção precoce de sinais de deterioração, permitindo uma boa acurácia na tomada de decisão. Diante disto, neste trabalho objetivou-se avaliar a qualidade de grãos armazenados com diferentes teores de água iniciais, de forma hermética e não hermética, assim como a sua relação com a dinâmica de níveis de CO_2, temperatura e umidade relativa na massa de grãos. Com efeito, foi conduzido um experimento em delineamento inteiramente casualisado, esquema fatorial 2 × 3 × 6, que corresponde a duas condições de armazenamento (hermético e não hermético), três teores de água iniciais (14, 16 e 18%, bu), seis tempos de armazenamento (0, 30, 60, 90 e 120 dias) e três repetições. Ao longo do armazenamento foram monitoradas as concentrações de CO_2, temperatura e umidade relativa na massa de grãos e no ambiente externo, por meio de sensores de CO_2. Igualmente foram avaliadas as propriedades físicas, cor, composição proximal, perda de matéria seca, atividade de água, integridade do grão por meio de imagens de raios X e microscopia eletrônica de varredura, danos por insetos e fungos, assim como a qualidade do óleo extraído ao longo dos 120 dias de armazenamento. Os dados foram avaliados por meio modelos de regressão, teste t, correlação e análise multivariada, utilizando o software RStudio 4.3.2®. Concluiu-se que a temperatura, umidade relativa e concentrações de CO_2 foram influenciados pelas condições de armazenamento, sendo os valores crescentes com o aumento do teor de água inicial e tempo de armazenamento; a condição de maior teor de água foi em geral mais prejudicial para a qualidade do grão, assim como do óleo extraído, com maior intensidade para os grãos armazenados de forma hermética. Em relação a classificação dos grãos, para o teor de água de 14% bu, o armazenamento pode ser realizado até os 120 ou 90 dias para a condição hermética ou não hermética, sendo 30 dias o máximo tolerável para as condições de teor de água de 16 e 18% bu.

Palavras-chave: *Zea mays* L.; perda de matéria seca; sensor de CO_2; composição proximal; armazenamento hermético

1. GENERAL INTRODUCTION

Brazil is one of the world's largest grain producers and is responsible for significant export demand, with a volume of 115.72 million tons of corn grains in the 2023/2024 season, representing an increase of 44.56% compared to the 2013/2014 season (CONAB, 2025). This upward trend puts pressure on storage capacity, which stands at 75% of total grain production, far short of the ideal target of 120% set by the FAO (An and Ouyang, 2016). In this context, different techniques for monitoring grain quality based on temperature, moisture content and respiration rate have been tested and adopted by farmers, exporters and managers with a view to safe storage, thus minimizing the deficit in relation to storage capacity.

According to Kaushik and Singhal (2018), the use of temperature sensors is a method of grain management that is considered fast, less expensive and accurate for measuring temperature, but limited for detecting the presence of insects, as they can develop in a close temperature range. Grain deterioration caused by fungi, mites and insects can be detected by monitoring the CO_2 concentration in the intergranular air, which increases its concentration because of respiratory activity and can be detected using sensors.

In stored products such as grains, for non-hemetic condition, CO_2 concentrations in the range of 600 to 1500 ppm indicate the start of fungal growth and between 1500 and 4000 ppm the level of infestation (by fungi and insects) is considered serious, with significant impacts on quality (Kaushik and Singhal, 2018). In the same context, Abalone et al. (2011) reported 5% (50 thousand ppm) of CO_2 concentration as reference in stored wheat grains with an initial moisture content of 13% wb, in temperature of 20 to 30 °C would be considered a reference, while 100 thousand ppm represents intense biological activity in grain mass.

Souza et al. (2024) reported CO_2 concentrations close to 1300 ppm in stored corn grains with an initial moisture content of 18% wb, with a dry matter loss of more than 0.5% reached after 18 days of storage. For the initial moisture content of 14% wb, the maximum CO_2 concentration was close to 600 ppm, with a dry matter loss of more than 0.5% reached after 61 days, showing a positive correlation between CO_2 concentration, initial moisture content and dry matter loss.

A lot of research has been dedicated to studying the behavior of CO_2 in the grain mass, but the indication of the correlation between CO_2 concentrations and quantitative losses is still incipient, limiting its practical applicability, especially with regard to storage alternatives, which include the use of hermetic systems, such as bag silos, a common alternative accessible to different levels of production (Barrettino et al., 2019). Hermetic storage systems have stood out, among other aspects for their role in reducing insect and fungal infestation, thus contributing to less deterioration, depending on the initial condition of the product, especially in the context of small farmers, who can easily adopt the technology through small hermetic packages, with a capacity of up to 100 kg each (Odjo et al., 2022).

Based on Baributsa and Ignacio (2020), a good grain storage system must guarantee the preservation of grain integrity, with less loss of quality. And the use of hermetic infrastructures, usually in bags, has been adopted mainly in some countries in sub-Saharan Africa and Asia. This technology includes the use of metal or polyethylene silos, bags and other forms and in different sizes, which can reach up to 300 tons, whose main characteristic is associated with the creation of unfavorable conditions for the development of insect pests, thus minimizing deterioration factors.

The knowledge of the different storage methods and the conditions under which the stored product is monitored directly affects the storage unit manager's decision as to whether or not to continue with storage, considering the offer of better marketing prices or extending availability over time (Souza et al., 2024; Taher et al., 2019).

The correlation between the CO_2 concentration generated by grain deterioration under different storage conditions can provide a primary tool for the development of grain management strategies and platforms for the rapid detection of damage to stored grain and the application of the necessary preventive or corrective measures to guarantee quality (Souza et al., 2024; Bilhalva et al., 2023; Souza et al., 2023).

The technical and practical limitations of post-harvest grain management are still a challenge for farmers in terms of guaranteeing grain quality and value. It is clear from previous research that changes in CO2 concentration in stored grain environments can be associated with the development of hot spots in the grain mass, resulting in deterioration and loss of quality (Souza et al., 2024; Bilhalva et al., 2023). The use of CO_2 sensors located close to these points can detect changes in gas concentration and thus indicate the source of potential deterioration in combination with integrated temperature and relative humidity sensors.

1.1 Corn grain storage systems

In general, grains can be stored for a long period under conditions of low moisture content and temperature (Moses et al., 2015). Storage conditions are important in maintaining the quality and biological activity of the stored product, with temperature, relative humidity and CO_2 and O_2 concentrations being among those that have the greatest influence on the granular mass, in addition to the initial moisture content, which conditions various parameters during storage. In addition, initial moisture content has been identified as a crucial factor in the respiration rate of grains, both for hermetic and non-hermetic systems (Daba et al., 2024; Souza et al., 2024; Souza et al., 2023; Bilhalva et al., 2023; Valle et al., 2021a).

Certain levels of temperature fluctuation and relative humidity in the granular mass can promote a series of metabolic reactions, including respiration. A storage system able to maintain the internal air condition in the granular mass is useful to limit the deterioration degree (Zhang et al., 2014). Zhang et al. (2014) also point out that the CO_2 concentration in large warehouses or silos are influenced by the volume of the facility and the structures used for collection, and the effect is diluted for longer evaluation periods.

Leal et al. (2023) also showed the advantage of monitoring temperature, relative humidity and CO_2 levels in the granular mass for early detection of quality loss in wheat grains stored in vertical silos and lower metabolic activity for products stored with a water content close to 12% wb. Early detection of grain deterioration signs in vertical silos is useful for preserving quality (Bilhalva et al., 2023).

Hermetic storage, which is very common in the context of small farmers in Mexico (Odjo et al., 2022) or bag silos with a capacity of more than 200 tons in South America (Valle et al., 2021a), helps to maintain grain quality and minimize quality losses. Bag silos have been a common alternative in countries with underdeveloped storage systems or to address the low capacity for grain storage in conventional systems, such as vertical silos and granaries (Barrettino et al., 2019).

The hermetic storage ecosystem has the potential to increase CO_2 concentrations and reduce O_2 concentrations, as long as good sealing is guaranteed, which can generate an oxygen-poor environment, which is why it is important to have a physical barrier to the entry of gases, including water vapor (Ochandio et al., 2017). Valle et al. (2021b) also point out that faulty seals in hermetic packaging provide favorable conditions for the occurrence of fungi during the storage of wet grains, although to a lower degree. According to Lutz et al. (2022), although the deterioration of stored grains is expected to increase over storage time, lower initial moisture contents provide better conditions for grains stored in hermetic systems, such as bag silos. And the levels of CO_2 increase and O_2 decrease inside the hermetic packaging depend on the interaction between the initial moisture content and the temperature in the grain mass (Valle et al., 2021a; Chelladurai et al., 2016).

1.2 Respiration and grain quality

Measuring respiration rates is one of the most important ways of establishing management techniques for stored products. A decrease in O_2 levels or an increase in CO_2 contributes to a reduction in insect damage to corn grains, provided that a physical barrier against insect entry and initial infestation control is guaranteed (Dowell and Dowell, 2017). The respiration rate is associated with CO_2 levels generated in the grain mass, because of the interaction between the biotic and abiotic factors present in the grain mass.

Chidananda et al. (2014) found that increasing moisture content and temperature were positively correlated with the rate of grain respiration, being it proportionally lower for conditions of moisture content between 12 and 14% wb, as well as temperature, providing a lower respiration rate and, consequently, better quality in pulse grains. This behavior was also observed by Souza et al. (2023) in soybeans stored in prototype silos with moisture contents ranging from 12 to 16% wb for 90 days and corn grains stored for the same period with moisture contents of 14, 16 and 18% wb (Souza et al., 2024).

Assessing CO_2 concentration is one of the most efficient ways of evaluating the activity of insects and microorganisms in the grain mass, as an indicator of grain deterioration or early detection of sources of deterioration (Fleurat-Lessard, 2017). Grain deterioration is associated with the generation of CO_2, water vapor, heat and distinct odors, as a reflection of grain metabolism, fungi, insects and mites in the grain mass. Increased CO_2 levels in stored grain indicate that insects, fungi or excessive respiration are present, so increased CO_2 levels in grain are a reliable indicator of deterioration and, consequently, corrective measures can be taken in real time (Bilhalva et al., 2023; Neethirajan et al., 2020).

The fungi metabolic rate is highly influenced by the initial moisture content of the grain and their growth is inhibited below a certain threshold of water activity (a_w), usually below 0.85 (Valle et al., 2021a). For safe grain storage, moisture content and temperature values must be compatible to maintain an a_w below the threshold for the development of insects and microorganisms (Valle et al., 2021a; Fleurat-Lessard, 2017). The increase in respiratory activity in the granular mass causes an increase in water vapor, thus allowing for greater fungi proliferation. According to Zhang et al. (2014), the amount of CO_2 produced by grain respiration is relatively low and does not interfere with monitoring the amount generated by the presence of insects and fungi.

Physical properties, proximal composition, oil quality, and incidence of insects and fungi are among the attributes of greatest interest in assessing grain quality and its association with CO_2 concentrations (Coradi et al., 2022; Bilhalva et al., 2023; Erasto et al., 2023; Souza et al., 2024). Bulk density, true density and porosity are fundamental to design of grain conservation and storage projects (Garcia-Lara et al., 2019). These properties are strongly affected by moisture content, including thousand-grain weight, which has also been used to define quality.

For Garbaba et al. (2017), among the precautions necessary for preserving the corn grains quality, the implementation of an effective pest management program is an important tool in preserving the nutritional quality of stored grains and secondary metabolites associated with fungi. The quality of edible oil is generally associated with a higher ratio of unsaturated to saturated fatty acids, with a particular emphasis on linoleic acid (Sanjeev et al., 2014).

According to Winkler-Moser & Breyer (2011), the oxidative stability of oils is affected by many factors, including fatty acid composition, antioxidant concentration and stability, and the presence of pro-oxidant compounds such as free fatty acids, lipid peroxides, or pro-oxidant metals. This situation gives corn oil greater stability during storage and cooking (Singh et al., 2014). According to Bilhalva et al. (2023), increased lipid acidity is directly associated with increased grain deterioration intensity.

1.3 Management and application of CO_2 sensors in the grain mass

Regardless of the control measure adopted to ensure grain quality, it is necessary to manage the parameters associated with quality loss, such as moisture content, temperature, relative humidity, CO_2 and O_2 concentrations. In addition to management actions, CO_2 can also be used as a fumigant to control the insect population in the granular mass, and it is important to ensure adequate concentration, distribution and uniformity in the application (Kaushik and Singhai, 2019).

CO_2 monitoring can be used effectively to measure the respiratory activity of the ecosystem composed of grains and other biotic agents. CO_2 or gas sensors in general are a useful tool for identifying infestation spots in the grain mass and can be inserted inside the grain mass to measure the intergranular composition of the air and early detection of deterioration of stored grain due to the action of any biotic agent (Kaushik and Singhai, 2019; Fleurat-Lessard, 2017). Nowadays, sensors are essential for determining the grain mass condition, even making it possible to obtain information in real time, with the possibility of making more effective decisions quickly. When deterioration occurs due to the development of insect pests, heat, water vapor and increased CO_2 levels are generated (Kaushik and Singhai, 2019).

The release of CO_2 is correlated with the moisture content of the grain. CO_2 concentrations of 400 to 500 ppm are synonymous of safe storage, values close to 1000 ppm usually indicate the existence of some problem in the grain mass (Fleurat-Lessard, 2017) and between 1100 and 5000 ppm indicate severe infestation by fungi and/or insects (Kaushik and Singhai, 2019), so its measurement is essential for preventing losses during storage. According to Zhu et al. (2022) the measurement of CO_2 levels has recently been used as one of the techniques for determining insect infestation levels, allowing for the lowest level of losses.

The data collected from the sensors provides information about the environmental parameters of the grain mass after pre-processing. With wireless technology, the information can be accessed via computer, laptop or smartphone (Kaushik and Singhai, 2019). Grain storage systems in silos, which include temperature management, moisture content, relative humidity and CO_2 concentration, insect incidence, among others, by means of automated sensors, are fundamental for maintaining the quality and longevity of stored products (Singh and Fielke, 2017).

2. OBJECTIVES

2.1 General objective

- ✓ Evaluating the quality of corn grains stored in hermetic and non-hermetic environments, as well as the relationship with the dynamics of the conditions of temperature, relative humidity and CO_2 concentrations generated in the grain mass.

2.2 Specific objectives

- ✓ Determine CO_2 concentrations, temperature and relative humidity in function of storage conditions for corn grains with different initial moisture contents;
- ✓ Determine the dry matter loss and water activity in stored grains in function of storage conditions;
- ✓ Evaluating the proximal composition and integrity of corn grains in function of storage conditions;
- ✓ Evaluating the physical characteristics and color of corn grains in function of storage conditions;
- ✓ Assess the effect of different storage conditions on corn grains using X-ray and SEM images;
- ✓ Quantify the levels of fungal and insect infestation in corn grains stored in hermetic and non-hermetic environments;
- ✓ Evaluate the quality of oil extracted from corn grains stored under different conditions;

- ✓ Relating the different quality attributes of corn grains and their relationship with different storage conditions.

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3 CHAPTER I

PHYSICAL PROPERTIES AND QUALITY OF CORN GRAINS STORED AT DIFFERENT INITIAL MOISTURE CONTENTS UNDER HERMETIC AND NON-HERMETIC CONDITIONS

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Abstract

The aim of this study was to evaluate the dynamics of the CO_2 concentration and its relationship with the quality of corn grains stored at different initial moisture contents under different conditions. The experiment was conducted in a completely randomized design, with a 2 × 3 × 5 factorial scheme and 3 replications. A sensor was inserted into the grain mass to measure CO_2, temperature and relative humidity levels at one-hour intervals for up to 120 days, and quality assessments were performed every thirty days via physical properties and grain classification (official Brazilian standard IN 60/2011). The data were subjected to analysis of variance, followed by a t test for storage conditions and linear regression for initial moisture content and storage time. The variation in temperature, relative humidity and CO_2 resulted in greater metabolic activity for the non-hermetic condition and higher initial moisture content; grains stored with an initial moisture content of 14% wb presented lower levels of deterioration, with higher bulk density values and lower grain mass porosity; color variation increased as a function of time and initial moisture content; grains stored under hermetic conditions changed to type 2 at 120 days for an 18% wb initial moisture content, whereas in the non-hermetic storage, the changes began after 30 days for 16 and 18% wb, whereas for 14% wb, the change occurred at 120 days. The integrated use of temperature sensors, combined with relative humidity and CO_2 monitoring, makes CO_2 sensors valuable tools for preventing quality loss during storage.

Keywords: *Zea mays* L.; Hermetic storage; Grain classification; CO_2 dynamics

3.1 Introduction

Corn is among the three most produced and consumed cereals in the world, namely, wheat, rice and corn. This cereal plays a leading role in livestock production and the bioethanol industry, whereas wheat and rice are mostly used for human food (García-Lara and Serna-Saldivar, 2019).

Water activity is fundamental for preserving the quality of agricultural products because of its effects on chemical and enzymatic reactions and biochemical processes (Pham et al., 2018). Grain deterioration is associated with the generation of CO_2, humidity, heat and distinct odors, reflecting the metabolism of grains, fungi, insects and mites in the grain mass. The generation of CO_2 essentially results from the aerobic metabolism of corn grains and their interaction with biotic and abiotic factors (Bilhalva et al., 2023).

Aerobic respiration in the grain mass occurs with the consumption of dry matter in the presence of oxygen and the release of water vapor and carbon dioxide. To avoid compromising quality, the magnitude of dry matter loss must not exceed 0.5% (Bern et al., 2019).

Monitoring the temperature, relative humidity and equilibrium moisture content of a grain mass and measuring CO_2 levels are important tools for detecting deterioration risk during storage (Lutz and Coradi, 2023). They are also used as indicators to determine the need for grain cooling aeration (Bilhalva et al., 2023). Leal et al. (2023) showed the importance of monitoring temperature, relative humidity and CO_2 levels in the grain mass for early detection of quality loss in wheat grains stored in vertical silos and lower metabolic activity for products stored with a moisture content close to 12% wb.

An effective monitoring system is essential for guaranteeing quality and making strategic decisions about the ideal time for marketing, which is fundamental for maximizing financial returns and consumer satisfaction (Bilhalva et al., 2023; Leal et al., 2023). For example, when evaluating the relationship between CO_2 levels and dry matter loss in wheat grains in vertical silos, Leal et al. (2023) reported a more effective response in terms of respiration intensity and dry matter loss and preservation of grain quality.

Reductions in the bulk density and thousand-grain mass of corn stored in vertical silos with moisture contents between 16 and 18% wb were observed as a result of the increase in the respiration rate (Bilhalva et al., 2023; Souza et al., 2024). Khalid et al. (2024) reported the maintenance of moisture content conditions in the hermetic storage of corn seeds, and in contrast, those in non-hermetic storage presented an increase in moisture content.

Hermetic storage is a very common practice among small farmers in Mexico (Odjo et al., 2022), including bag silos with a capacity of more than 200 tons in South America (Barrettino et al., 2019; Valle et al., 2021a). Hermetic systems are also very common in some sub-Saharan African and Asian countries because of their practicality in accommodating small volumes, in addition to the use of metal or plastic silos, bags and other forms that can reach 300 tons, whose main purpose is to control insect pests, thus minimizing deterioration factors (Baributsa and Ignacio, 2020).

Physical properties reflect quality standards and are associated with the type of corn endosperm. The true and bulk density, as well as the intergranular porosity, are fundamental parts of the design of grain storage projects (García-Lara et al., 2019).

Classification is also a fundamental element in defining the quality of grains, thus defining the degree of their acceptability on the market. The classification process considers different categories of defects, such as moldy grains, which can be seen by the darkening of the germ (Paulsen et al., 2019). In Brazil, for example, the quality standard for corn grains was defined by IN 60/2011, of December 22nd, 2011 (Mapa, 2011), which established the official standard for classifying corn. According to this standard, criteria are established that allow the acceptance or rejection of corn lots. The same categories of acceptance products are considered in official standards or Argentina, China, the United State of America and South Africa; however, each level is specifically considered (Paulsen et al., 2019).

Although temperature determination via thermocouples or digital sensors is a very common tool, localized measurements are less accurate because of the low thermal conductivity of grains, as the heat transmission process occurs more slowly (García-Lara et al., 2019; Leal et al., 2023). Magan et al. (2020) reported greater sensitivity to changes in CO_2 levels with the introduction of a bag of wet grains than with changes in temperature. Therefore, CO_2 measurement is more sensitive for detecting biological activity than temperature is (Souza et al., 2023; Souza et al., 2024). In stored products such as grains, CO_2 levels in the range of 600 to 1500 ppm indicate the beginning of fungal growth, and between 1500 and 4000 ppm, the level of infestation (by fungi and insects) is considered serious for quality preservation (Kaushik and Singhai, 2018).

In view of these findings, the aim of this study was to evaluate the behavior of CO_2 levels, temperature and relative humidity and their relationships with quality and to evaluate the quality of corn grains by means of physical properties and commercial classification to establish the types or grades according to the characteristics of each defect as a function of initial moisture content, condition and storage time. This study aims to address how specific levels of CO_2, temperature and relative humidity in the grain mass are linked to deterioration in grain levels during storage and to anticipate possible preventive measures to minimize the loss of quality in stored grains.

3.2 Material and methods

The work was carried out via a completely randomized design with a 2 × 3 × 5 factorial scheme and 3 replications, corresponding to two storage conditions (SC: hermetic and non-hermetic), three initial moisture contents (IMC: 14, 16 and 18% on a wet basis, wb) and five storage times (ST), namely, 0, 30, 60, 90 and 120 days, corresponding to thirty treatments (SC × IMC × ST), defined in ascending order, from hermetic to the non-hermetic storage, followed by IMC in descending order (18, 16 and 14%, wb) and ascending order for ST (0, 30, 60, 90 and 120 days) (as shown in Table A1).

The BRS284 corn grains were harvested in the municipality of Rio Verde, Goiás, Brazil (17° 48’ 16.73” S; 50° 54’ 23.96” W, mean altitude of 748 m), with an initial moisture content of 18% wb. The grains were subsequently dried with natural ventilation at a temperature and relative humidity of 24.0±2.73 ºC and 41.49±7.08%, respectively, until they reached the preestablished initial moisture contents of 16 and 14% wb. The moisture content of the grains was determined via an oven with forced air circulation, in which 15 g samples were heated at a temperature of 103 ± 1 ºC, for 72 h, with three replications (ASABE, 2010).\Storage under non-hermetic (NH) conditions was carried out in bulk in experimental silos at the Laboratório de Pós-Colheita de Produtos Vegetais of the Instituto Federal Goiano - Rio Verde Campus between July and November 2023. The prototype experimental silos were made of metal plates with dimensions of 0.60 × 0.60 × 0.30 m, with the capacity to store 0.108 m^3 of grain volume, equivalent to approximately 80 kg of corn grain.

Hermetic (H) storage was carried out in multilayer, low-density hermetic packaging with two polyethylene films, between which a plastic layer highly impermeable to oxygen was pressed, with a thickness of 78±2 μm and a barrier to gas exchange, water absorption and the entry of insects, with seal-type closure (GrainPro, Super Grain bag). To enable periodic evaluations without altering hermetic conditions, four packages with a capacity of 30 kg each were adopted, which were used for evaluation during each storage period (30, 60, 90 and 120 days).

The temperature (T), relative humidity (RH) and CO_2 concentration were monitored via sensors, which were placed inside each of the storage packages (prototype experimental silos and hermetic packaging), using a pipe structure, fully perforated at the base and open at the top, at a depth of 25 cm from the grain mass. To ensure greater representativeness and reduce heterogeneity, all the grain samples were homogenized in Boerner-type equipment before and after the drying process to reach initial moisture contents of 16 and 14% wb, respectively, for both storage conditions.

To measure temperature (T), relative humidity (RH) and CO_2 in hermetic packaging, CO2Meter sensors were used: model CM-0025 K33 BLG 30% + RH/T (bio-logger, GasLab®), which is based on non-dispersive infrared (NDIR) technology and is suitable for detecting high levels of CO_2 in confined environments, with the capacity to detect up to 300±20 thousand ppm (30 ± 2%). The sensor used is capable of recording data in real time via software (GasLab®) installed on a computer, with the functionality to be used as portable equipment. Measurements were taken at one-hour intervals throughout the evaluation period, and the intervals for T, RH and CO_2 monitoring were adjusted from previous studies (Bilhalva et al., 2023; Leal et al., 2023, Garcia-Cela et al., 2020; Souza et al., 2024).

Extech Instruments model CO210 sensors were used for non-hermetic storage, with the capacity to record 0 to 10 thousand ppm (≈1%). The sensor is also capable of recording data in internal memory, can be downloaded by the software Extech CO210 Datalogger Ver3.0®, and is also based on non-dispersive infrared (NDIR) technology. Extech Instruments model CO210 sensors placed outside of the grain mass in the same storage environment were also used to measure the temperature (T), relative humidity (RH) and CO_2 concentration.

3.2.1 Physical properties of the grains

The physical properties of the grains were determined in terms of true density (TD), bulk density (BD), intergranular porosity (POR) and thousand-grain mass (TGM). Bulk density (kg m^{-3}) was determined using a hectoliter weight scale with a container of known volume (1 L), dividing the value of the mass (kg) by the volume (m^3). Intergranular porosity (%) was determined by the direct method (Mohsenin, 1986) using a 100 mL beaker and low-density liquid (hexane, density of 0.675 g mL^{-1}) to fill the empty spaces. The true density (kg m^{-3}) was calculated via the mathematical relationship established by Mohsenin (1986) between the bulk density, true density and intergranular porosity (Eq. 1).

$$\rho_u = \frac{\rho_{ap}}{1 - \varepsilon} \tag{1}$$

where ρ_u is the true density (kg m^{-3}), ρ_{ap} is the bulk density (kg m^{-3}), and ε is the intergranular porosity (decimal).

The thousand-grain mass was determined by weighing eight 100-grain samples from each replication. The value was subsequently obtained by dividing the total mass by the number of grains, and the result was multiplied by one thousand (Brasil, 2009; Carvalho et al., 2021).

3.2.2 Color assessment

Corn grain color was assessed using a spectrophotometer (Color Flex EZ, Hunter LabReston, Canada), by analyzing the L^*, a^* and b^* coordinates using three samples of ground grains for each replication. The results of the reading of the L^*, a^* and b^* coordinates were converted into Chroma (C^*, Eq. 2), hue angle (H^*, Eq. 3) and color difference (ΔE, Eq. 4) (Demirhan and Özbek, 2009). For each replication, three readings were taken per sample.

$$C^*=\sqrt{(a^*)^2+\left(b^*\right)^2} \tag{2}$$

$$H^*=\begin{cases} \tan^{-1}\left(b^*/a^*\right);\ a>0 \\ 180+\tan^{-1}\left(b^*/a^*\right);\ a<0 \end{cases} \tag{3}$$

$$\Delta E=\sqrt{\left(L^*_0-L^*_t\right)^2+(a^*_0-a^*_t)^2+\left(b^*_0-b^*_t\right)^2} \tag{4}$$

where L^*_0, a^*_0, b^*_0 are the initial values of the coordinates L^*, a^* and b^*, L^*_t, a^*_t, b^*_t are the coordinate values of L^*, a^* and b^* by t-period, L^* is the black/white coordinate, a^* is the green/red coordinate, b^* is the blue/yellow coordinate, C^* is Chroma, H^* is the hue angle (°), and ΔE is the color difference.

3.2.3 Grain classification

Grain classification was carried out using the official classification according to the Brazilian normative instruction IN 60/2011 of December 22nd, 2011 (Mapa, 2011), which established the official standard for corn classification. The samples were collected during each evaluation period, homogenized and quartered to obtain 250 g of samples per replicate, which were then subjected to the evaluation process. Initially, after weighing, each sample was placed on a set of two sieves with circular openings measuring 5 and 3 mm and a base (without perforations). This was followed by continuous, uniform movements for 30 s to separate and quantify the total impurities and broken grains contained in each sample.

For the impurity content, all the residues and fragments retained in the base and foreign materials that were retained on the 5- and 3-mm-mesh sieves were counted, then deducted and converted to a percentage value in relation to the mass of the working sample. For broken grains, the grains that passed through the 5 mm mesh sieve and were retained on the 3 mm mesh sieve were counted, and their percentage was determined as a function of the total mass of the working sample.

After the impurities were separated, the resulting sample was weighed to separate the defect grains (burnt, shriveled or immature, fermented, sprouted, chalky and moldy) and the weevil-damaged grains (Mapa, 2011). Each category of defect grains was weighed, and its percentage content was determined. The values of each defect were then used to classify the grains according to type, taking into account SC, IMC and ST, thus establishing four categories (type 1, type 2, type 3 and out of type), which correspond to a decreasing order of quality established in IN 60/2011 (Mapa, 2011).

3.2.4 Statistical analysis

The data are presented as the means ± standard deviations and were analyzed in a completely randomized design with a $2 \times 3 \times 5$ factorial scheme and three replications. The comparisons were carried out by *t-test* for SC and linear regression analyses for IMC and ST according to the results of analysis of variance (ANOVA) at $p<0.05$. Pearson's correlation analysis was also performed at a level of $p<0.05$ by *t-test*, using the RStudio 4.3.2® statistical package.

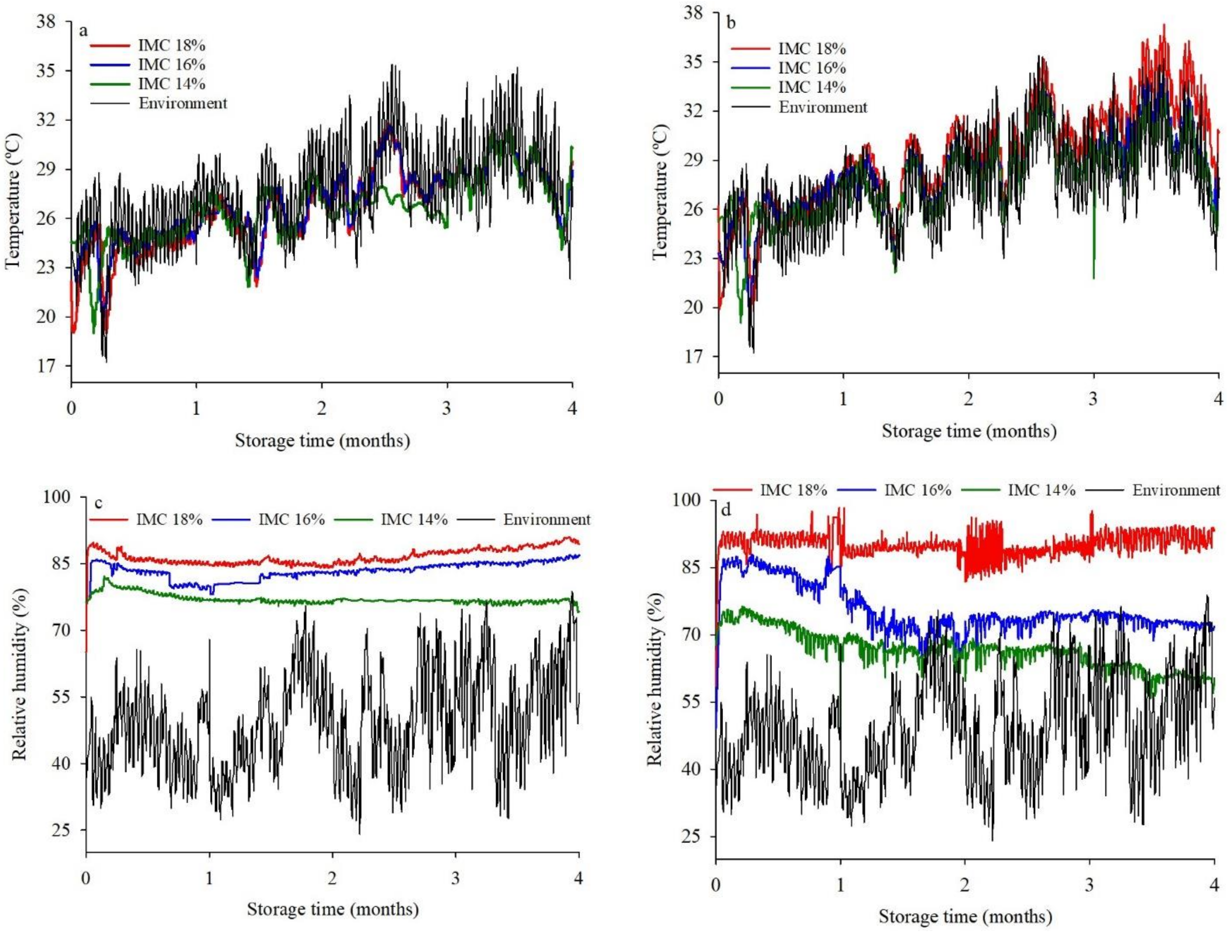
For the T, RH and CO_2 concentration monitoring data, graphs were plotted as a function of time, for each ST and IMC and, for the CO_2 concentrations under the hermetic conditions, the data were analyzed using linear regression. Furthermore, the data were subjected to multivariate analysis using principal component analysis and cluster analysis to determine the relationships between the different response variables and their relationships with the independent variables.

3.3 Results and discussion

3.3.1 Storage condition characterization

Fig. 1 shows the values for temperature, relative humidity and CO_2 concentration recorded in the mass of corn grains in hermetic and non-hermetic storage as a function of the IMC. Overall, there was a change in the distribution of the values observed, with a greater impact on the relative humidity and CO_2 concentration. With respect to temperature, the values recorded for hermetic storage were lower for most of the period than those reported for the grain mass, regardless of the IMC (Fig. 1a).

In non-hermetic storage, slight increases were observed, with a greater proportion of grains stored with an IMC of 18% wb (Fig. 1b). Especially toward the end of storage, the increase in temperature was proportional to the increase in the IMC, but oscillations prevailed, which are associated with the behavior observed in the environment.



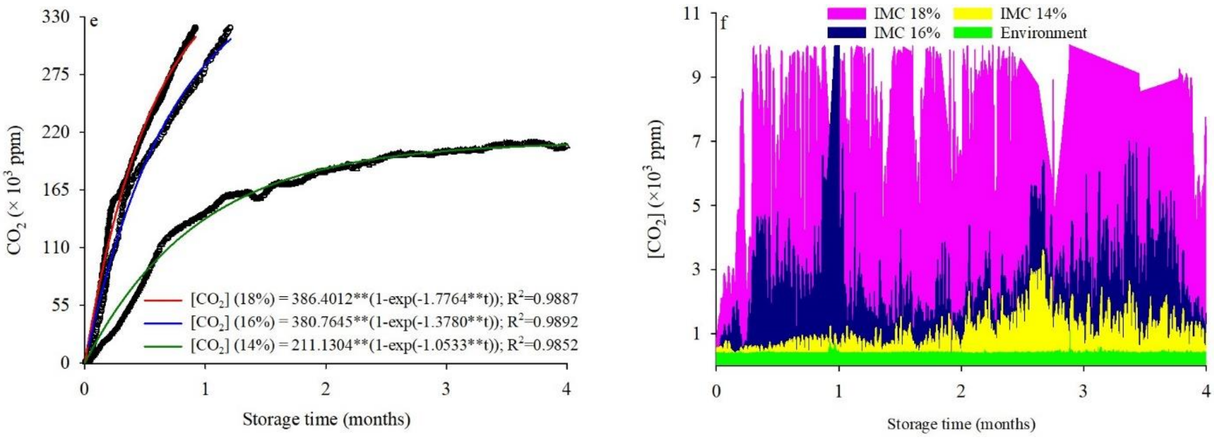


Fig. 1. Values of temperature (a, b), relative humidity (c, d) and CO_2 concentration (e, f) recorded in the mass of corn grains under hermetic and non-hermetic storage conditions as a function of different initial moisture contents. **Significant at $p<0.05$ by t-test.

The trend in temperature values under both conditions shows that metabolic activity is more intense in grains stored under non-hermetic conditions. Metabolic activity is associated with the consumption of organic matter through respiration, generating carbon dioxide, water vapor and heat, which is converted into an increase in temperature in the grain mass, with dissipation conditioned by low thermal conductivity (Bilhalva et al., 2023). Generally, the influence of storage conditions has been mentioned, with T, RH and CO_2 being fundamental for accurate information on the condition of the stored product and early decision making aimed at preserving quality (Bilhalva et al., 2023; Souza et al., 2024).

The relative humidity tended to increase as a function of initial moisture content, and the measured values were always higher than those observed in the environment due to the increase in relative humidity conditions in the grain mass, which was more accentuated for non-hermetic storage conditions, where higher absolute values were recorded, with means of 90.11, 76.28 and 67.44% for non-hermetic storage and 86.19, 82.81 and 77.23% in hermetic storage for 18, 16 and 14% wb, respectively (Fig. 1a and b). On the other hand, there was a trend toward stability in terms of the variation in the values observed under hermetic conditions and a reduction in the initial moisture contents of 16 and 14% wb, but these values were always greater than those measured in the environment, with a mean value of 48.72% (Fig. 1c).

With respect to relative humidity, the highest CO_2 concentration values were observed for the highest moisture content, with 320 thousand ppm reached by 30 days in the hermetic environment, 6563.84 ppm for the environment and the lowest for the environment, with a value of 429.77 ppm (Fig. 1e and f). Although CO_2 monitoring was carried out until the end of storage, the evaluation of hermetic conditions was conditioned by the sensor's maximum recording capacity (320 thousand ppm), which reached approximately 0.99 months (30 days) and 1.33 months (40 days) for IMCs of 18 and 16% wb, respectively. For the moisture content of 14% wb, the maximum value reached on the basis of the model fit was 208.01 thousand ppm, which was observed at 4 months (120 days) of storage.

The trend of CO_2 generation in the grain mass was consistent with more intense levels of respiration under hermetic conditions with higher initial moisture contents, reducing the time to reach the peak, thus correlating with the data observed for T and RH, reflecting the rate of respiration within the grain mass, the magnitude of which is influenced by the combination of product characteristics, biotic factors and abiotic factors.

The CO_2 peak was generally in line with the initial moisture content, thus justifying the reduction in time as the initial moisture content increased (Valle et al., 2021a; Souza et al., 2024). For Abalone et al. (2011), the concentration of gases, including the ratio of CO_2 and O_2, can be used as an indicator to detect problems in bag silos or hermetic packaging in general; values above the standard indicate excessive biological activity, with direct consequences for dry matter consumption. From this perspective, these authors state, for example, that values of 5% (50 thousand ppm) of CO_2 in stored wheat grains with an initial moisture content of 13% wb and a temperature of 20 to 30 °C would be considered a reference, whereas 10% (100 thousand ppm) would be associated with intense biological activity.

Under hermetic storage conditions, the O_2 present in the atmosphere is consumed, while CO_2 is generated until aerobic activity ceases (Valle et al., 2021a). However, for conditions with high levels of moisture content and water activity, CO_2 levels continue to rise even in the absence of O_2 as a result of the fermentative activity carried out by facultative microorganisms that maintain their activity in this environment - anaerobic respiration, as opposed to what happens under conditions with low moisture content, where fermentative activity is not expected.

Valle et al. (2021a) also noted that the success of using a non-hermetic storage system lies in the waterproofing capacity so that a critical level of oxygen is reached, from which it is expected that benefits will result, since, even at smaller levels, small changes in the interstitial concentration would not be enough to inhibit the biological activity of the grains and microorganisms present in the mass of the grains. Owing to the presence of higher O_2 concentrations, the rate of aerobic respiration is more intense at the beginning, making the environment anaerobic and unsuitable for aerobic organisms.

In the non-hermetic storage, the highest CO_2 values were observed in grains stored with the highest initial moisture content (18% wb), and the lowest values were observed for grains stored with an initial moisture content of 14% wb. The average values recorded for non-hermetic storage were 756.67, 1933.75 and 6563.84 ppm for initial moisture contents of 14, 16 and 18% wb, respectively. For Aby and Maier (2020), these values represent concern or the presence of metabolic activity in the grain mass, since, in general, CO_2 levels between 600 and 1500 ppm are linked to the presence of insects and/or fungi or an increase in the moisture content of the product. When they reach ranges of 1500 to 4000 ppm, the situation is considered serious, thus requiring mitigation actions to control it.

The variations generated over the evaluation period are the result of gas exchange between the grain mass and the external environment, resulting in the CO_2 generated being diluted by the mixture of air present in the upper surface layer, which has lower concentrations. In hermetic storage, the variation is not expected due to the insulating effect produced by the waterproofing of hermetic packaging, as long as it remains properly sealed, and the increasing or stabilizing trend is also an indication of the capacity to seal out gases and water vapor. High values of stored grain moisture content are a challenge and have been linked, for example, to higher levels of metabolic activity, culminating in increased dry matter losses in stored corn grains with different moisture contents (Souza et al., 2024).

Measuring CO_2 levels has become essential to ensure that the quality of the stored product is maintained as a complement to monitoring T and RH (Leal et al., 2023; Souza et al., 2024). In general, the respiration rate tends to increase when the initial moisture content of most cereals is above 14% wb (Lutz and Coradi, 2023).

Based on the reference of 50 thousand ppm (reached in 80 days) and 100 thousand ppm of CO_2 concentration as a reference for the wheat grains, which were stored hermetically with a moisture content of 13% wb and a temperature of 20 to 30 °C, as reported by Abalone et al. (2011), and the studies of Valle et al. (2021a), which link greater metabolic activity to grain size, revealed that the CO_2 values mentioned here would be reached in less time, thus supporting the dynamic behavior of the data in this study.

According to the analysis of variance (as shown in Table A2), overall, all the variables were influenced by the SC × IMC × ST interaction, with the exception of the color variables a^*, b^*, hue angle and color difference (ΔE); however, all the pairwise interactions were significant except for the SC × IMC and IMC × ST interactions for hue angle.

The influence of SC on grain quality has been reported by several authors, with T and RH being the most important parameters for assessing quality (Valle et al., 2021a; Valle et al., 2021b; Bilhalva et al., 2023; Mabasso et al., 2023). Recently, the use of CO_2 sensors has also increased as a useful and complementary tool for decision-making on control actions, even in cases where aeration of stored grains is necessary (Lutz and Coradi, 2023; Souza et al., 2024). The integration of these tools provides a comprehensive and effective monitoring system for the efficient management of stored grains.

Post-harvest losses can be minimized by adopting appropriate conservation and processing techniques, thus reducing deterioration levels (Ikegwu et al., 2022). The condition of heating of the grain mass occurs as a consequence of heating generated by respiration activity, the intensity of which depends on the initial condition of the product and the storage conditions.

Leal et al. (2023), when evaluating the quality of wheat grains stored in vertical silos, reported that CO_2 is a potential indicator for the early detection of evidence of grain deterioration, which allows action to be taken before the degree of deterioration, detected by a substantial increase in temperature, intensifies, considering that the grain has a low capacity to conduct heat, so its effectiveness depends greatly on the positioning of the sensor or thermometry cable close to the heating point.

3.3.2 Physical properties and color change analysis

Under hermetic conditions, the moisture content was not significantly influenced by storage time, unlike under conditions in which the moisture content decreased and the initial moisture content increased (Fig. 2a and b). This is due to the presence of a physical barrier against gas exchange and moisture loss, thus also reducing variations in the relative humidity of the intergranular atmosphere (Ngoma et al., 2024).

The increase in moisture content was greater under the non-hermetic condition conditions (0.8919 and 0.8402% for non-hermetic and hermetic conditions, respectively), reflecting a greater tendency toward greater metabolic activity. The presence of an impermeable physical barrier to gas exchange in hermetic storage is associated with the creation of an environment unsuitable for aerobic organisms.

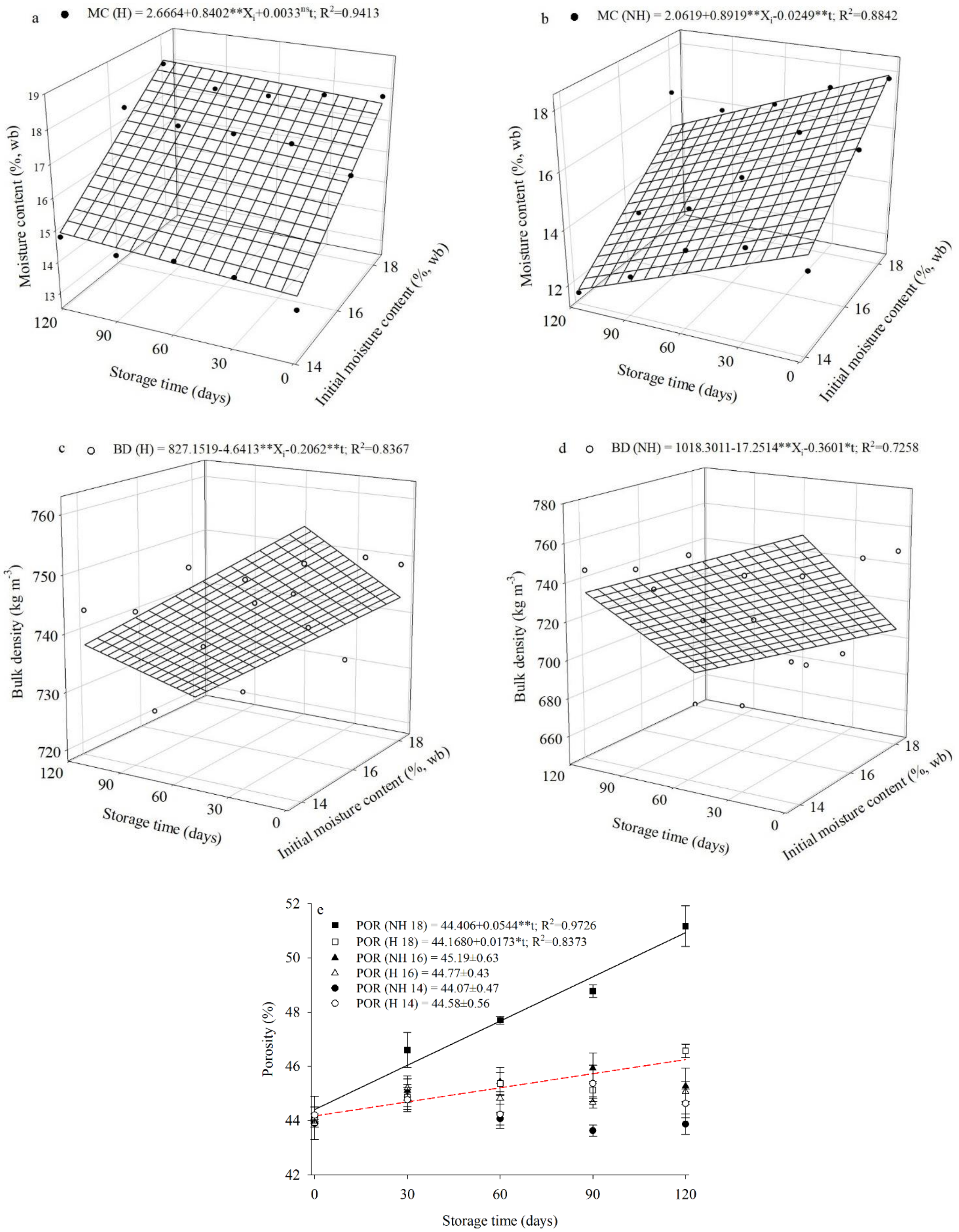


Fig. 2. Average values of the grain moisture content (a, b), bulk density (c, d) and porosity (e) of corn grains stored under hermetic and non-hermetic storage conditions as a function of different initial moisture contents and storage times. *Significant at $p<0.05$; **Significant at $p<0.01$.

Hermetic storage technology, usually in hermetic packaging, has been used effectively to minimize post-harvest losses in sub-Saharan African and Asian countries, mainly for lower moisture contents aimed at long storage periods (Baributsa and Ignacio, 2020). The moisture content values during non-hermetic storage were influenced by both factors (Fig. 2b). The increase and loss of moisture is characteristic of stored products, which are influenced by the combination of storage conditions and initial characteristics.

The trend recorded for grains stored hermetically is considered typical because of the absence of gas exchange between the internal and external environments. Khalid et al. (2024) also reported that the moisture content of corn seeds stored with an initial moisture content of 13.5% wb was maintained, whereas the moisture content of those stored in conventional form increased due to the high initial relative humidity, in contrast to the behavior observed in this experiment. This discrepancy results from the prevalence of conditions favorable for moisture loss during the period in which the study was carried out because hygroscopic equilibrium is reached at relatively low values (Figs. 1a, b, c and d).

The moisture content values were always greater for hermetic conditions (as shown in Table A3); however, the reduction was lower for the initial moisture content of 18% wb than for conditions, thus generating more favorable conditions for deterioration processes linked to the greater availability of moisture and the presence of oxygen, including insects and fungi, which intensify their activity (Fleurat-Lessard, 2017).

The true density under both storage conditions behaved randomly. The absolute values for lower moisture contents were always higher than those measured for higher moisture contents, with values of 1354.27, 1335.01 and 1335.34 kg m^{-3} in hermetic storage and 1346.92, 1307.16 and 1305.14 kg m^{-3} in the non-hermetic storage, for moisture contents of 14, 16 and 18% wb, respectively, being mostly higher for hermetic storage (as shown in Table A3).

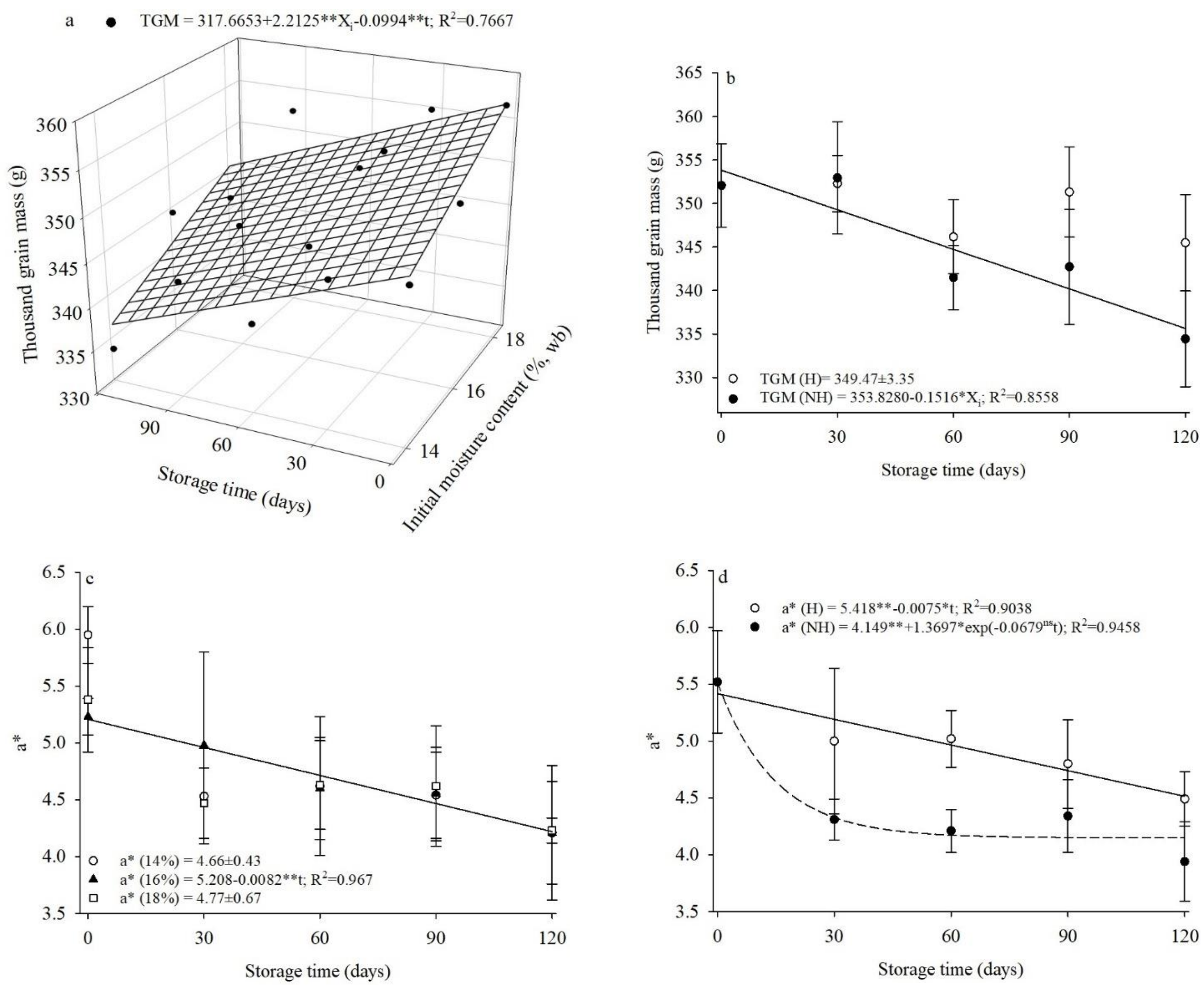
The BD values were negatively affected by the initial moisture content and storage time, regardless of the storage conditions (Fig. 2c and d), with the highest values almost always observed for the hermetic condition for moisture contents of 18 and 16% wb, whereas for the moisture content of 14% wb, the values were similar for almost the entire period. On the other hand, the reduction in dry matter is supported by the higher rates in the non-hermetic storage.

BD is considered a quality parameter and is linked directly to the dry matter content of the grain. Souza et al. (2024) also reported a reduction in BD values over the storage time of corn grains stored in prototype experimental silos in the same range of initial moisture contents.

They also reported an increase in electrical conductivity values and a reduction in germination, as well as evidence of dry matter loss.

On the other hand, the porosity values tended to increase with increasing storage time for a moisture content of 18% wb under both conditions (Fig. 2e). For the moisture contents of 16 and 14% wb, the values observed during storage did not follow a defined trend, with the lowest values for the moisture content of 14% wb.

Thousand-grain mass is also used as a quality parameter for stored grains. In this context, the TGM values increased with increasing initial moisture content and decreased with increasing storage time (Fig. 3a), reflecting the loss of dry matter due to grain respiration, a behavior consistent with the results observed in relation to TD, BD and POR, with greater values for higher IMCs under both conditions, i.e., 50.93 and 46.24% for the on-hermetic and hermetic conditions, respectively, during the final storage time.



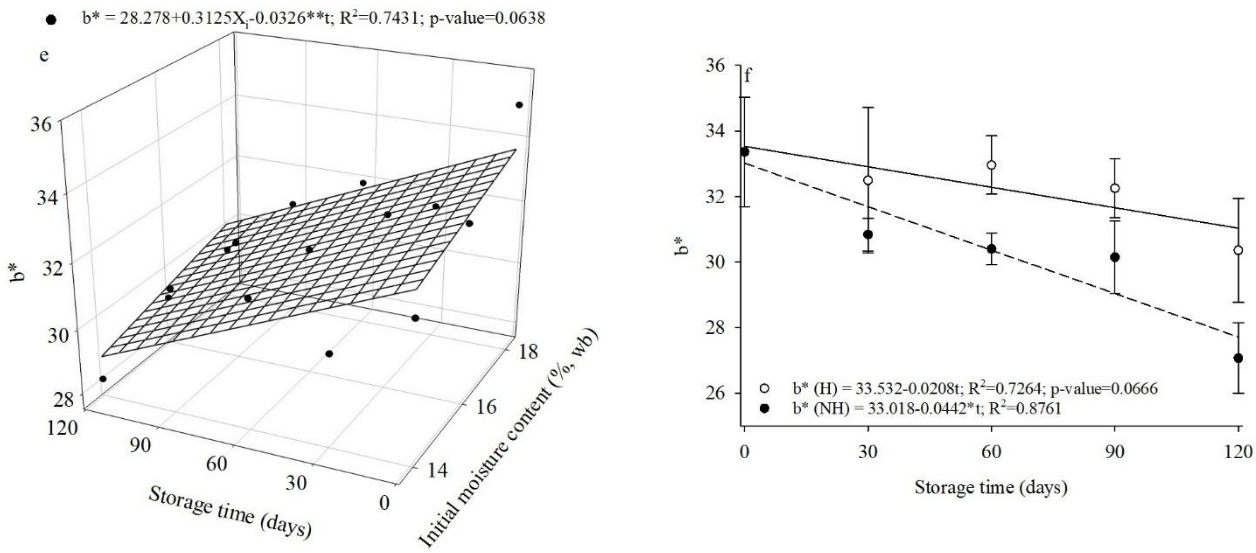


Fig. 3. Average values for thousand-grain mass as a function of initial moisture content and storage time (a), storage time and conditions (b); a^* as a function of storage time for each initial moisture content (c) and each storage condition (d); and b^* as a function of storage time and initial moisture content (e) and as a function of storage time for each initial moisture content (f). **Significant at $p<0.01$.

Considering the two storage conditions, there was a reduction in TGM for the non-hermetic condition over time (Fig. 3b), whereas in hermetic storage, the values oscillated, and the average was 349.47 ± 3.35 g. This value is within the range reported by García-Lara et al. (2019), who reported magnitudes of 240--370 g for yellow corn grains. The initial moisture content tended to increase with increasing IMC, with the highest values occurring under hermetic conditions (as shown in Fig. A1). The grains with a higher moisture content are heavier because, as the grains lose moisture, they tend to shrink and decrease in volume.

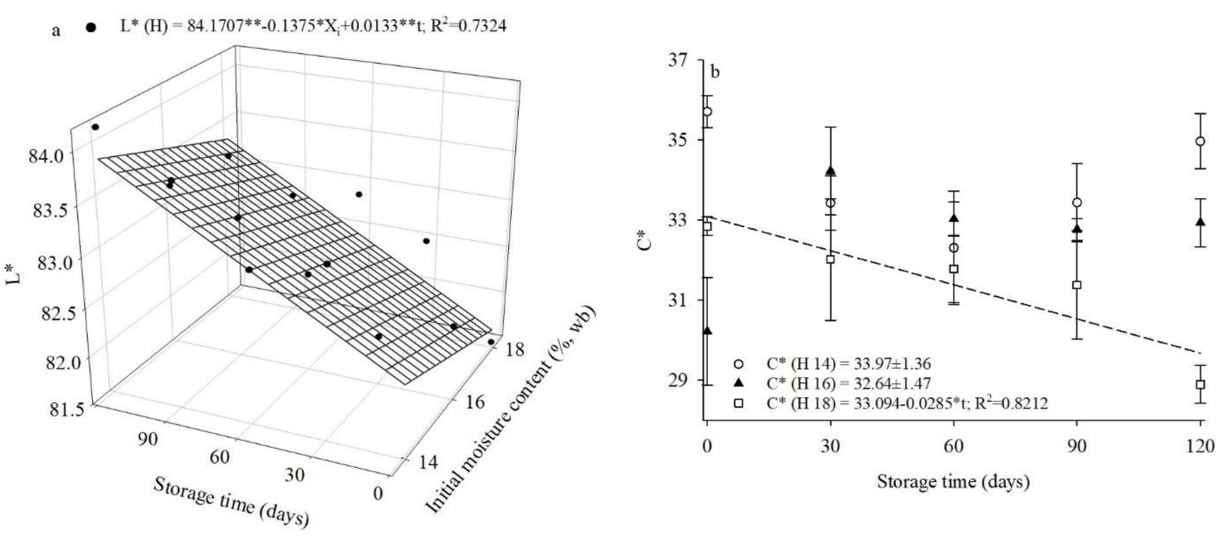
The reduction in TGM under the non-hermetic conditions is consistent with the studies by Souza et al. (2024), who evaluated the quality of corn grains stored under environmental conditions and reported a loss of dry matter, which was accentuated for grains with a relatively high initial moisture content. Higher TGM values are desirable, especially for wet starch processes or for obtaining larger flakes via dry milling (Paulsen et al., 2019).

Figs. 3c-f show the results of the a^* and b^* color parameters as a function of initial moisture content, storage conditions and storage time. The a* values decreased as the storage time increased to 16% wb, and the values varied in terms of moisture content between 14 and 18% wb (Fig. 3c). With respect to storage time, there was also a reduction in a^* values, with the rate of reduction under the non-hermetic storage condition being more intense at the beginning and slowing down toward the end (Fig. 3d).

The trend observed for a^* was also the same for b^*, with the influence of the initial moisture content being less preponderant than that of the combination of storage conditions and time (Figs. 3c, d, e and f). The reduction in the b^* coordinate is linked to the loss of yellow color, an important characteristic for defining quality, considering the typical color of the cultivar in the study, and the intensity was greater for the non-hermetic condition, with a rate of 0.0442, than for the hermetic condition, with a rate of 0.0208.

Throughout the storage period, the a^* and b^* values were always greater for hermetic storage, i.e., there was less tendency for grains stored non-hermetically to lose their yellow color. Similar behavior in relation to time was observed by Mabasso et al. (2023), who evaluated the storage of corn grains in conventional form for a period of 270 days.

The L^* value under hermetic conditions decreased as the initial moisture content increased, in contrast to the storage time (Fig. 4a). However, the effect of the initial moisture content on this variable was more intense than the effect of time, thus promoting greater browning of the grains over the storage time for higher initial moisture contents.



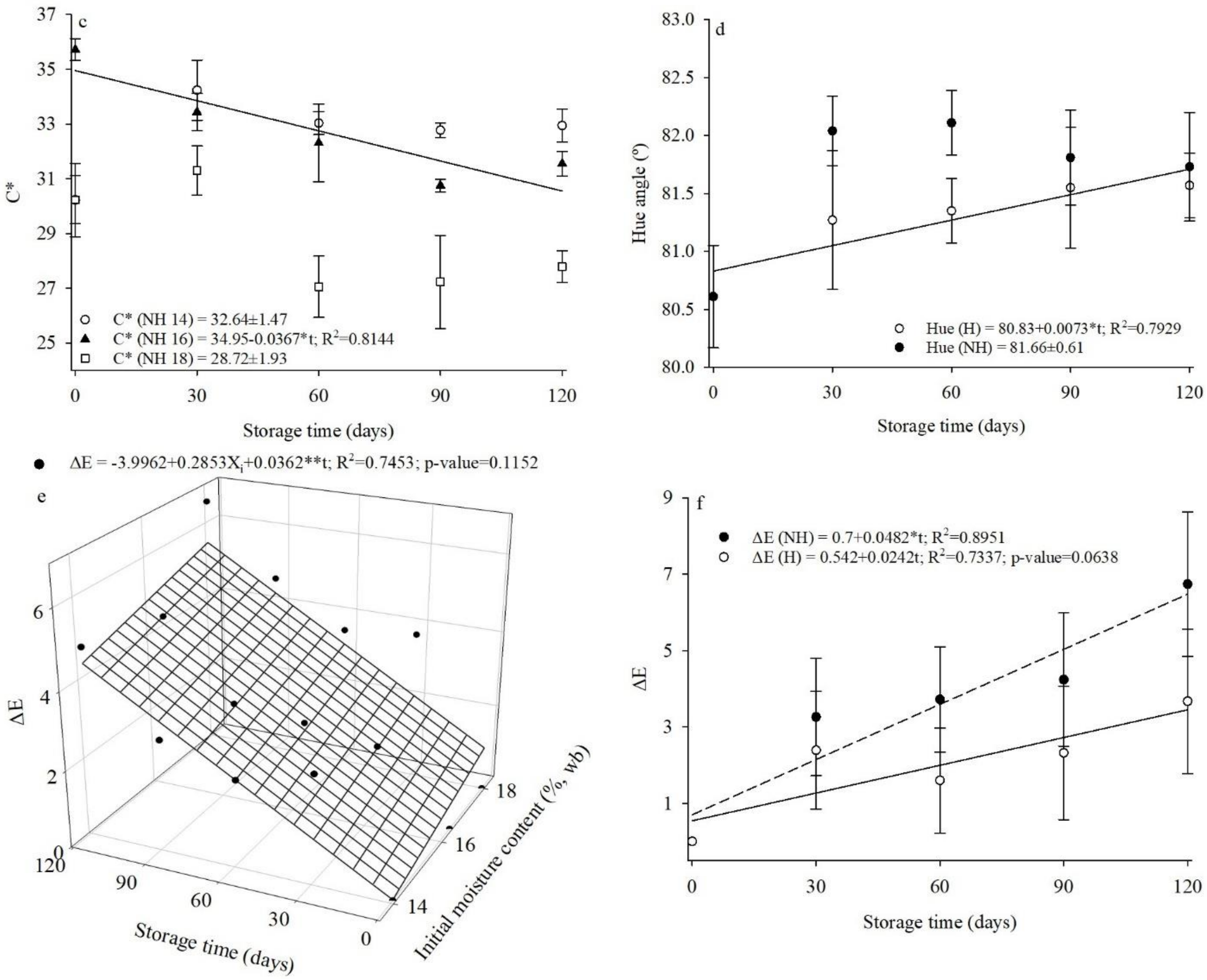


Fig. 4. Average values of L^* (a) and C^* (b, c), hue angle (d) and ΔE (e, f) as a function of the initial moisture content, time and storage conditions of corn grains. *Significant at $p<0.05$; **Significant at $p<0.01$.

In non-hermetic storage, this trend was not observed (Fig. 4b), but the measured values were generally lower, especially for the 18% wb moisture content (as shown in Table A5), indicating that the grains under this condition tended to darken more. This relationship is also evidenced by the combination of chroma and hue angle values (Figs. 5c and d), with a reduction in saturation and tonality, since the lower the chroma value is, the lower the saturation. On the other hand, the hue angle values are consistent with the results observed for the a^* variable, as the loss of red color is highlighted.

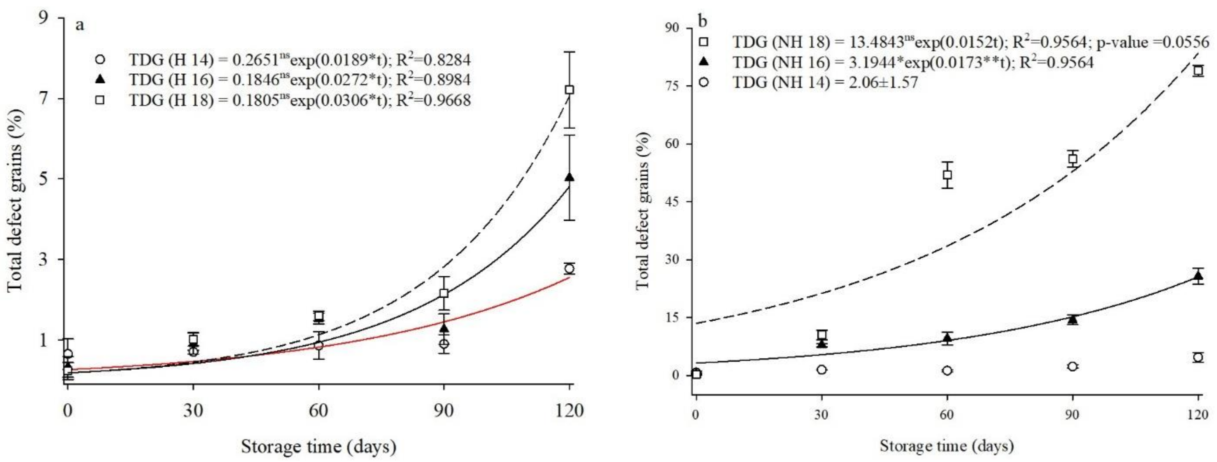
Changes in color, oxidative processes and even the degradation of internal membranes are among the metabolic reactions that lead to the deterioration of stored products (Wang et al., 2022). Over time, metabolic processes cause alterations in grains, which depreciate their quality, especially under the non-hermetic conditions, where respiration activity is substantially more intense and harmful (Groot et al., 2022).

Higher color variation values for non-hermetic conditions are partially justified by the level of variation under these conditions, since controlling T and RH is fundamental to managing the speed of grain deterioration processes (Mabasso et al., 2023). On the other hand, for Valle et al. (2021a), the use of a hermetic storage system has the potential to generate benefits, as long as a critical oxygen level is reached, at which point the biological activity of the grains and aerobic microorganisms is inhibited.

3.3.3 Grain classification analysis

Grain classification is an important element in the perception of quality, and standards are generally established by official classification standards, such as the Brazilian standard IN 60/2011 (Mapa, 2011). Fig. 5 shows the average values of the total percentage of defects and fermented and moldy grains as a function of the initial moisture content and storage time under both storage conditions.

The values for the total percentage of defect grains (TDG) increased exponentially over storage time for each initial moisture content under the two storage conditions, with the exception of grains stored non-hermetically with a moisture content of 14% wb (Figs. 6a and b), and the maximum values for TDG were approximately 7.5 and 80% for hermetic and non-hermetic storage, respectively, considering the higher IMC. The rate was greater for the combination of non-hermetic storage × higher initial moisture content (18% wb).



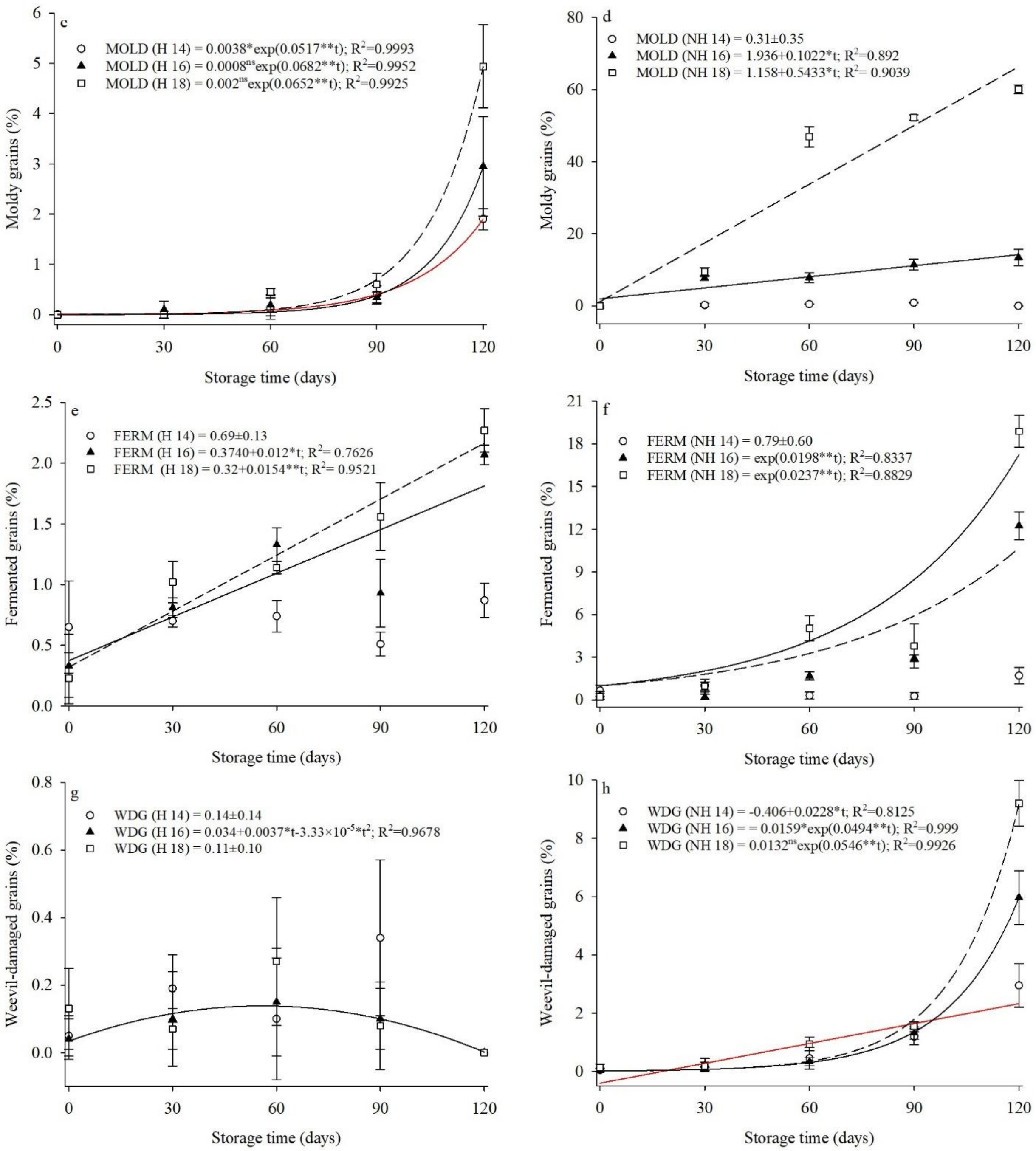


Fig. 5. Average values of the total defect grains (a, b), moldy grains (c, d), fermented grains (e, f), and weevil-damaged grains (g, h) as a function of storage time for each initial moisture content in hermetically and non-hermetically stored grains. *Significant at $p<0.05$; **Significant at $p<0.01$.

The total percentage of defect grains is derived from the combination of fermented, moldy, immature and shriveled grains. As defects made the greatest contribution to TDG, an increasing trend was also observed with increasing storage time (Figs. 6c, d, e and f).

For the initial moisture content of 14% wb, the percentage of moldy and fermented grains was random, and the same was found for both conditions, 0.79 ± 0.60 and 0.69 ± 0.13%

for non-hermetic and hermetic conditions, with lower absolute values overall (as shown in Table A6), compared with those observed for IMCs of 16 and 18% wb.

Respiration is associated with the metabolic activity generated in the grain mass due to the action of the grains, microorganisms and/or insects present, the intensity of which depends on the availability of moisture, as well as the level of oxygen from the perspective of an aerobic process (Valle et al., 2021a), although there was no significant correlation between MC and MOLD, WDG or TDG (as shown in Table A8). Valle et al. (2021a) reported that aerobic respiratory activity, which is characteristic of a wide range of fungi, can be affected by restrictive oxygen conditions, a common condition after a certain period of hermetic storage, thus leading to a reduction in the rate of CO_2 generation.

The incidence of moldy grains is associated with the presence of fungi, which have the ability to multiply and develop even under conditions of lower water activity, compared with what generally occurs in the field, and their action is generally more evident when the grains are stored with moisture contents between 13 and 20% wb or at relative humidity levels between 70 and 90% (Nishimwe et al., 2020), values consistent with those observed in the stored grains for both conditions, i.e., 66.35 and 4.99% in non-hermetic and hermetic storage, respectively, for the higher IMC conditions (18% wb).

Fungal spores can be lodged in storage equipment or in preinfested grains in the field, which then develop quickly under favorable conditions, leading to substantial and irreversible damage to the grains (Mohapatra et al., 2017). On the other hand, infestations from the field develop more quickly, even under conditions of low moisture content and temperature, than do preinfestation infestations.

As shown in the data, the increase in CO_2 levels, as a result of greater respiration in the grain mass and metabolic activity, is strongly associated with the greater presence of fungi, since the presence of moldy grains (damage caused by fungi) was the most significant contributor to the total number of defects, TDG × MOLD ($r=0.990$, $p<0.05$).

According to Magan et al. (2020), changes in temperature are a consequence of previous changes in CO_2 levels, which are more easily detectable because of the low thermal conductivity that characterizes biological materials in general, making them good thermal insulators.

The incidence of weevil damage to grains is linked to the presence of insects in the grain mass, leading to typical damage, which is the partial absence of mass. In this context, there is a trend toward lower values for grains stored hermetically (Figs. 6g and h), which are almost imperceptible (as shown in Table A6). This is due to the efficiency of the physical barrier of the packaging, which is able to prevent the entry and exit of gases and moisture vapor, thus creating an unsuitable environment for the development and multiplication of insects in the grain mass.

Under the non-hermetic storage, the percentage of weevil-damaged grains increased exponentially for moisture contents of 16 and 18% wb and linearly for a moisture content of 14% wb (Fig. 5h), which corresponded to maximum values of 9.25, 5.97 and 2.33% of grain weevil-damaged grains for IMCs of 18, 16 and 14% wb, respectively. According to Navarro and Navarro (2020), post-harvest losses are almost inevitable, continuing to occur even under conditions of low moisture content but at reduced rates and becoming almost imperceptible under favorable conditions between the product and the storage system. For hermetic storage, the values were almost imperceptible, always remaining below 0.3%, which is in accordance with the results observed in this study (Fig. 5g).

According to IN 60/2011 (Mapa, 2011), corn grains are classified as type 1 (TDG<6% or WDG<2%), type 2 (6%<TDG<10% or 2%<WDG<3%), type 3 (10%<TDG<15% or 3%<WDG<4%) and out of type (15%<TDG<20% or 4%<WDG<8%). For grains stored with an initial moisture content of 14% wb, under hermetic conditions, the grains remained classified as type 1, as the increase in deterioration level was below the reference value for changing types, especially TDG, as one of the criteria for defining type. For the same moisture content and in non-hermetic storage, there was only a change from type 1 to type 2, with the incidence of weevil-damaged grains being the major defect for changing the type at 120 days (as shown in Table A7).

The grains stored with an initial moisture content of 16% wb, under hermetic storage, also maintained their characteristics as type 1, and the increase in defect levels was within the standard, with only a change from type 1 to type 2 at 120 days, for 18% wb.

For grains stored non-hermetically with initial moisture contents of 16 and 18% wb, the levels of defects, mainly TDG, changed to type 2 and type 3 at 30 days, respectively. By 120 days, both groups had altered to out-of-type, but the process was more accelerated for IMCs of 18% wb. On the basis of this trend, the reduction in moisture content during storage was clearly not enough to limit the magnitude of defects, including the percentage of weevil-damaged grains.

3.3.4 Correlation analysis

The temperature, moisture content and conditions under which the product is stored affect the levels of CO_2 generated, resulting in an increase in the respiration rate of the grain mass, as well as the development of fungi and consequent deterioration of the grain (Lutz and Coradi, 2023).

TDG and crunched grains, which are important for establishing the type, are among the variables that are best correlated with the others. An increase in TDG led to a decrease in BD ($r=-0.864$, $p<0.05$) and TD ($r=-0.452$, $p<0.05$) and an increase in POR ($r=0.884$, $p<0.05$). With respect to color, TDG was negatively correlated with L* ($r=-0.652$, $p<0.05$), indicating that an increase in TDG promoted darkening of the grains as a result of an increase in the percentage of fermented and moldy grains, which made the color of the grains darker, with correlation values of 0.817 and 0.990, respectively. This correlation shows a close relationship between the physical property variables and grain classification, allowing consistency in establishing the type (as shown in Table A8).

The increase in the percentage of moldy grains, as well as weevil-damaged grains, is associated with a greater loss of dry matter, thus reflecting a reduction in bulk density, which is consistent with the correlation between MOLD × BD ($r=-0.876$, $p<0.05$) and an increase in granular porosity, MOF × POR ($r=0.878$, $p<0.05$). The same trend was observed by Bilhalva et al. (2023) as a consequence of increased metabolic activity and respiration rates, with greater dry mass consumption, which was consistent with reductions in BD and TD, whereas POR increased as a function of storage time, regardless of the IMC.

Paulsen et al. (2019) reported that, within the moldy grain category, certain levels of darkening can be observed in the corn grain germ, which also contributes to the increase in darkening indices, which is consistent with the inverse relationship between L^* and TDG.

The color difference was also positively correlated with the classification variables, with values ranging from $r=0.672$ to $r=0.736$, thus reinforcing the relationship between deterioration and color difference, since a greater color difference indicates the occurrence of deterioration processes, which are easily detected by consumers (Wang et al., 2022).

Fig. 6a shows the results of the principal component analysis for the physical properties and grain classification. The first three components represent approximately 76.84% of the accumulated variance and are, therefore, the components with relevant information about the behavior of the study variables, i.e., those that retain the greatest contributions.

3.3.5 Multivariate statistical analysis

As the individual variance of each principal component decreases, so does the contribution of the variables, making it less relevant for describing the kind of variability obtained by the different variables. One of the criteria used to define the number of principal components is their ability to retain a great deal of variability in information about the variables, with a minimum of 70% of accumulated variance or eigenvalues greater than one usually being considered (Santos et al., 2019; Yeshitila et al., 2023).

a

b

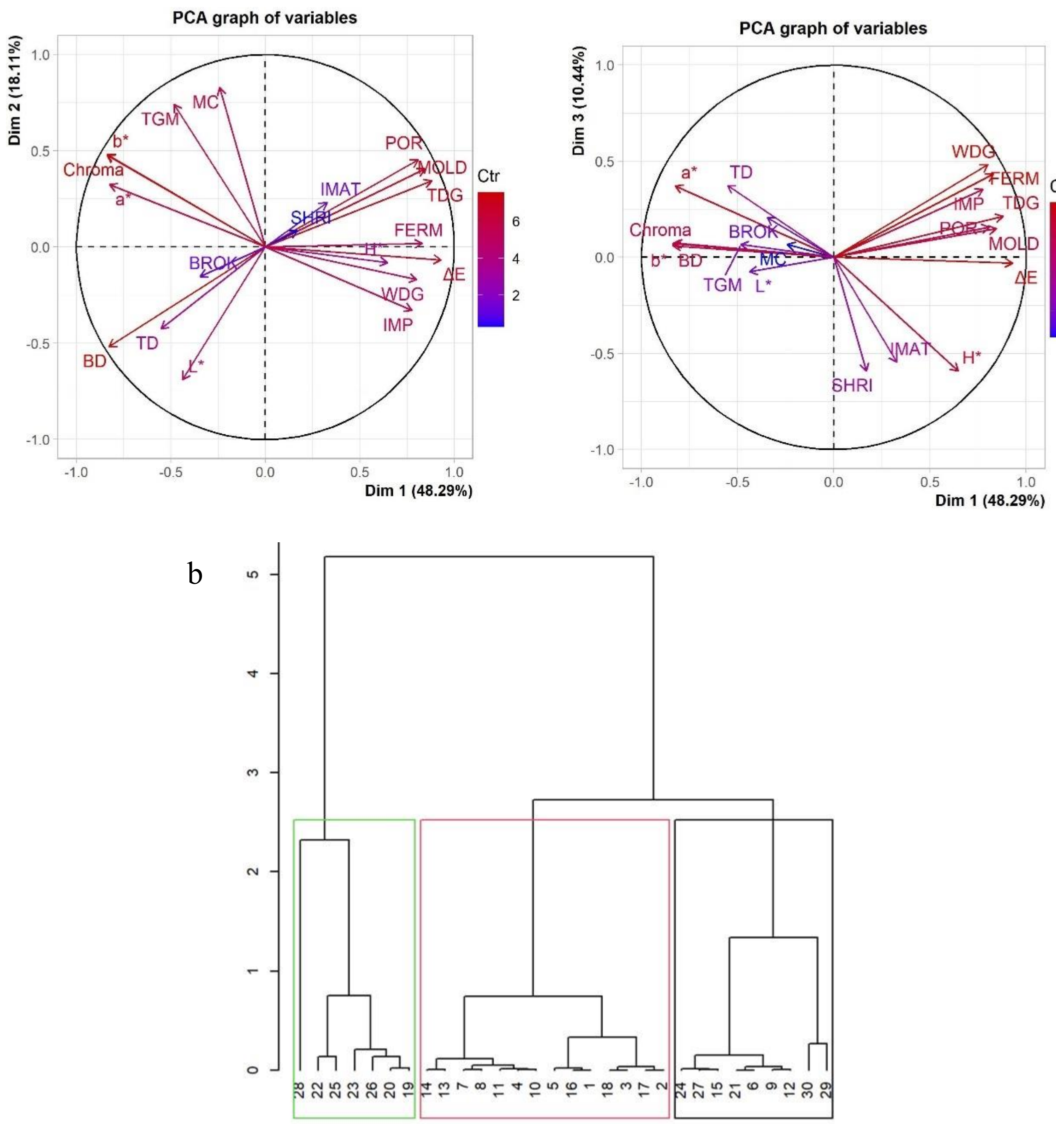


Fig. 6. Map of principal component analysis (a) and cluster analysis of treatments for the storage of corn grains as a function of initial moisture content and storage conditions (b). a: The total variation explained by each dimension is shown on the axis labels; b: Cluster 1 (black), cluster 2 (red), cluster 3 (green).

The first, second and third principal components (Dim 1, Dim 2 and Dim 3) explained 48.29, 18.11 and 10.44% of the variance, respectively. The contribution of the variables is proportional to the magnitude of their individual variances in terms of the number of variables and the strength of the correlation (as shown in Table A9). TDG ($r=0.880$, $p<0.05$), moldy (MOLD) ($r=0.845$, $p<0.05$), fermented (FERM) ($r=0.831$, $p<0.05$), weevil-damaged grains (WDG) ($r=0.802$, $p<0.05$), color variation ($r=0.929$, $p<0.05$), intergranular porosity (r=0, 808, $p<0.05$), BD ($r=-0.829$, $p<0.05$), b^* ($r=-0.838$, $p<0.05$), a^* ($r=-0.824$, $p<0.05$) and chroma ($r=-0.839$, $p<0.05$) were among the variables that correlated best with Dim 1. For Dim 2, MC ($r=0.829$, $p<0.05$), BD ($r=-0.517$, $p<0.05$), TGM ($r=0.742$, $p<0.05$) and L^* ($r=-0.689$, $p<0.05$) stood out among the variables. Dim 3 correlated best with TD ($r=0.374$, $p<0.05$), a^* ($r=0.372$, $p<0.05$), WDG ($r=0.703$, $p<0.05$), FERM ($r=0.434$, $p<0.05$) and hue angle ($r=-0.592$, $p<0.05$).

Considering the three principal components, the relationships were also consistent in terms of the magnitude of the correlation, as well as the number of variables retained for each component. The direction of the arrows and the magnitude are associated with the type of correlation or contribution that each variable has in relation to the principal component, which decreases from red to blue.

The data from the PCA analysis was subjected to cluster analysis, in which clusters were defined according to the similarity between the individual observations (treatments). The distribution is shown in Fig. 6b, where it is possible to see which observations are part of each cluster.

Cluster 1 includes treatments such as H×14×30, H×14×30, H×14×60, NH×14×30 and NH×14×60. Within this cluster, the treatments with the lowest initial moisture content stand out, 14% wb, under both storage conditions and at different storage times, mostly fitting into type 1, although treatments T29 and T30 also fit within this cluster. The treatments are characterized by higher values for L^*, ΔE, BD, and TD and lower values for MC, TGM, b^*, chroma and POR, which are generally favorable to better quality levels. The inclusion of T29 and T30 may be related to the fact that the classification variables have less influence in defining cluster 1, such as TDG and WDG, which are important in establishing the type.

Cluster 2 is largely composed of treatments such as H×16×30, H×18×0 and NH×18×0, characterized by higher values of a^*, b^*, Chroma, BD, TD, TGM and MC and lower values of hue angle, ΔE, POR, TDG, MOLD, WDG and FERM. According to the classification of the grains and correlation, cluster 1 is also mostly made up of grains with a low degree of deterioration, classified as type 1. In this cluster, only T13 has a different type (type 2), which may be associated with the predominance of physical property variables, most of which correspond to hermetic storage, with moisture contents of 16 and 18%.

Cluster 3, defined by treatments with moisture contents of 16 and 18% in a non-hermetic storage, included grains with relatively high levels of deterioration, which were classified as type 2, type 3 and out of type. Both the physical properties and classification variables stand out here, defined by higher values for MOLD, POR, TDG, hue angle, ΔE, FERM and WDG and lower values for BD, L^*, TD, a^*, chroma, b^* and TGM, a correlation that is quite consistent with the observations regarding the dynamics of each of the variables analyzed above.

The separation between clusters 1 and 2 is not very obvious, but both differ from that of cluster 3 because cluster 3 has higher deterioration rates. Grains with initial moisture contents of 16 and 18% wb are stored under non-hermetic conditions, indicating that the moisture content factor can be considered to a certain extent in hermetic storage, but its negative effect is quite pronounced when the grains are stored non-hermetically.

Even under conditions with a moisture content of 14% wb, for non-hermetic storage, intervention in the grain mass is important, especially with respect to the proliferation of insects and associated damage, in view of the increased incidence of weevil-damaged grains in the final phase of storage (Fig. 5h).

In hermetic storage, for higher initial moisture contents, storage should be limited, as this condition is expected to have a more intense respiration rate, favorable to the development of facultative microorganisms (Valle et al., 2021a), thus reducing the possible benefits generated by the depletion of O_2 in the grain mass.

To maintain the integrity of the grains, the use of CO_2 sensors, combined with more usual monitoring based on thermocouples or even temperature sensors, is very useful because of their sensitivity in detecting points of deterioration in the grain mass, regardless of the storage system, although there is still the challenge of correctly sizing the number of points that would be feasible. On the other hand, the hermetic storage system proved to be more effective than the non-hermetic storage system and could be stored for up to 90 days without substantial damage, in terms of the degree of defects, but for an MC of 18% wb, better results were expected for grains with a moisture content of less than 16% wb over time.

Grains stored in a non-hermetic system present a high risk of deterioration with an increase in initial moisture content, so corrective measures are expected to be taken from 30 days onward for MCs lower or higher than 16% wb; for MCs equal to or lower than 14% wb, action could be delayed until 90 or 120 depending on the temperature and RH

3.4 Conclusion

The storage conditions, initial moisture content and storage time influenced the dynamics of the temperature, relative humidity and CO_2 concentration generated under each condition. Corn grains stored under non-hermetic conditions tended to have increased metabolic activity, especially those stored with initial moisture contents of 18 and 16% wb. The grains stored with an initial moisture content of 14% wb showed lower levels of deterioration regardless of the storage conditions, with higher values of bulk density and lower porosity of the grain mass. In general, grains stored with a moisture content of 14% wb presented better preservation quality up to 120 days of storage, with hermetic conditions being more favorable in terms of the degree of deterioration and change in physical properties.

The physical properties and classification attributes of the grains showed strong and consistent interactions with the levels of deterioration and the dynamics of the conditions observed throughout storage under both conditions analyzed, with a higher incidence of type 2 to out-of-type grains stored non-hermetically with moisture contents of 16 and 18% wb.

Monitoring the grain mass by means of carbon dioxide concentration was more efficient than monitoring the temperature and relative humidity, better demonstrating the relationship between the respiration rate and the degree of deterioration found in the grain mass by means of physical properties and grain classification according to IN 60/2011, reinforcing the findings of previous studies, which mentioned the use of CO_2 sensors as promising tools for early detection of hot spots or intense biological activity, which intensifies with increasing moisture content, regardless of storage conditions.

Authorship contribution statement

Geraldo Acácio Mabasso: conceptualization, data curation, formal analysis, investigation, methodology, project administration, writing-original draft, writing-review and editing. **Osvaldo Resende**: Supervision, conceptualization, funding acquisition, investigation, methodology, project administration, review–original draft. **Diene Gonçalves Souza**: conceptualization, investigation, methodology, review–original draft. **Elivânio dos Santos Rosa**, **Adrielle Borges de Almeida**, **Jaqueline Ferreira Vieira Bessa**, **Juliana Aparecida Célia**, **Joainny Martins Leite**, **Lara Fernanda Leite**: methodology, project administration and research.

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Declaration of competing interest

The authors declare that there are no known competing financial interests or personal relationships that may have impacted the work reported in this manuscript.

Data availability

The data will be made available upon request.

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SUPPLEMENTARY MATERIAL (CHAPTER I)

Physical properties and quality of corn grains stored at different initial moisture contents under hermetic and non-hermetic conditions

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Table A1. Description of treatments according to storage condition, storage time and initial moisture content

Treatment Nr	Cod	SC	ST	IMC
1	H-18-0	H	0	18
2	H-16-0	H	0	16
3	H-14-0	H	0	14
4	H-18-30	H	30	18
5	H-16-30	H	30	16
6	H-14-30	H	30	14
7	H-18-360	H	60	18
8	H-16-60	H	60	16
9	H-14-60	H	60	14
10	H-18-90	H	90	18
11	H-16-90	H	90	16
12	H-14-90	H	90	14
13	H-18-120	H	120	18
14	H-16-120	H	120	16
15	H-14-120	H	120	14
16	NH-18-0	NH	0	18
17	NH-16-0	NH	0	16
18	NH-14-0	NH	0	14
19	NH-18-30	NH	30	18
20	NH-16-30	NH	30	16
21	NH-14-30	NH	30	14
22	NH-18-360	NH	60	18
23	NH-16-60	NH	60	16
24	NH-14-60	NH	60	14
25	NH-18-90	NH	90	18
26	NH-16-90	NH	90	16
27	NH-14-90	NH	90	14
28	NH-18-120	NH	120	18
29	NH-16-120	NH	120	16
30	NH-14-120	NH	120	14

Table A2. Analysis of variance of physical properties and classification of grains stored under different conditions and initial moisture contents

Source of variation	MC	TD	BD	POR	TGM	a^*	b^*	L^*
SC	1097.66^{**}	64.71^{**}	1867.75^{**}	56.75^{**}	73.40^{**}	54.75^{**}	108.49^{**}	220.82^{**}
IMC	2002.71^{**}	54.25^{**}	2403.95^{**}	139.12^{**}	86.87^{**}	0.79^{ns}	16.32^{**}	181.45^{**}
ST	127.50^{**}	12.58^{**}	698.98^{**}	41.51^{**}	76.42^{**}	40.85^{**}	66.17^{**}	25.45^{**}
SC × IMC	83.35^{**}	7.17^{**}	822.39^{**}	70.96^{**}	3.31^{*}	4.49^{*}	14.40^{**}	77.53^{**}
SC × ST	188.68^{**}	7.71^{**}	124.92^{**}	4.96^{**}	17.38^{**}	4.19^{**}	8.93^{**}	23.78^{**}
IMC × ST	18.11^{**}	7.03^{**}	158.05^{**}	22.32^{**}	5.87^{**}	3.07^{**}	5.82^{**}	24.27^{**}
SC × IMC × ST	17.64^{**}	7.37^{**}	103.82^{**}	10.51^{**}	2.09^{**}	1.47^{ns}	1.79^{ns}	8.45^{**}
CV (%)	1.33	0.97	0.33	1.09	0.76	6.79	2.79	0.40
	Chroma	H^*	ΔE	FERM	WDG	MOLD	TDG	
SC	106.47^{**}	22.96^{**}	95.71^{**}	524.91^{**}	573.06^{**}	5153.30^{**}	1596.90^{**}	
IMC	15.20^{**}	1.96^{ns}	39.16^{**}	246.11^{**}	3.92^{*}	3126.66^{**}	767.97^{**}	
ST	65.06^{**}	27.88^{**}	103.95^{**}	438.27^{**}	165.77^{**}	784.79^{**}	577.68^{**}	
SC × IMC	13.82^{**}	2.21^{ns}	20.21^{**}	157.36^{**}	6.01^{**}	2877.53^{**}	454.29^{**}	
SC × ST	8.60^{**}	3.82^{**}	10.55^{**}	291.12^{**}	202.14^{**}	559.51^{**}	111.07^{**}	
IMC × ST	5.69^{**}	1.79^{ns}	2.95^{**}	99.29^{**}	8.02^{**}	439.85^{**}	92.91^{**}	
SC × IMC × ST	1.76^{**}	1.37^{ns}	1.83^{ns}	72.71^{**}	6.76^{**}	392.09^{**}	38.74^{**}	
CV (%)	2.86	0.47	27.74	22.23	29.84	11.79	9.10	

CV Coefficient of variation (%); MC Moisture content (%, wb); FERM Percentage of fermented grains (%); WDG Percentage of weevil-damaged grains (%); MOLD Percentage of moldy grains (%); TDG Percentage of total defect grains (%). *Significant at $p<0.05$, **Significant at $p<0.01$ and ns Not significant by F-test.

Table A3. Average values of moisture content, true density, bulk density and porosity of corn grains stored under hermetic and non-hermetic conditions with different initial moisture contents

		Moisture content (%, wb)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
	18	18.00^{a}	18.00^{a}	17.80^{a}	17.43^{b}	17.52^{a}	16.55^{b}	17.50^{a}	16.04^{b}	18.06^{a}	16.41^{b}
	16	16.45^{a}	16.45^{a}	17.11^{a}	16.72^{b}	17.13^{a}	14.81^{b}	17.10^{a}	13.29^{b}	17.41^{a}	12.74^{b}
	14	14.08^{a}	14.08^{a}	14.65^{a}	14.43^{a}	14.75^{a}	13.92^{b}	14.55^{a}	12.55^{b}	14.76^{a}	11.52^{b}
		True density (kg m^{-3})									
	18	1340.54^{a}	1340.54^{a}	1325.96^{a}	1291.87^{b}	1357.25^{a}	1301.36^{b}	1315.28^{a}	1269.34^{b}	1337.70^{a}	1322.60^{a}
	16	1342.55^{a}	1342.55^{a}	1350.17^{a}	1257.97^{b}	1346.25^{a}	1307.03^{b}	1325.64^{a}	1310.14^{a}	1310.42^{a}	1318.09^{a}
	14	1354.99^{a}	1354.99^{a}	1361.92^{a}	1370.67^{a}	1350.10^{a}	1356.60^{a}	1362.26^{a}	1327.15^{b}	1342.06^{a}	1325.19^{a}
IMC		Bulk density (kg m^{-3})									
	18	749.35^{a}	749.35^{a}	730.96^{a}	689.82^{b}	741.47^{a}	680.51^{b}	721.62^{a}	650.22^{b}	714.76^{a}	645.87^{b}
	16	753.13^{a}	753.13^{a}	739.85^{a}	693.47^{b}	742.68^{a}	713.08^{b}	733.42^{a}	708.35^{b}	719.84^{a}	721.42^{a}
	14	756.05^{a}	756.05^{a}	752.23^{a}	752.49^{a}	752.90^{a}	758.79^{a}	744.22^{a}	748.00^{a}	743.05^{a}	743.78^{a}
		Porosity (%)									
	18	44.10^{a}	44.10^{a}	44.87^{b}	46.60^{a}	45.37^{b}	47.70^{a}	45.13^{b}	48.77^{a}	46.57^{b}	51.17^{a}
	16	43.90^{a}	44.20^{a}	45.20^{a}	45.10^{a}	44.83^{a}	45.43^{a}	44.67^{b}	45.93^{a}	45.07^{a}	45.27^{a}
	14	44.20^{a}	43.90^{a}	44.77^{a}	44.87^{a}	44.23^{a}	44.07^{a}	45.37^{a}	43.63^{b}	44.63^{a}	43.87^{b}

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the *t-test*.

Table A4. Average values of thousand grains mass (TGM), a*, b*, hue angle (H*) and color difference (ΔE) of corn grains stored in hermetic and non-hermetic conditions

IMC	TGM		a*		b*		ΔE	
	H	NH	H	NH	H	NH	H	NH
18	352.62^{a}	349.78^{b}	5.04^{a}	4.49^{b}	33.24^{a}	30.48^{b}	2.44^{b}	5.13^{a}
16	350.32^{a}	345.20^{b}	5.08^{a}	4.36^{b}	32.74^{a}	30.27^{b}	1.13^{b}	3.04^{a}
14	345.48^{a}	339.22^{b}	4.78^{a}	4.55^{a}	30.87^{a}	30.34^{a}	2.40^{a}	2.60^{a}

ST	TGM		a*		b*		h*		ΔE	
	H	NH	H	NH	H	NH	H	NH	H	NH
0	352.07^{a}	352.07^{a}	5.52^{a}	5.52^{a}	33.36^{a}	33.36^{a}	80.61^{a}	80.61^{a}	0.00^{a}	0.00^{a}
30	352.29^{a}	352.94^{a}	5.00^{a}	4.31^{b}	32.49^{a}	30.84^{b}	81.27^{b}	82.04^{a}	2.39^{b}	3.26^{a}
60	346.17^{a}	341.49^{b}	5.02^{a}	4.21^{b}	32.96^{a}	30.40^{b}	81.35^{b}	82.11^{a}	1.60^{b}	3.72^{a}
90	351.32^{a}	342.72^{b}	4.80^{a}	4.34^{b}	32.25^{a}	30.15^{b}	81.55^{a}	81.81^{a}	2.32^{b}	4.24^{a}
120	345.49^{a}	334.44^{b}	4.49^{a}	3.94^{b}	30.36^{a}	27.07^{b}	81.57^{a}	81.73^{a}	3.67^{b}	6.74^{a}

Values following by different superscript small letters in the row indicate significant difference at $p<0.05$ by the t-test.

Table A5. Average values of L* and color saturation (chroma) of stored corn kernels as a function of conditions and initial moisture content

		L*									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	81.56a	81.56a	82.54a	80.98b	82.92a	80.51b	82.79a	79.13b	83.11a	80.09b
	16	82.27a	82.27a	82.01a	81.86a	82.52a	80.52b	82.98a	81.31b	83.19a	82.62b
	14	81.48a	81.48a	83.24a	83.44a	83.05a	83.08a	83.76a	83.57a	84.14a	83.84a
		Chroma									
	18	35.71a	35.71a	33.44a	30.75b	34.23a	30.71b	32.94a	29.85b	31.78a	27.05b
	16	33.43a	33.43a	34.97a	31.55b	33.03a	30.47b	32.85a	30.23b	31.38a	27.23b
	14	32.31a	32.31a	30.22a	31.13a	32.77a	30.89b	32.02a	31.30a	28.90a	27.79a

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the t-test.

Table A6. Average values of fermented, weevil-damaged, moldy and total defect grains as a function of initial moisture content, conditions and storage time

		Fermented grains (%)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	0.23a	0.23a	1.02a	0.97a	1.14b	5.04a	1.56b	3.80a	2.27b	18.89a
	16	0.33a	0.33a	0.81a	0.22a	1.33a	1.69a	0.93b	2.89a	2.07b	12.22a
	14	0.65a	0.65a	0.70a	1.02a	0.74a	0.31a	0.51a	0.27a	0.87b	1.71a
		Weevil-damaged grains (%)									
	18	0.13a	0.13a	0.19a	0.17a	0.27b	0.94a	0.08b	1.54a	0.00b	7.28a
	16	0.04a	0.04a	0.07a	0.22a	0.15a	0.33a	0.10b	1.10a	0.00b	9.28a
	14	0.05a	0.05a	0.10a	0.16a	0.10b	0.45a	0.34b	1.42a	0.00b	2.95a
		Moldy grains (%)									
	18	0.00a	0.00a	0.00b	9.48a	0.45b	46.92a	0.60b	52.30a	4.94b	60.09a
	16	0.00a	0.00a	0.10b	7.64a	0.19b	7.85a	0.34b	11.41a	2.95b	13.45a
	14	0.00a	0.00a	0.00a	0.25a	0.12a	0.46a	0.39a	0.84a	1.90a	0.01b
		Total defect grains (%)									
	18	0.23a	0.23a	1.02b	10.45a	1.60b	52.00a	2.16b	56.10a	7.21b	78.98a
	16	0.26a	0.26a	0.91b	7.85a	1.53b	9.55a	1.27b	14.36a	5.03b	25.70a
	14	0.65a	0.65a	0.70a	1.27a	1.86a	0.77a	0.90a	1.11a	2.77a	1.72b

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the t-test.

Table A7. Classification of corn grains according to type, in accordance with the Brazilian standard IN 60/2011 as a function of initial moisture content, time and storage conditions

		Classification of grains									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	Type 1	Type 1	Type 1	**Type 3**	Type 1	**OT**	Type 1	**OT**	**Type 2**	**OT**
	16	Type 1	Type 1	Type 1	**Type 2**	Type 1	**Type 2**	Type 1	**Type 3**	Type 1	**OT**
	14	Type 1	Type 1	Type 1	Type 1	Type 1	Type 1	Type 1	Type 1	Type 1	**Type 2**

OT out of type

Table A8. Correlation analysis between physical property variables and corn grain classification as a function of initial moisture content, storage conditions and storage time

	TD	BD	POR	TGM	a*	b*	L*	Chroma	H*	ΔE	FERM	WDG	MOLD	TDG
MC	-0.148^{ns}	-0.232*	0.215*	0.746*	0.388*	0.579*	-0.249*	0.573*	-0.126^{ns}	-0.204^{ns}	-0.091^{ns}	-0.270*	0.067^{ns}	0.037^{ns}
TD		0.731*	-0.296*	-0.098^{ns}	0.402*	0.282*	0.479*	0.288*	-0.434*	-0.410*	-0.214*	-0.171^{ns}	-0.485*	-0.452*
BD			-0.868*	-0.002^{ns}	0.513*	0.441*	0.666*	0.446*	-0.483*	-0.720*	-0.622*	-0.512*	-0.876*	-0.864*
POR				-0.067^{ns}	-0.423*	-0.411*	-0.589*	-0.414*	0.356*	0.708*	0.712*	0.590*	0.878*	0.884*
TGM					0.494*	0.651*	-0.205^{ns}	0.648*	-0.239*	-0.412*	-0.354*	-0.476*	-0.163^{ns}	-0.210*
a*						0.883*	-0.046^{ns}	-0.046^{ns}	0.892*	-0.776*	-0.471*	-0.456*	-0.442*	-0.468*
b*							0.003^{ns}	0.999*	-0.592*	-0.787*	-0.600*	-0.633*	-0.477*	-0.524*
L*								0.001^{ns}	0.064^{ns}	-0.204^{ns}	-0.356*	-0.268*	-0.688*	-0.652*
Chroma									-0.607*	-0.790*	-0.597*	-0.629*	-0.477*	-0.524*
H*										0.616*	0.275*	0.216*	0.333*	0.336*
ΔE											0.703*	0.672*	0.704*	0.736*
FERM												0.937*	0.728*	0.817*
WDG													0.632*	0.723*
MOLD														0.990*

*Statistically significant at $p<0.05$, **Statistically significant at $p<0.01$ and ns Statistically not significant by t-test

Table A9. Eigenvalues, variance and correlation analysis between the variables of physical properties and classification with the principal components (Dim 1, Dim 2 and Dim 3) of corn grains as a function of initial moisture content, storage conditions and storage time

Variable	Dim 1	Dim 2	Dim 3
Eigenvalues	9.18	3.44	1.98
Individual variance	48.29	18.11	10.44
Cumulative variance	48.29	66.40	76.84
MC	-0.242^{ns}	0.829**	0.067^{ns}
TD	-0.553**	-0.423**	0.374**
BD	-0.829**	-0.517**	0.072^{ns}
POR	0.808**	0.452**	0.157^{ns}
TGM	-0.484**	0.742**	-0.067^{ns}
a^*	-0.724**	0.324^{ns}	0.372**
b^*	-0.837**	0.481**	0.059^{ns}
L^*	-0.438**	-0.689**	-0.074^{ns}
Chroma	-0.839**	0.477**	0.072^{ns}
H*	0.647**	-0.080^{ns}	-0.592**
ΔE	0.929**	-0.067^{ns}	-0.029^{ns}
FERM	0.831**	0.183^{ns}	0.434**
WDG	0.802**	-0.169^{ns}	0.703**
MOLD	0.845**	0.406**	0.148^{ns}
TDG	0.880**	0.345^{ns}	0.213^{ns}
IMAT	0.326^{ns}	0.235^{ns}	-0.545**
BROK	-0.346^{ns}	-0.152^{ns}	0.205^{ns}
IMP	0.776**	-0.328^{ns}	0.353^{ns}
SHRI	0.170^{ns}	0.084^{ns}	-0.591**

*Statistically significant at $p<0.05$, **Statistically significant at $p<0.01$ and ns Statistically not significant by t-test

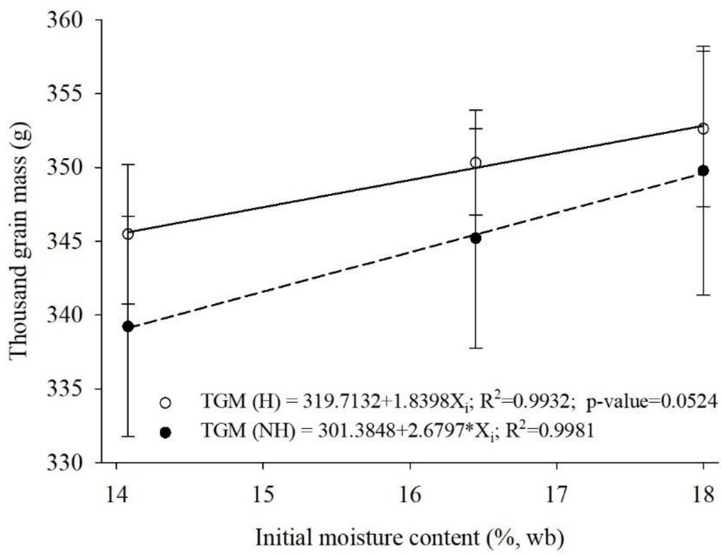

Fig. A1. Average values for thousand-grain mass as a function of conditions and initial moisture content. *Statistically significant at $p<0.05$.

4 CHAPTER II

PHYSICOCHEMICAL PROPERTIES, STRUCTURAL ANALYSIS AND CO_2 CONCENTRATIONS OF CORN GRAINS STORED UNDER DIFFERENT CONDITIONS

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Abstract
This study aimed to evaluate the effects of storage conditions (hermetic and non-hermetic), initial moisture content (14, 16, and 18% wb), and storage time (0, 30, 60, 90, and 120 days) on corn grains quality. During the storage period, the concentration of CO_2, temperature, relative humidity, proximal composition, dry matter loss, starch, and insect damage were evaluated. The BRS284 corn grains were harvested and stored with an initial moisture content of 18, 16, and 14% wb. The [CO_2], temperature, and relative humidity were monitored by sensors in grain mass and ambient air for up to 120 days, at one-hour intervals. The results indicated increases in [CO_2], temperature, and relative humidity in the grain mass, with increased storage time and higher moisture content. The rates of dry matter loss increased for both conditions, more intense for non-hermetic storage, no insect was observed in grains stored hermetically. The ether extract and protein contents decreased with rising moisture content and storage time, while starch granules tended to compact with increasing moisture content.

Keywords: *Zea mays* L.; X-ray; scanning electron microscopy; hermetic and non-hermetic; proximal composition

4.1 Introduction

Postharvest losses of agricultural products are often linked to inadequate storage technology and processing methods (Ikegwu et al., 2022). Losses can be minimized through appropriate conservation and processing techniques, along with improved market management, reducing the rate of deterioration and increasing availability.

Under conditions of sufficiently low metabolic activity and the absence of insects, grain can be stored for long periods, minimizing losses (Navarro and Navarro, 2020).

These losses include a reduction in quantity, changes in physical appearance, physicochemical composition, fungal growth and/or the presence of insects, as well as unpleasant odors.

Aerobic respiration in the grain mass is linked to dry matter loss, oxygen consumption, and the release of water vapor and CO_2, all of which accelerate deterioration. This process can lead to dry matter losses exceeding 0.5%, a critical threshold for safe storage (Bern et al., 2019). Monitoring via sensors helps in the management of grain quality and early detection of contamination and insect infestation. It also reveals a correlation between CO_2 concentration and the risk of deterioration (Souza et al., 2024). Non-destructive techniques to assess the quality of agricultural products have attracted researchers' interest due to their accuracy, reliability, and economic and environmental benefits (Jimoh et al., 2023).

CO_2 monitoring is a useful tool for managing stored grain quality. It enables managers of storage units to make informed decisions to mitigate the effects of biological activity on a larger scale. Ziegler et al. (2021) highlight practicality and simplicity as essential elements to ensure the adoption and preservation of quality over long periods. Levels of CO_2 between 600 and 1,500 ppm indicate the presence of insects and/or fungi, as well as an increased moisture content of the grain mass, and become more critical when levels of CO_2 reach between 1,500 and 4,000 ppm, requiring urgent mitigation actions (Aby and Maier, 2020).

Sensitivity in the measurement of CO_2 levels has been reported in several studies, for example, Magan et al. (2020), observed changes with the introduction of a bag of wet grains, which later influenced temperature variations. This is because biological activity is more easily detected through respiration. While respiratory activity also causes an increase in temperature, but its diffusion is slower due to the low thermal conductivity of the grains (Mabasso et al., 2024; Souza et al., 2024).

Quality can be altered by storage time and conditions (Scariot et al., 2020). During storage, grains are subjected to the actions of insects and microorganisms, as well as deterioration reactions that cause loss of mass (Leal et al., 2023). In addition, SEM can also be used effectively to assess the structural arrangement of particles (Sharma and Bhardwaj, 2019; Mabasso et al., 2023).

Hermetic storage is characterized by ease of handling, greater availability, suitability for both small and large volumes, durability, preservation of biochemical composition, and effectiveness in limiting the development of fungi and mycotoxins

(Nishimwe et al., 2020). Hermetic systems, such as bag silos, are characterized by the absence of gas exchange and a physical barrier to water vapor, creating an environment less favorable for aerobic organisms (Bartosik et al., 2023).

Given these findings, this study aimed to evaluate the effects of storage conditions (SC) (hermetic and non-hermetic storage), initial moisture content (IMC) (14, 16 and 18% wb) and storage time (ST) (0, 30, 60, 90 and 120 days) on the quality of stored corn grains, through proximal composition, dry matter loss (DML), structural analysis through images (SEM and X-rays), as well as its relationship with the variation in concentration of CO_2, temperature and relative humidity in the grain mass.

4.2 Material and methods

4.2.1 Experimental design

The study was carried out at the Laboratory of Postharvest of Vegetable Products (LPCPV), IF Goiano - Campus Rio Verde - Goiás, in a completely randomized design, with a factorial scheme of 2 × 3 × 5 and 3 repetitions, which corresponds to two storage conditions (hermetic and non-hermetic storage), three initial moisture contents (14, 16 and 18% wb) for the corn grains (Mabasso et al., 2024; Souza et al., 2024; Bilhalva et al., 2023; Valle et al., 2021) and five storage times (0, 30, 60, 90 and 120 days), total of 30 treatment, as combination of storage condition (SC), initial moisture content (IMC) and storage time (ST).

4.2.2 Monitoring of environment parameters

The BRS284 corn grains were mechanically harvested with an IMC of 18% wb. The grains were then dried by natural ventilation at T and RH values of 24.0±2.73 °C and 41.49±7.08%, respectively, to obtain two lots of grains with IMCs of 16 (24 h) and 14% wb (72 h). The moisture content was determined by oven method at a T of 103±1 °C for 72 h, and three repetitions with approximately 15g were performed (ASABE, 2003). After reaching the defined moisture contents, the grains were subjected to storage under the two established conditions with homogenized samples, in variable environmental conditions.

Non-hermetic storage (NH) was carried out in experimental metal silos with a capacity of 0.108 m^3 (0.60 × 0.60 × 0.30 m). Hermetic storage (H) carried out in multilayer, low-density hermetic packaging with two polyethylene films, which are pressed into a plastic layer that is highly impermeable to oxygen, has a thickness of 78±0.1 µm and is composed of multiple barriers for gas exchange, water vapor absorption, and insect entry (GrainPro, SuperGrainBag®), with a vapor transmission rate of less than 5 g^{-2} day^{-1} (Bakhtavar et al., 2019). For each IMC condition, a sufficient number of packages were adopted to allow hermeticity, with approximately 30 kg of grains in each package, where the samples were taken for each evaluation period, without altering the hermetic conditions in the packaging.

The T, RH, and CO_2 concentrations were monitored via sensors placed inside the granular mass at one-hour intervals. For hermetic storage, sensors (GasLab 2.1®), model K33 BLG (bio-logger) were used, which is based on non-dispersive infrared (NDIR) technology and is suitable for detecting high levels of CO_2, with a capacity of up to 30±2% (300,000±20,000 ppm). For NH, sensors from Extech Instruments, model CO210 (0 to 10,000 ppm), were used.

4.2.3 Quality grain analysis

4.2.3.1 Dry matter loss

The DML was determined via three samples of 100 g each per repetition for each treatment, which were enveloped in Voil wraps and randomly placed inside the grain mass. To determine the magnitude of the DML, weighing was carried out at established intervals, and the moisture content was determined (Eq. 1), the evaluations were performed in 30-day intervals until 120 days.

$$DML = \frac{m_0 \times (1 - MC_0) - m_i \times (1 - MC_i)}{m_0 \times (1 - MC_0)} \times 100 \qquad (1)$$

where DML is dry matter loss (%), m_0 and m_i are the initial and actual mass of the sample at 30, 60, 90, and 120 days of storage (g), MC_0 and MC_i are the initial and present moisture content of the sample at 30, 60, 90 and 120 days of storage (decimal, wb).

4.2.3.2 Proximal composition of corn grains

For the proximal composition, the carbohydrate (CHO), protein, ether extract (EE), total mineral, crude fiber (CF) and starch contents were determined during storage, at 30-day intervals, for the two storage conditions (SC) and at each IMC, considering three repetitions. The evaluation was carried out via near infrared reflectance (NIR) spectroscopy, BUCHI model NIRFlex 500 (Buchi Labortechnik, Flawil, Switzerland). The CHO content was determined by subtracting the sum of the other constituents of the proximal composition.

4.2.3.3 Electrical conductivity and germination

The electrical conductivity (EC) was determined using four samples of 50 grains per repetition, as a total of 200 grains or 600 grains per treatment. Each sample was placed in a 200 mL disposable cup and weighed on a semi-analytical scale with a resolution of 0.001 g. After adding 75 mL of deionized water, the samples were placed in a DBO chamber at a T of 25 °C for 24 hours. The readings were taken on a conductivity meter ($\mu S\ cm^{-1}$) and then converted to $\mu S\ cm^{-1}\ g^{-1}$ by dividing the values by the mass of each sample (Vieira and Krzyzanowski, 1999).

For germination (GM), four samples of 50 grains per repetition were used, which correspond to total of 200 grains per repetition or 600 grains per treatment. The grains were placed on Germitest® paper moistened with distilled water at a ratio of 2.5:1 and then placed in a GM chamber with a 12-hour photoperiod at a temperature of 25±1 °C. For quantification, counts were made on the 4^{th} and 8^{th} days of the test, according to the Rule for Seed Analysis as reported by Lutz and Coradi (2023).

4.2.3.4 Assessment of insect damage via X-ray

Insect damage was determined via images obtained from X-ray analysis. For each combination of IMC × SC, in 30-day intervals, five repetitions of forty grains were used per evaluation period, which were placed on transparent acrylic plates (15 cm × 10.5 cm) and fixed with transparent double-sided adhesive tape. The plates were then subjected to radiation via X-ray image analysis equipment (Faxitron HP 43855A) at 30 kV for 10 seconds. The captured images were then analyzed to identify the damage associated with the insects, counting the grains with evidence of the presence of insects inside (larvae, pupae or adults) or typical perforations and galleries (Eq. 2).

$$ID = \frac{n}{N} \times 100 \quad (2)$$

where ID is the insect damage (%), n is the number of grains with evidence of the insect presence in the sample; and N is the total number of grains observed.

4.2.3.5 Grain analysis by scanning electron microscopy

Scanning electron microscopy (SEM) was performed at the beginning and end of the 120-day storage time (ST). Before analysis, the corn grains were first ground in a Tecnal TE-650/1 Willye knife mill with a 1 mm diameter sieve. After grinding, the samples were degreased via the Soxhlet extraction method, AOAC 920.39 (AOAC, 2019). The images were then taken at different resolutions on a Jeol JSM7 100F scanning electron microscope (SEM-FEG) from the Laboratory Multiuser of High-Resolution Microscopy of the Federal University of Goiás, with an electron acceleration voltage of 5 keV in secondary electron detection (SED) mode.

4.2.4 Statistical analysis

The data were analyzed via RStudio 4.4.1® (easyonova, MASS) software in a completely randomized 2 × 3 × 5 factorial design with three repetitions. The normality and homoscedasticity were performed by the significance of p-value ($p<0.05$), according to Shapiro-Wilk test and Bartlett test. A t-test was used to compare the SC at 5% significance ($p<0.05$). Linear regression models were fitted and tested for IMC and ST based on the significance of the coefficients via the t-test at 5% significance ($p<0.05$) and the magnitude of the coefficient of determination (R^2). Additionally, the data were subjected to Pearson's correlation analysis at a significance level of $p<0.05$.

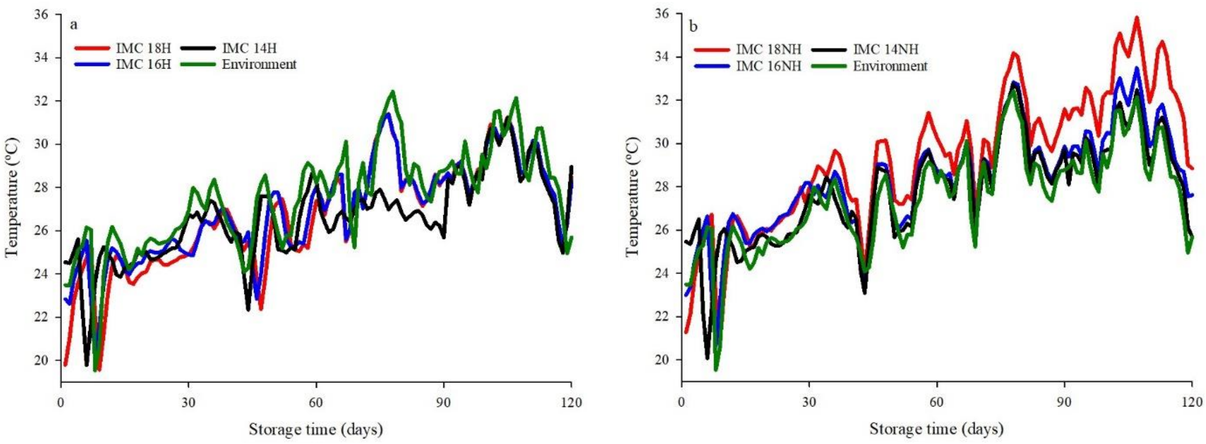
4.3 Results and discussion

4.3.1 Effect of storage conditions on concentration of CO_2, temperature and relative humidity

In general, the T values were proportionally greater for the higher IMC condition, with the lowest magnitudes recorded for the environmental air condition, with an increasing trend over the ST. For the grains stored hermetically, the highest T values were recorded mostly for the environment, with the lowest recorded for the grains stored with an IMC of 14% wb (Fig. 1a). This increase in the ST was more intense, especially toward the end of storage, close to 90-120 days, for the IMC of the grains of 18% wb, where there was a greater distance between the curve and the others for the NH (Fig. 1b).

The rise in T is one of the consequences of the increase in respiration, so it can be inferred that respiratory activity was more intense for the higher moisture content conditions for NH, where significant increases in T were observed with environmental T, contrary to what was observed for hermetic storage, in which the values were always lower and similar for the IMC conditions of 16 and 18% wb (Fig. 1b).

The same behavior was observed by Coradi et al. (2022) in hermetic storage, using bag silo prototypes, for IMCs of 13 and 18% wb, with higher T and RH values for the higher IMC, in the condition of controlled temperature.



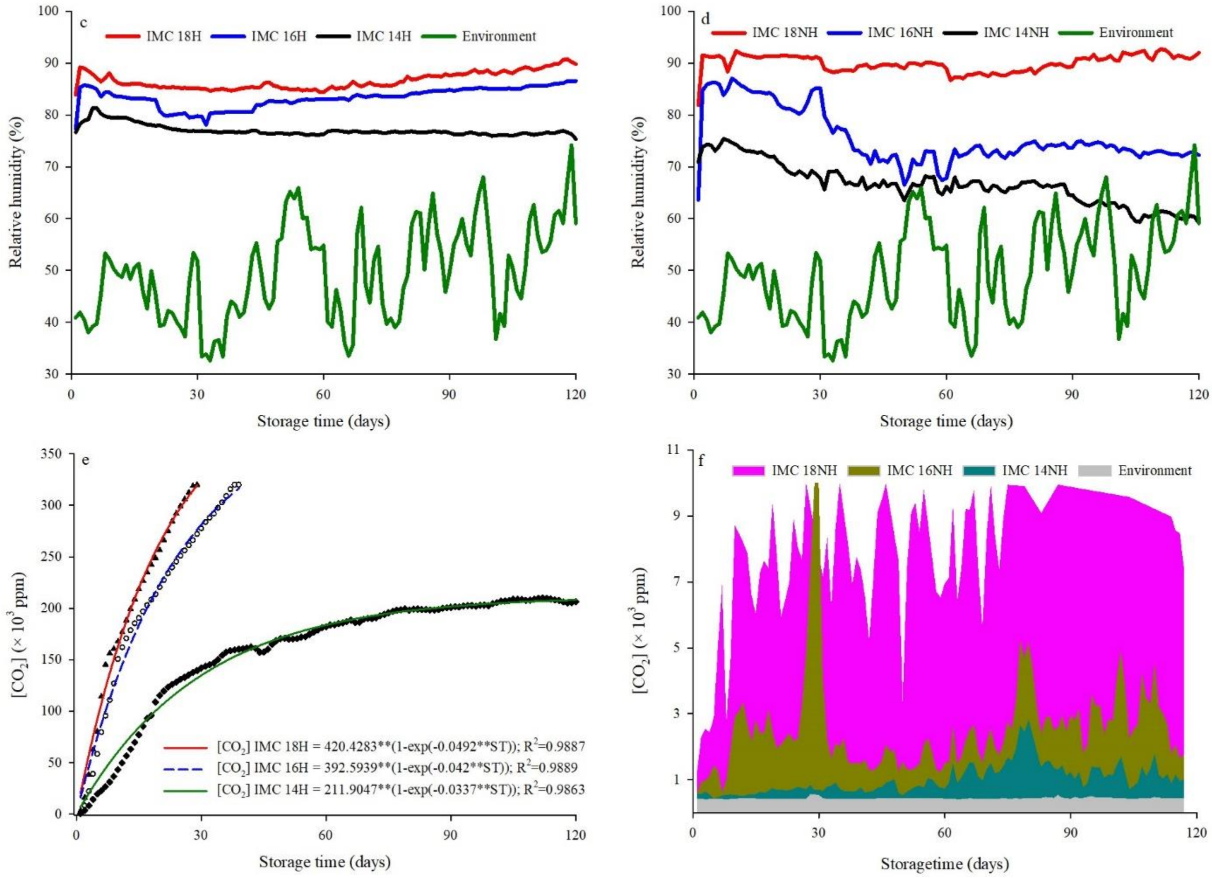


Fig. 1. Mean daily values of temperature (a, b), relative humidity (c, d), and CO_2 concentration (e, f) in the external environment and inside the mass of corn grains stored under hermetic and non-hermetic conditions. **: significant at p<0.01 by t-test; ST: Storage time; IMC: Initial moisture content; H: Hermetic storage; NH: Non-hermetic storage.

For RH, the recorded values were consistently greater for all IMCs than for the environment, most notably for the IMC of 18% wb (Fig. 1c-d), with values approaching 90%. The variation was greater under NH. For IMCs of 16 and 14% wb in the NH, the values decreased, contrary to the behavior observed for the IMC of 18% wb. The values for 16% wb were close to the range of 75 - 80%, and for 14% wb, they were in the range of 65 - 70%. These results were similar to those reported by Coradi et al. (2022), but with an IMC of 13% and a constant environmental temperature of 30 °C.

For CO_2, the measured values were always greater for the granular mass, reflecting respiratory activity with the external environment, which is consistent with the behavior of T and RH. The values were also higher for greater moisture contents, regardless of SC. However, they were significantly higher under hermetic conditions, with a more rapid growth rate in the initial phase (Fig. 1e-f).

At initial moisture content of 18 and 16% wb, in grain stored hermetically, the maximum value of CO_2 (320 × 10^3 ppm) was reached with approximately 29 and 40 days of storage, respectively. For the IMC of 14% wb, the maximum value was reached at 120 days of storage and was 208.19 × 10^3 ppm, which is 65% lower than that recorded for 18 and 16% wb, a result of less respiration rate of the grains mass for this condition. Under hermetic storage conditions, metabolic activity is controlled. However, in environments with higher humidity or an elevated initial moisture content, facultative microorganisms may be present, leading to a significant increase in CO_2 levels even in the absence of oxygen. Additionally, the rate of increase is higher at the beginning of the process (Valle et al., 2021).

In NH, the CO_2 concentration varied with increasing IMC, with values closer to 10,000 ppm for an IMC of 18% wb. The variation during storage was due to gas exchange between the granular mass and the external environment, but the dynamic of the recorded values was maintained with the initial condition of the product, with mean values of 7,428.97, 2,494.07 and 1,002.07 ppm for IMCs of 18, 16 and 14%, respectively, and 431.00 ppm for environmental air (Fig. 1f).

The variations in T, RH and CO_2 indicate more intense respiration activity for higher IMCs based on the magnitude of the values of the byproducts associated with respiration. According to Diarra and Amoah (2019), hermetic storage systems, such as SuperGrainBag® packaging, are more effective for storing corn grains because they allow the creation of an environment with a reduced oxygen concentration and T at levels that are favorable for controlling insects and inhibiting the presence of fungi, especially under conditions of low product moisture content, thus minimizing the level of mass loss.

Although T is a commonly used tool for monitoring the quality of stored grains, localized measurements are less accurate because of the low thermal conductivity of the granular mass, as the heat transmission process occurs slowly (Leal et al., 2023; Garcia-Lara et al., 2019). Garcia-Lara et al. (2019) noted that in the case of biotic activity caused by microorganisms and insects, the heat generated can cause T to rise above the ignition T, which can lead to spontaneous combustion. Additionally, Magan et al. (2020) and Souza et al. (2024) reported that changes in T occur later, with changes in CO_2 concentration being easier to detect, as a result of the low thermal conductivity of biological materials in general. Thus, a greater lag was identified between the values observed for the external and internal conditions of the granular mass in this study.

Another relevant factor is the distance between thermometry sensors or cables. According to Aby and Maier (2020), there is no consistent scientific evidence regarding optimal spacing, which poses risks for identifying deterioration outbreaks in advanced stages if they occur far from the sensor's detection range. Therefore, combining T measurements with CO_2 concentrations is advantageous for early detection and timely implementation of corrective actions (Souza et al., 2024; Ferreira et al., 2024; Coradi et al., 2022).

Monitoring SC, through T, RH and CO_2 concentrations, for example, also provides indicators to determine the need for aeration and, consequently, grain cooling, which is an important factor in containing any T increase in the mass of a grain (Bilhalva et al., 2023). High respiration rates, which result in increases in the concentrations of CO_2, T, and RH in the grain mass, have the potential to negatively impact grain quality during storage, especially in environments with relatively high temperatures and high grain moisture contents (Coradi et al., 2022).

4.3.2 Effect of storage conditions on dry matter loss, electrical conductivity and germination

For all the variables analyzed, there was an interaction between SC, IMC and ST (Table A1). The DML increased with increasing ST and IMC, with the rate of increase being more significant under SC, thus resulting in greater deterioration under these conditions (Table A2, Fig. 2a-b). Higher DML values are associated with a higher respiration rate, which is consistent with the measurements of T, RH, and CO_2 concentrations, although the T values under hermetic conditions remained below the environmental T.

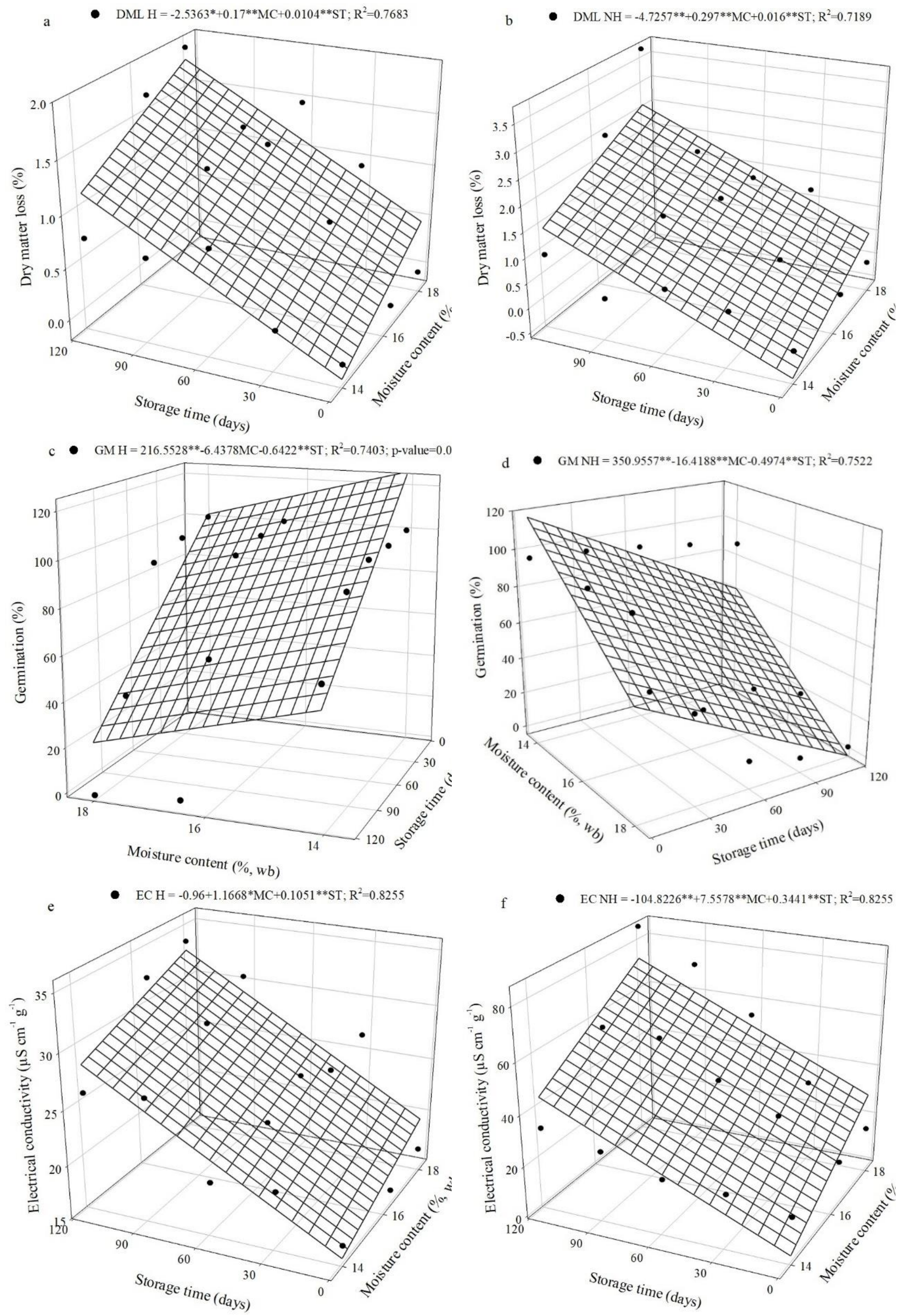


Fig. 2. Mean values of dry matter loss (a, b), germination (c, d) and electrical conductivity (e, f) in corn grains stored under hermetic and non-hermetic storage conditions. * and **: Significant at $p<0.05$ and $p<0.01$ by t-test; ST: Storage time; MC: moisture content.

Estimating the DML in stored grains is crucial for making informed decisions about grain quality and the optimal time for their sale, aiming to maximize returns for producers or storage units (Leal et al., 2023; Bilhalva et al., 2023). Leal et al. (2023) reported a positive correlation between CO_2 concentration and DML during wheat grain storage, underscoring the importance of this trend for assessing grain quality.

GM and EC had opposite effects, with values decreasing as the IMC and ST increased, in contrast to the increase in EC values (Table A2, Fig. 2c-f). This shows that the increase in ST and IMC contributed to greater metabolic activity, which resulted in a greater DML and consequently a greater release of leachates or damage to the membranes, causing some of their nutrient reserves to leak out. This relationship was also evidenced by the correlations between DML × EC ($r=0.784$, $p<0.05$), DML × GM ($r=-0.743$, $p<0.05$), and EC × GM ($r=-0.802$, $p<0.05$) (Table A3).

Bakhtavar et al. (2019), evaluating the effect of IMC between 8 and 14% wb, reported a reduction in the GM of corn seeds at an IMC of 14% wb, which was associated with the maintenance of the moisture content during storage, as a result of the effectiveness of the barrier offered by hermetic packaging to lose water.

The GM is not negatively affected by high levels of CO_2, as long as the moisture content is below the critical value. However, when the moisture content of grains increases, a CO_2-rich environment can become detrimental because of an increase in the enzymatic activity of glutamine decarboxylase (Navarro and Navarro, 2020).

4.3.3 Insect damage and structural changes

Insect damage was observed in grains stored non-hermetically, with an exponential and proportional increase in the IMC (Fig. 3a). At 120 days of storage, the maximum values recorded were 15.24, 44.35 and 55.70% for IMCs of 14, 16 and 18% wb, respectively.

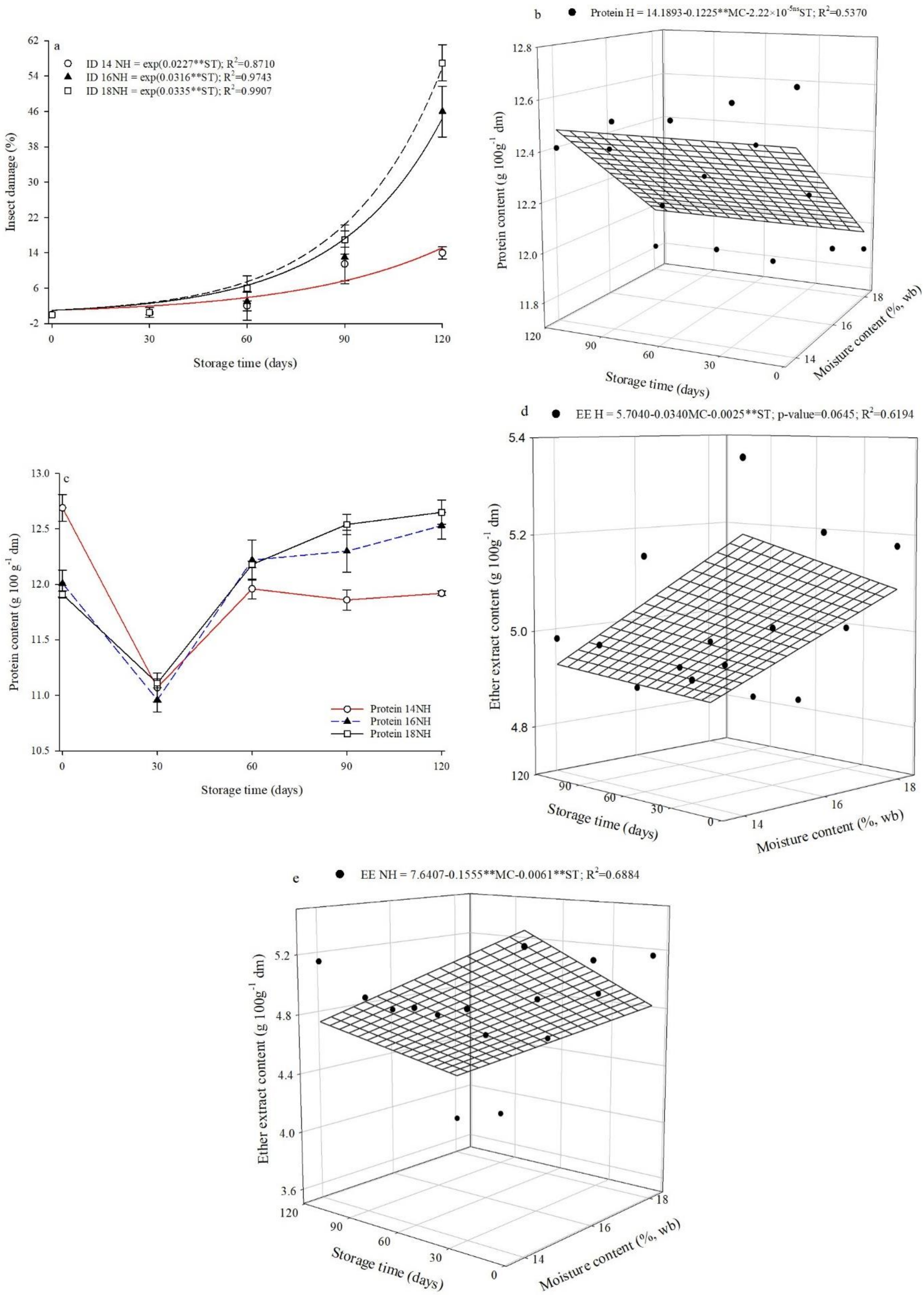


Fig. 3. Mean values of insect damage (a), protein content (b, c) and ether extract content (d, e) in hermetically and non-hermetically stored corn grains. **: Significant at $p<0.01$ by t-test; ns: Not significant; ST: Storage time; MC: moisture content.

For hermetic storage, no signs of insect presence or damage were observed (Fig. 4a, b, c), which contrasts with the observations made regarding signs of insect damage under NH (Fig. 4d, e, f). Although the presence of insects was expected under both SCs, considering the CO_2 concentration, which is much higher than 600 ppm (Aby and Maier, 2020), the same does not apply to hermetic storage because the physical barrier to gas exchange generates an oxygen-depleted and CO_2-rich environment. A similar finding was reported by Mabasso et al. (2024), in an experiment carried out under the same conditions, linked to the initial level of infestation in the beginning, as well as the prevalence during the storage. Kiobia et al. (2020), evaluating different packaging for stored corn grains, also found an absence of live insects in corn grains stored in a hermetic condition, using GrainPro® packaging, due to the effectiveness of physical barberries and increase in [CO_2], which turn the environment lethal for aerobic organisms.

Kuyu et al. (2022) also associated the incidence of insects in stored corn grains with the availability of oxygen present in the NH. For Bakhtavar et al. (2019), this aspect also has a significant influence on the viability of the embryo and, consequently, a proportional reduction in the GM, since the corn germ, where the embryo is located, is the preferred food for stored grain insect pests. Damage to the embryo can also be associated with the action of microorganisms and oxidative reactions, meaning that GM can be affected not only by the balance of nutrient reserves but also by the viability of the embryo.

Diarra and Amoah (2019) reported a positive effect of the SuperGrainBag® storage system on insect control in stored corn grains, achieving total insect mortality at 52 days and significantly reducing damage. Similarly, Suleiman et al. (2018) reported total insect mortality in corn grains pre-infested with *Sitophilus zeamais* at 60 days of storage, regardless of the IMC.

Insect damage increased from 30 days onward, likely due to the completion of the insect life cycle. Suleiman et al. (2018) reported an increase in the number of live *Sitophilus zeamais* with increasing moisture content, ranging from 14 to 20% wb in the first 30 days of NH. However, the values were greater for IMCs of 14 and 16% wb at 60 days for those of 18 and 20% wb at 30 days, likely due to greater fungal infestation. The levels of damage were greater at higher moisture contents (18 and 20% wb), and this study also revealed a greater degree of insect damage at these moisture levels, which was associated with intense fungal activity.

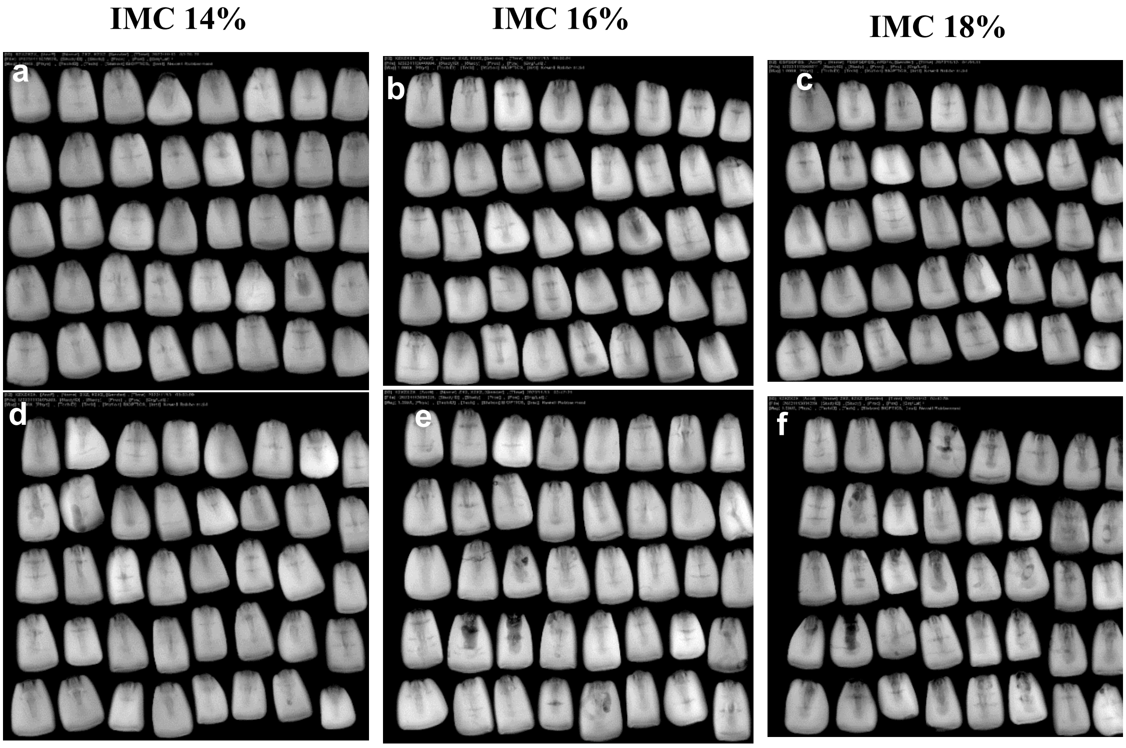


Fig. 4. X-ray images of corn kernels stored in hermetic (a, b, c) and non-hermetic (d, e, f) conditions after 120 days for initial moisture contents of 14, 16 and 18% wb

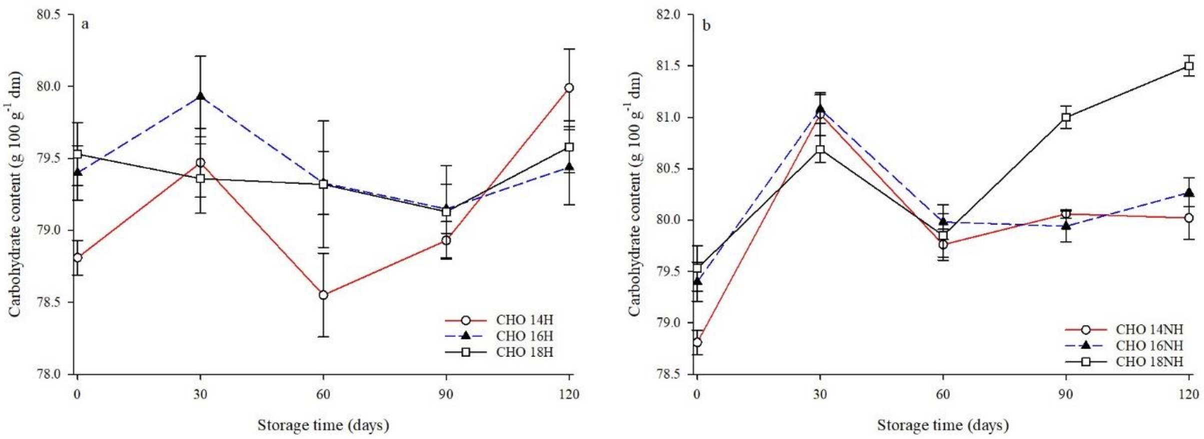
The high incidence of fungi is also associated with a loss of quality, leading to a reduction in seed GM, which is a reflection of the increased consumption of important nutrient reserves, including carbohydrates, proteins, and lipids, during the GM process (Erasto et al., 2022). According to Navarro and Navarro (2020), grains severely infested by insect pests require actions to control the insect population through fumigation and, subsequently, aeration to lower the intergranular T, an extremely useful action in NH, in which significant levels of infestation and altered SC are expected.

The level of insect damage was negatively influenced by GM ($r=-0.479$, $p<0.05$) and positively influenced by DML ($r=0.697$, $p<0.05$) and EC ($r=0.779$, $p<0.05$), indicating greater metabolic activity and consequent loss of nutrient reserves as the level of damage increased in grains stored non-hermetically.

For the hermetic storage system, the protein content decreased with increasing ST and IMC, with the effect of IMC being the factor with the greatest contribution (Fig. 3b). Concerning the NH, no trend was observed for all IMCs over the ST (Fig. 3c), with mean values ranging from 11.90±0.58 to 12.02±0.48 g 100 g^{-1} dm for IMCs of 14 and 18% wb, respectively. For the EE, the values recorded throughout storage were negatively influenced by the increase in both factors under the two SC, with the rate reduction being greater in the NH (Fig. 3d-f). A similar trend was also observed in conventionally stored corn grains with a moisture content of 14% wb, with the lowest value recorded at 270 days of storage (Mabasso et al., 2023).

The results observed concerning the protein content, especially the EE ($r=-0.647$, $p<0.05$), are in line with the levels of insect damage since both constituents of dry matter are mostly found in the germ. Ziegler et al. (2021) reported that changes in the proximal composition during storage are primarily due to the metabolism of the grain and microorganisms.

The CHO, total mineral, CF, and starch contents did not show a consistent trend with the STs for each IMC, except for the starch content, which increased at an IMC of 14% wb under NH (Fig. 5a-h). Generally, the CHO content was lower under hermetic conditions (Table A4), which was also observed for the starch content. This was expected since carbohydrates are primarily composed of starch ($r=0.634$, $p<0.05$). Conversely, the CF content was generally greater under hermetic conditions (Table A4). According to Kuyu et al. (2022), higher values of one constituent of the proximal composition are associated with lower values of at least one other constituent, reflecting the moisture content and condition of the product.



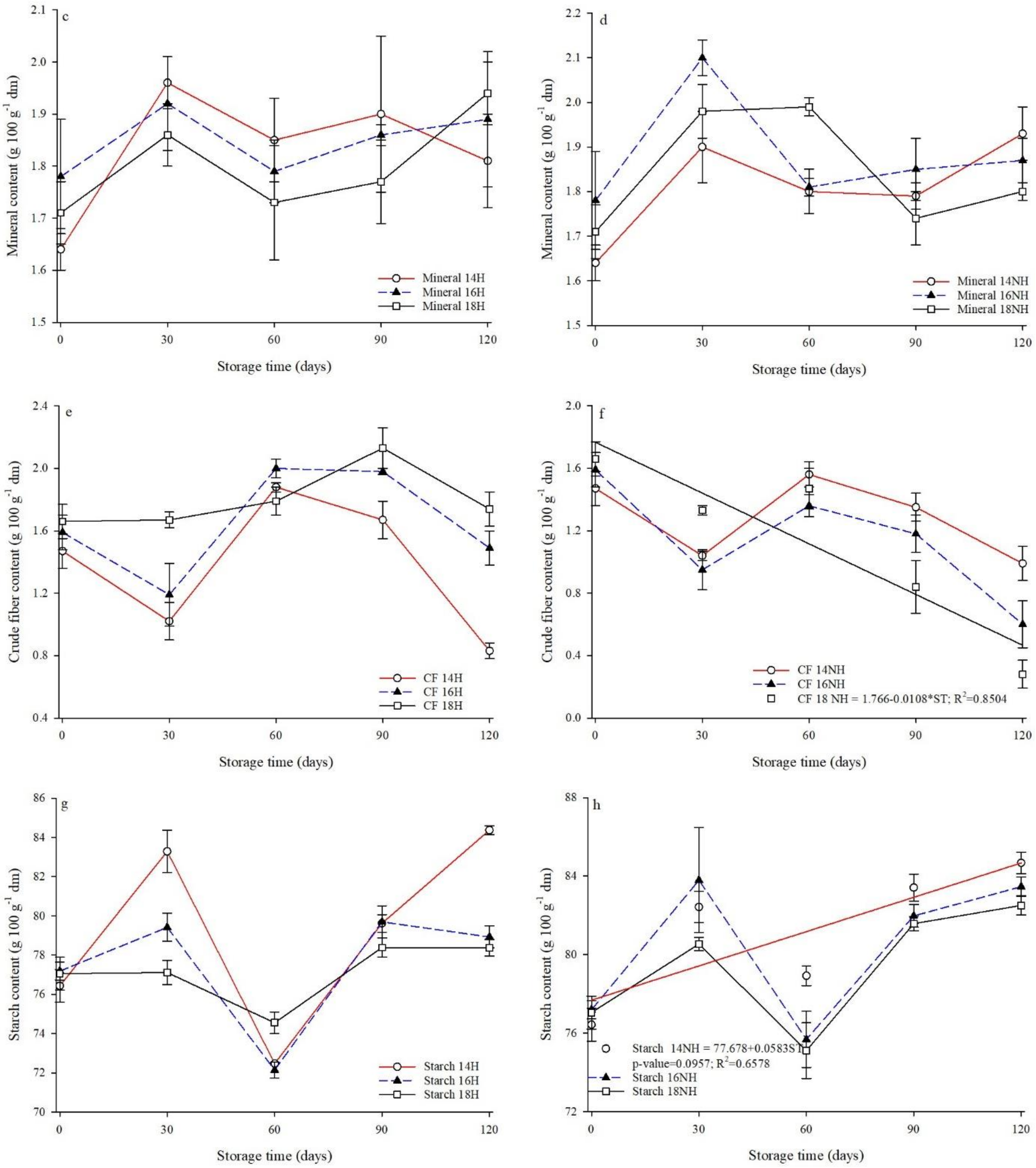


Fig. 5. Mean carbohydrate (a, b), total mineral (c, d), crude fiber (e, f) and starch (g, h) contents of corn grains stored under hermetic and non-hermetic conditions as a function of storage time and different initial moisture contents. *: Significant at $p<0.05$ by t-test; ST: Storage time.

According to Garcia-Cela et al. (2020), the endosperm of corn corresponds to approximately 80 to 82% of the dry matter of the grain and is mostly composed of 86 to 89% starch. From this perspective, the values for the present study are relatively low, regardless of SC, but the oil content is within the range referenced by Kuyu et al. (2022), which ranges from 3–5% db. These values also contrast with the CHO and starch contents obtained under the best SC, which was 70.7% starch content for the maize seeds stored in the SuperBag® packaging, and 61.27% for grains stored in the Jute bag with a moisture content of 14% wb (Bakhtavar et al., 2019), which are equivalent to starch contents of 79.23±4.92 and 81.18±3.41 g 100 g^{-1} dm for H and NH, respectively (Fig. 5g-h).

The degrees of correlation between EE × CHO ($r=-0.665$, $p<0.05$), CF × CHO ($r=-0.770$, $p<0.05$) and CF × Starch ($r=-0.702$, $p<0.05$) are consistent with the observed standards, in which the highest CF and EE contents mostly coincide with the lowest CHO and starch values. The relationship between protein × CHO ($r=-0.418$, $p<0.05$) was relatively low, i.e., the degree of dependence between the two variables was less important than the relationship between EE × CHO ($r=-0.665$, $p<0.05$), a relatively strong correlation, which can be explained by the fact that no clear trend was observed to the CHO content during storage.

Fig. 6 shows SEM images of corn grains at 0 and 120 days of storage under both H and NH. The comparison was based on the size and degree of dispersion or agglomeration of starch granules at the initial moisture content and after 120 days of storage. For an IMC of 14% wb, small, agglomerated structures are visible. In contrast, at IMCs of 16 and 18% wb (Fig. 6a, d, g), small, enlarged structures are present. There was also a trend toward greater compaction of starch granules at IMCs of 16 and 18% wb before storage than the spherical shape observed at an IMC of 14% wb. This compaction is a consequence of less stable structures at higher moisture content.

The grains stored under hermetic conditions also maintained the same trend to time zero but with a proportionally more pronounced fiber matrix for the IMC of 14% wb and a slight tendency to form polygonal structures at the IMC of 18% wb (Fig. 6b, e, h).

After 120 days of storage, agglomeration of starch granules was observed in the grains stored under NH. This included the involvement of fibrous structures and compacted granules at IMCs of 16 and 18% wb. The granular structures with a moisture content of 14% wb were typically spherical, whereas those with IMC of 18% wb were polygonal (Fig. 6c, f, i). In terms of size, the starch granules generally followed a similar trend but were smaller at an IMC of 14% wb before and after storage under NH (Fig. A1).

The mean diameter of the starch granules obtained for this study was 11.76 ± 2.73 µm. According to Garcia-Cela et al. (2020), the endosperm of corn is mostly composed of elongated cells filled with starch granules between 3 and 25 µm in diameter, surrounded by a protein matrix in mature grains.

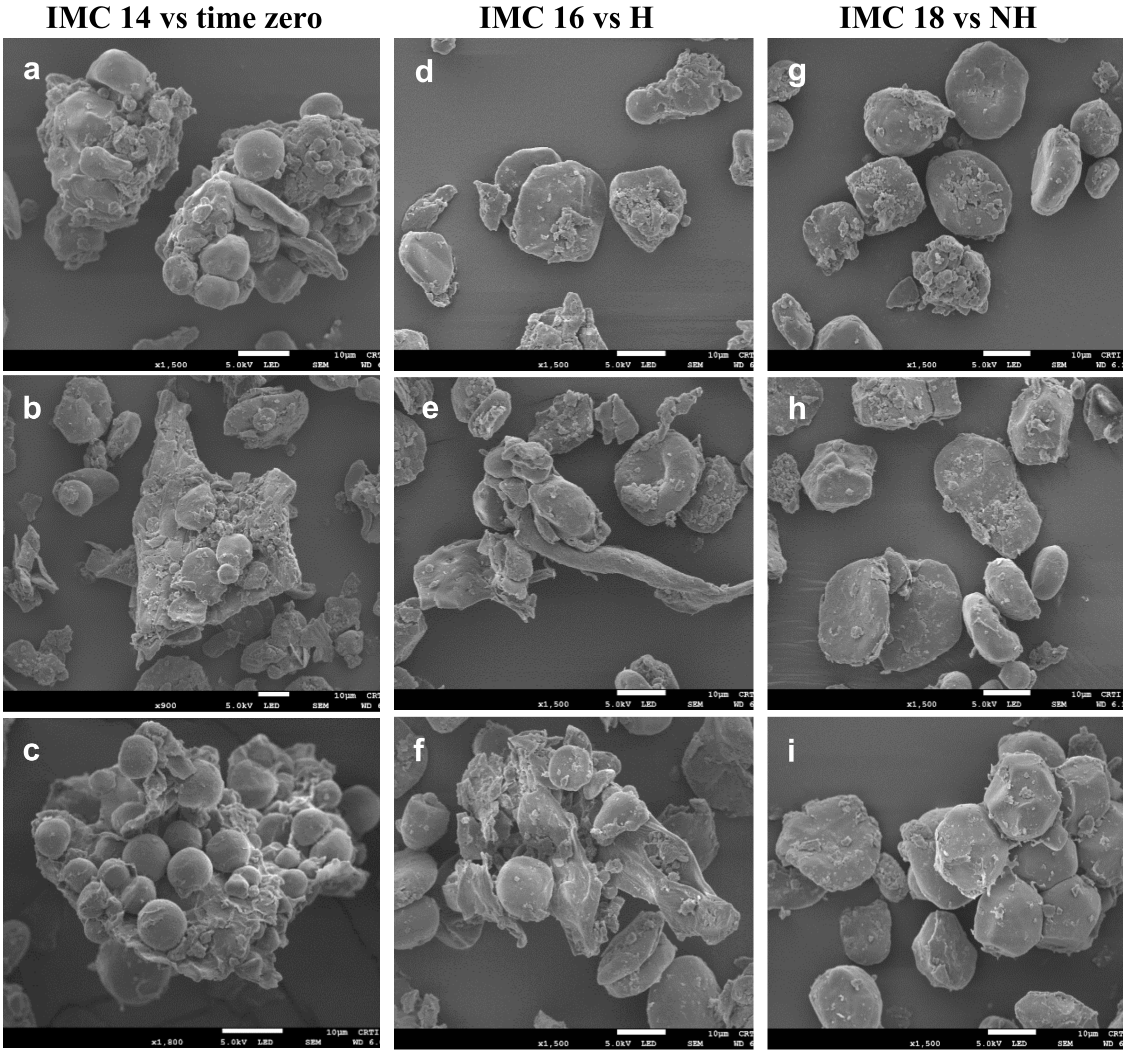


Fig. 6. Scanning electron microscopy of corn grains stored with initial moisture contents of 14 (time zero: a, b, c), 16 (120 days hermetic: d, e, f) and 18% (120 days non-hermetic: g, h, i) at the beginning and after 120 days of storage

Generally, as highlighted in several previous studies, adopting hermetic storage systems and incorporating CO_2 sensors for grain quality monitoring are essential tools that enable grain storage unit managers to make quick and well-informed decisions. These tools help identify the most effective measures to ensure grain quality, considering, for example, the temporary or long-term use of bag silos, depending on the initial moisture content of the corn grains.

Due to its practicality and the possibility of using various types of materials and dimensions (Baributsa and Ignacio, 2020), adoption of hermetic storage becomes widespread, especially in the context of small-scale farmers, where implementing more robust storage structures is often a challenge. This system helps reduce post-harvest losses while maintaining costs compatible with the reality of these farmers, as long as corn grains are stored dry, with a moisture content not exceeding 14% wb (Mabasso et al., 2024; Dijkink et al., 2022). Hermetic storage systems also offer an effective alternative to pesticides, preserving grain quality by minimizing insect damage and enhancing its overall value, with environmental benefits (Dijkink et al., 2022).

4.4 Conclusion

The values of CO_2 concentration, temperature, and relative humidity increased with the increase in the storage time and initial moisture content, with greater values for temperature and relative humidity for grains stored non-hermetically.

Hermetic packaging proved to be more effective in controlling insects, a crucial factor in limiting metabolic activity. Thus, it represents a viable alternative for small-scale farmers, who often lack the resources to adopt more robust storage systems, such as vertical silos, mainly in regions of high postharvest losses.

The DML and EC increased with increasing IMC and ST under both conditions, with higher values under NH. The ether extract and protein contents were the proximal composition variables most influenced by the combination of IMC, SC and ST, with values decreasing as the IMC and ST increased. The sizes of the starch granules were generally similar and within the range that characterizes the product and more compact at higher moisture contents.

The monitoring system based on RH and CO_2 concentrations was more effective in detecting metabolic changes in the grain mass, particularly for DML, ID, EC, and GM. Overall, the increase in the concentrations of CO_2, T and RH in the grain mass, associated with longer STs and higher IMCs, has the potential to negatively impact grain quality, especially under NH conditions, so the storage of corn grain with high IMC must be limited.

Authorship contribution statement

Geraldo Acácio Mabasso: conceptualization, data curation, formal analysis, investigation, methodology, project administration, writing-original draft, writing-review and editing. **Osvaldo Resende**: Supervision, conceptualization, funding acquisition, investigation, methodology, project administration, review-original draft. **Diene Gonçalves Souza**, **Valdiney Cambuy Siqueira**: conceptualization, investigation, methodology, review–original draft. **Maria Lúcia Ferreira Simeone**, **Arthur Almeida Rodrigues**, **Adrielle Birges de Almeida**, **Jaqueline Ferreira Vieira Bessa**, **Juliana Aparecida Célia**: investigation, methodology and research.

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Declaration of competing interest

The authors declare that there are no known competing financial interests or personal relationships that may have impacted the work reported in this manuscript.

Data availability

Data will be made available on request.

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SUPPLEMENTARY MATERIAL (CHAPTER II)

Physicochemical properties, structural analysis and CO_2 concentrations of corn grains stored under different conditions

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Table A1. Summary of analysis of variance for loss of matter (DML, %), proximal composition and insect damage (ID, %), electrical conductivity (EC, μS cm^{-1} g^{-1}), and germination (GM, %) of corn grains stored under different conditions and initial moisture contents

VS	ID	DML	Protein	Mineral	CF	EE	CHO	Starch	EC	GM
SC	718.33**	13.32**	99.53**	1.57ns	369.70**	136.48**	382.49**	209.7**	1862.66**	843.60**
IMC	19.06**	250.90**	25.68**	3.49*	11.44**	132.89**	28.33**	21.81**	1035.62**	1787.83**
ST	173.20**	450.29**	105.87**	26.32**	132.65**	108.83**	75.52**	256.23**	1180.17**	1478.46**
SC × IMC	10.34**	10.86**	81.76**	1.60ns	62.02**	58.14**	9.33**	4.01*	457.14**	361.99**
SC × ST	160.37**	13.44**	107.53**	2.60*	47.07**	17.88**	29.19**	13.54**	245.45**	335.38**
IMC × ST	5.10**	24.39**	24.93**	2.27*	8.62**	17.67**	10.10**	10.29**	86.42**	178.55**
SC × IMC × ST	5.47**	7.42**	10.92**	3.91**	17.30**	18.24**	9.35**	5.73**	61.77**	47.39**
CV (%)	43.32	12.79	0.91	3.96	7.62	1.85	0.26	1.03	2.50	4.64

VS: Source of variation; SC: Storage conditions (H, NH); IMC: Initial moisture content (%, wb); ST: Storage time (days); CV: Coefficient of variation (%); CF: Crude fiber content (g 100 g^{-1} dm); EE: Ether extract content (g 100 g^{-1} dm); CHO: Carbohydrate content (g 100 g^{-1} dm). * and **: Significant at $p<0.05$ and $p<0.01$ by F-test; ns: Not significant.

Table A2. Mean values of dry matter loss, germination, and electrical conductivity of corn grains stored under hermetic and non-hermetic conditions with different moisture contents

		Dry matter loss (%)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	0a	0a	0.98b	1.32a	1.51a	1.37a	1.18b	1.73a	1.89b	3.68a
	16	0a	0a	0.71a	0.47a	1.35a	1.50a	0.92a	1.02a	1.64b	2.38a
	14	0a	0a	0.18a	0.49a	0.82a	0.66a	0.21b	0.61a	0.68a	0.85a
		Electrical conductivity (μS cm^{-1} g^{-1})									
IMC	18	17.05a	17.05a	27.13b	31.91a	22.21b	56.08a	30.94b	73.09a	33.50b	85.31a
	16	16.30a	16.30a	26.46b	30.22a	20.47b	40.17a	28.84b	53.13a	32.17b	53.71a
	14	16.66a	16.66a	20.17a	19.89a	19.73a	20.35a	26.16a	26.18a	25.56b	30.70a
		Germination (%)									
	18	99.33a	99.33a	94.17a	44.00b	88.17a	10.33b	35.00a	3.17b	0.33a	0.83a
	16	99.50a	99.50a	97.67a	40.33b	94.17a	22.67b	55.33a	26.83b	3.50b	16.50a
	14	98.83a	98.83a	97.00a	97.50a	96.50a	94.83a	89.17a	91.17a	59.50b	86.83a

Pairs of means followed by the same lowercase letter in the row for each storage time and initial moisture content do not differ by the t-test at $p<0.05$.

Table A3. Pearson's correlation analysis for dry matter loss, proximal composition, electrical conductivity, and germination of corn grains as a function of initial moisture content, storage conditions, and storage time

	Protein	Mineral	CF	EE	CHO	Starch	EC	GM	ID
DML	0.194^{ns}	0.177^{ns}	-0.349^{*}	0.7601^{*}	0.425^{*}	0.143^{ns}	0.784^{*}	-0.743^{*}	0.697^{*}
Protein		-0.452*	-0.066^{ns}	-0.186^{ns}	-0.418^{*}	-0.230^{*}	0.246^{*}	-0.078^{ns}	0.289^{*}
Mineral			-0.164^{ns}	0.024^{ns}	0.228^{*}	0.316^{*}	0.140^{ns}	-0.271^{*}	0.004^{ns}
CF				0.508^{*}	-0.770^{*}	-0.702^{*}	-0.583^{*}	0.342^{*}	-0.687^{*}
EE					-0.665^{*}	-0.262^{*}	-0.903^{*}	-0.715^{*}	-0.647^{*}
CHO						0.634^{*}	0.608^{*}	0.456^{*}	0.540^{*}
Starch							0.352^{*}	-0.264^{*}	0.433^{*}
EC								-0.802^{*}	0.779^{*}
GM									-0.479^{*}

*: Significant at $p<0.05$ by t-test; ns: Not significant

Table A4. Mean dry matter, protein, mineral, crude fiber, ether extract, carbohydrate and starch contents of stored corn grains as a function of initial moisture content, storage conditions and storage time

		Protein content (g 100 g^{-1} dm)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
	18	11.91a	11.91a	12.12a	11.11b	12.32a	12.18a	12.16b	12.54a	11.81b	12.65a
	16	12.01a	12.01a	11.94a	10.96a	11.95b	12.22a	12.11b	12.30a	12.32b	12.53a
	14	12.69a	12.69a	12.62a	11.07b	12.54a	11.96a	12.53a	11.56b	12.40a	11.92b
		Mineral content (g 100 g^{-1} dm)									
	18	1.71a	1.71a	1.86b	1.98a	1.73b	1.99a	1.77a	1.74a	1.94a	1.80b
	16	1.78a	1.78a	1.91b	2.09a	1.79a	1.81a	1.86a	1.85a	1.89a	1.87a
	14	1.64a	1.64a	1.96a	1.90a	1.85a	1.80a	1.90a	1.79a	1.81b	1.93a
		Crude fiber content (g 100 g^{-1} dm)									
	18	1.66a	1.66a	1.67a	1.33b	1.79a	1.47b	2.13a	1.84b	1.74a	0.28a
	16	1.59a	1.59a	1.19a	0.95b	2.00a	1.36b	1.98a	1.18b	1.49a	0.60b
	14	1.47a	1.47a	1.02a	0.04a	1.88a	1.56b	1.67a	0.36b	0.83a	0.99a
IMC		Ether extract (g 100 g^{-1} dm)									
	18	5.18a	5.18a	5.00a	4.88a	4.83a	4.51b	4.82a	3.88b	4.93a	3.77b
	16	5.21a	5.21a	5.02a	4.93a	4.93a	4.64b	4.91a	4.73b	4.85a	4.72a
	14	5.37a	5.37a	4.94a	4.96a	5.17a	4.92b	4.98a	4.94a	4.98b	5.14a
		Carbohydrate content (g 100 g^{-1} dm)									
	18	79.53a	79.53a	79.36b	80.69a	79.32b	79.55a	79.13b	81.00a	79.58b	81.50a
	16	79.40a	79.40a	79.93b	81.08a	79.33b	79.98a	79.15b	79.94a	79.44b	80.27a
	14	78.81a	78.81a	79.47b	81.03a	78.55b	79.76a	78.93b	80.06a	79.99a	80.02a
		Starch content (g 100 g^{-1} dm)									
	18	77.05a	77.05a	79.36a	80.54a	74.55a	75.11a	78.39b	81.58a	78.38b	82.51a
	16	77.19a	77.19a	79.42b	83.80a	72.14b	75.68a	79.70b	81.98a	78.93b	83.47a
	14	76.43a	76.43a	79.47b	82.43a	72.47b	78.92a	79.62b	83.42a	84.37a	84.68a

Pairs of means followed by the same lowercase letter in the row for each storage time and initial moisture content do not differ according to the t-test at $p<0.05$.

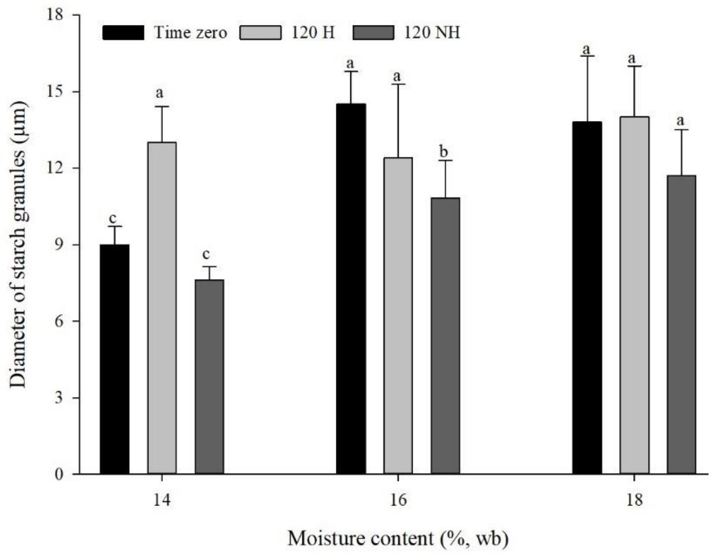

Fig. A1. Mean starch granule diameter values as a function of the initial moisture content and, storage conditions. Pairs of means followed by the same letter do not differ according to the Scott Knott test at $p<0.05$.

5 CHAPTER III

CONCENTRATION OF CO_2 IN HERMETIC AND NON-HERMETIC STORAGE AND EFFECT ON INCIDENCE OF INSECT, FUNGI AND OIL QUALITY OF CORN GRAIN WITH DIFFERENT MOISTURE CONTENTS

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Abstract
This study aimed to evaluate the dynamics of CO_2, temperature, and relative humidity in stored corn grains, as well as the quality of the grains and oil extracted over time. BRS284 corn grains were harvested and stored at moisture contents of 18, 16, and 14% wb, in both hermetic (GrainPro SuperGrainBag®) and non-hermetic (experimental silos) storage conditions. Quality was assessed at 0, 30, 60, 90, and 120 days using a 2 × 3 × 5 factorial layout with three replications, which correspond to storage conditions, initial moisture content and storage time, respectively. [CO_2], temperature, relative humidity, water activity, equilibrium moisture content, incidence of fungi and insect damage loss, ether extract content, acidity, peroxide and iodine indices, and fatty acid profiles were measured. Results showed that temperature, relative humidity, and [CO_2] increased with higher initial moisture content, with non-hermetic storage showing higher temperature (mean of 29.33±2.96 ºC) and relative humidity (mean of 89.99±1.39), while hermetic storage exhibited higher [CO_2] with 320×10^3 and 9435.34 ppm as maximum value for hermetic and non-hermetic storage, respectively. Grain quality and oil extraction were negatively affected by higher initial moisture contents (18 and 16% wb), particularly in non-hermetic storage (3.68 and 4.61 g $100g^{-1}$ dm of ether extract content), with more significant deterioration by 60 days. The fatty acid profile showed minor changes, with corn oil stability prevailing, and unsaturated-to-saturated fatty acid ratios ranging from 5.67 to 6.17.

Keywords: *Zea mays* L. *Aspergillus flavus*. Oil stability. *Sitophilus zeamais*. Respiration rate. Grain deterioration

Practical Application: This research highlights CO_2 monitoring as a valuable and complementary technique to thermometry for stored grain. It proves useful in the early detection of grain deterioration within corn storage units and reinforces the effectiveness of hermetic storage methods, for both temporary and long-term storage.

5.1 Introduction

The rise in CO_2 levels within stored grains mass, particularly in conventional systems lacking a physical barrier that restricts gas exchange and water permeability, is typically associated with the presence of insects, fungi, or excessive respiration in the grain. Therefore, monitoring CO_2 evolution serves as a reliable indicator of deterioration, enabling timely corrective actions to be taken (Neethirajan et al., 2010; Mabasso et al., 2024; Souza et al., 2024). According to Magan et al. (2020), temperature fluctuations often reflect changes in CO_2 concentrations, which are easier to detect since grain has low thermal conductivity, making it an effective insulator.

An effective grain storage system must ensure the preservation of product integrity while minimizing quality loss (Baributsa and Ignacio, 2020). Systems of grain storage, such as bag silos with a capacity of 200 tons, have been adopted as a way of dealing with low storage capacity, as an economically and technically viable solution (El-Kholy and Kamel, 2021; Valle et al., 2021). Hermetic storage systems are potentially aimed at containing the rate of respiration, when compared to conventional systems under the same conditions, thus contributing to a lower rate of deterioration during storage (Odjo et al., 2022).

The key challenge for safe storage in South America and Africa is reducing grain losses, particularly due to limited static capacity in relation to the volume of production (Nishmwe et al., 2020; Kamel et al., 2024). For hermetic storage, 5% of CO_2 in wheat grains with a moisture content of 13% wb is considered an initial sign of deterioration, whereas 10% represents intense biological activity. In non-hermetic storage, values from 600 to 1,500 ppm have been reported as indicative of fungal growth (Kaushik and Singhal, 2018).

Storage conditions are considered crucial in the metabolic activity and also define the start of the deterioration process as a function of the initial condition of the stored product. According to Zanon et al. (2022) corn grains can be harvested already pre-infested with aflatoxins, as a result of infestation by *Aspergillus flavus* while still in the field, with intensification during storage. Species of the genus *Fusarium* are dominant only under conditions of high levels of water activity (Mohapatra et al., 2017).

Storage conditions can significantly impact the quality of oil produced from corn grains. Ziegler et al. (2017) found that the acidity index of rice grain oil increased after six months of storage, primarily due to rising temperatures during storage. The oil content typically ranges from 3 to 5% of the grain's mass (Barrera-Arellano et al., 2019). Corn oil is composed of the common fatty acids with other oils, relatively stable due to its high content of antioxidant and phenolic compounds, and it has a low level of linolenic acid, which is more prone to oxidation (Barrera-Arellano et al., 2019; Wang and White, 2019).

The quality of corn oil is assessed using several parameters that help determine the efficiency of the refining process and its optimal application, whether for food or non-food purposes. Key indicators include free fatty acid content, peroxide value, iodine value, color, and others (Barrera-Arellano et al., 2019). Recently, a lot of research has been dedicated to investigating the behavior of CO_2 in the grain mass, given its relevance as a useful and complementary tool for managing stored grains, especially corn. However, issues concerning the correlation between CO_2 concentrations and quantitative and qualitative losses, especially the incidence of insects, fungi and oil quality, are still lacking mainly for corn oil (Ziegler et al., 2017; Barrera-Arellano et al., 2019; Valle et al., 2021; Bilhalva et al., 2023; Erasto et al., 2023; Lutz and Coradi, 2023; Kamel et al., 2024).

In this context, the aim of this study was to evaluate the application of a CO_2 sensor as a useful and practical tool for assessing the condition of grain mass in connection with temperature and relative humidity measurements, as well as the advantages of hermetic storage compared to non-hermetic storage. Additionally, this study was conducted to evaluate different grain quality parameters, such as water activity, fungal and insect damage, oil content, acidity, peroxide and iodine indices, and fatty acid profiles, for different initial moisture contents, conditions, and storage times.

5.2 Material and methods

The experiment was carried out in a completely randomized design, factorial layout 2 × 3 × 5, with three replications, which 2 corresponds to storage conditions (hermetic non-hermetic storage), 3 to initial moisture contents (14, 16 and 18%, wet basis

- wb) and 5 to storage times (0, 30, 60, 90 and 120 days). The experiment was conducted between the months of July and November 2023.

The corn grains, cultivar BRS284, were harvested on a farm in the municipality of Rio Verde - Goiás, Brazil (17° 48' 16.73" S; 50° 54' 23.96" W, mean altitude of 748 m), with an initial moisture content of 18.00±0.05% wb. Two-thirds of the total amount was then subjected to drying using natural ventilation with solar energy in a surface with plastic tarpaulin at a temperature of 24.0±2.73 ºC and a relative humidity of 41.49±7.08% for approximately 24 to 72 hours, until the pre-established initial moisture contents (IMC) of 16 and 14% wb were reached. The lots were divided to achieve the target moisture contents using a Gehaka Boerner homogenizer. To determine the moisture content, the corn samples were placed in a forced-air circulation oven (oven method) set at 103±1 ºC for 72 hours (ASABE, 2003).

Hermetic storage (H) was carried out using low-density multilayer hermetic packaging GrainPro, Super Grain Bag® (Fig. S1a), low-density hermetic packaging, with two polyethylene films, between which a plastic layer highly impermeable to oxygen is pressed, with a thickness of 78 ± 2 µm, with a barrier to gas exchange, water absorption and the entry of insects, with a seal-type closure. To ensure hermetic conditions were maintained, four 30 kg packages were used for each IMC, which were only opened during the 30-, 60-, 90- and 120-day storage times, for evaluation. During storage, the temperature (T), relative humidity (RH) and [CO_2] in the grain mass and in the external environment were monitored using CO_2 sensors. CM-0025 K33 BLG 30% + RH/T sensors (bio-logger, Gaslab 2.1®) were used in the hermetic packages, based on non-dispersive infrared (NDIR) technology (Ramachandran, 2022), measurement range of 30±2% of [CO_2]. The sensors were calibrated in agreement with the manufacturer and measurements were taken at one-hour intervals throughout the evaluation period (Bilhalva et al., 2023; Mabasso et al., 2024; Souza et al., 2024).

For the non-hermetic storage (NH), the grains were stored in prototype silos made from metal plates, with a grain volume capacity of 0.108 m^3 (0.60 × 0.60 × 0.30 m) (Fig. S1b). [CO_2], T and RH were monitored using Extech Instruments sensors, model CO210 Datalogger 3.0®, capable of recording [CO_2] in the range of 0 to 10000 ppm. This sensor was also used to measure T, RH and [CO_2] in the environment outside the grains mass. The data were then downloaded using the Extech CO210 Datalogger 3.0® software.

5.2.1 Water activity and equilibrium moisture content

Water activity was determined using the Hygropalm AW1, Rotronic model HP23-AW-A. Three measurements were taken, corresponding to the number of repetitions defined. The values were then used to determine the equilibrium moisture content, according to the modified Henderson model (Eq. 1) (Coradi et al., 2022).

$$EMC = \frac{1}{100} \times \left[\frac{\ln(1 - a_w)}{-A \times (T + B)}\right]^{\frac{1}{C}} \quad (1)$$

where EMC is the equilibrium moisture content (kg kg^{-1}, bs), a_w is the water activity, T is the temperature (ºC) and A, B, C are the model constants ($A=8.6541\times10^{-5}$; B=49.810 e C=1.8634).

5.2.2 Insect damage loss

The insect damage loss (IDL) was determined according to the methodology of Brasil (2009). Each set of two samples per repetition, with one hundred grains, was evaluated to identify the presence of eggs, larvae, pupae and/or adult insects, in two stages. The grains that appeared healthy were immersed in distilled water for 24 hours at ambient temperature in order to soften them and allow them to be cut to identify the different phenological stages of the insect (*Sitophilus zeamais*) using a stereoscopic magnifier (Feldmann Wild Leitz), model FWL - SMZ 7.5, with magnification from 0.8 to 5X by 10X/22.

5.2.3 Incidence of fungi

Fungal incidence was assessed using the blotter test method (Brasil, 2009) with modification (Lutz and Coradi, 2023), detecting Curvularia spp., Fusarium spp., Aspergillus flavus and Aspergillus niger (Erasto et al., 2023; Lutz and Coradi, 2023). Five samples of 20 grains per repetition were placed in germination boxes on moistened filter paper (100 grains per treatment). The boxes were incubated at 25±2 ºC with a 12-hour photoperiod. After seven days, grains were examined under a Feldmann Wild Leitz stereoscopic, to identify typical fungal growth structures (Brasil, 2009; Erasto et al., 2023).

5.2.4 Oil quality

The oil content (ether extract) was determined using the indirect method of Near Infrared Reflectance (NIR) spectroscopy using a BUCHI NIRFlex 500 device (Buchi Labortechnik, Flawil, Switzerland). To assess the quality of the oil, it was extracted using the Soxhlet method (Químis Q-328G26, Diadema, SP, Brazil), AOAC 920.39 (AOAC, 2019). Initially, the corn grains were ground in a Tecnal TE-650/1 willye-type knife mill with a 1 mm diameter sieve. Then, about 25 g of the crushed grains wrapped in filter paper were inserted into the extractor connected to a flat-bottomed flask, after adding about 400 mL of hexane (density of 0.675 g mL^{-1}). The extraction process was carried out for 8 hours, using a rotary evaporator, and the residue was taken to a forced circulation oven for 2 hours at 80 ºC. After extraction, the acidity index (AI, mg NaOH g^{-1}), peroxide index (PI, mg NaOH g^{-1}) and iodine index (II, g I_2 100 g^{-1}) were determined. The AI and PI were determined following the methodology of IAL (2008) with modifications, according to Eq. 2 (AI) and Eq. 3 (PI). The iodine index (II) was determined following the Hanus solution methodology according to Eq. 4 (Yildiz et al., 2019).

$$\mathrm{AI} = (\mathrm{V} \times \mathrm{f} \times 5.61)/\mathrm{m} \tag{2}$$

$$\mathrm{PI} = (\mathrm{V}_B - \mathrm{V}_S) \times \mathrm{f} \times 1000)/\mathrm{m} \tag{3}$$

$$\mathrm{II} = [(\mathrm{V}_B - \mathrm{V}_S) \times \mathrm{N} \times \mathrm{f} \times 12.69]/\mathrm{m} \tag{4}$$

where V is the volume of NaOH 0.1 M spends for titration (mL); f is the titrating solution correction factor (0.861 for AI, and 0.965 for PI and II), m is the oil mass sample (g), V_B, V_S are the volume of sodium thiosulfate solution 0.1 N in the titration of sample and blank (mL).

5.2.5 Fatty acid profile

The fatty acid profile was determined at the Biochemistry and Instrumental Analysis Laboratory of the Food Science Department, Escola Superior de Agricultura Luiz de Queiroz (ESALQ). The evaluation was carried out on samples of oil previously extracted using the Soxhlet method (Químis Q-328G26, Diadema, SP, Brazil), AOAC 920.39 (AOAC, 2019), mentioned above, considering two periods (initial and after 120 days of storage). Each sample was previously methylated according to the method of Hartman and Lago (1973), with adaptations based on the AOCS Ce 1b-89 method (2003).

The fatty acids were determined using a chromatograph (GC-2010 Plus, Shimadzu Co.), equipped with a SUPELCO 256 column (100 m × 0.25 mm × 0.2 µm), coupled to a flame ionization detector (FID). The temperature programming was 130 ºC (1.0 min) to 170 ºC (6.5 ºC min^{-1}), 170 ºC to 215 ºC (2.8 ºC min^{-1}), 215 ºC (15 min), 215 ºC to 230 ºC (40 ºC min^{-1}), 230 ºC (6 min). The injector and detector temperatures were 270 ºC and 280 ºC, respectively. Hydrogen was used as the carrier gas at a flow rate of 1.0 mL min^{-1}. Fatty acids of 6, 8, 10, 12, 14, 15, 16, 17, 18 (cis and trans), 20, 22 and 24 carbon atoms, saturated and unsaturated, were used as the standard.

5.2.6 Statistical analysis

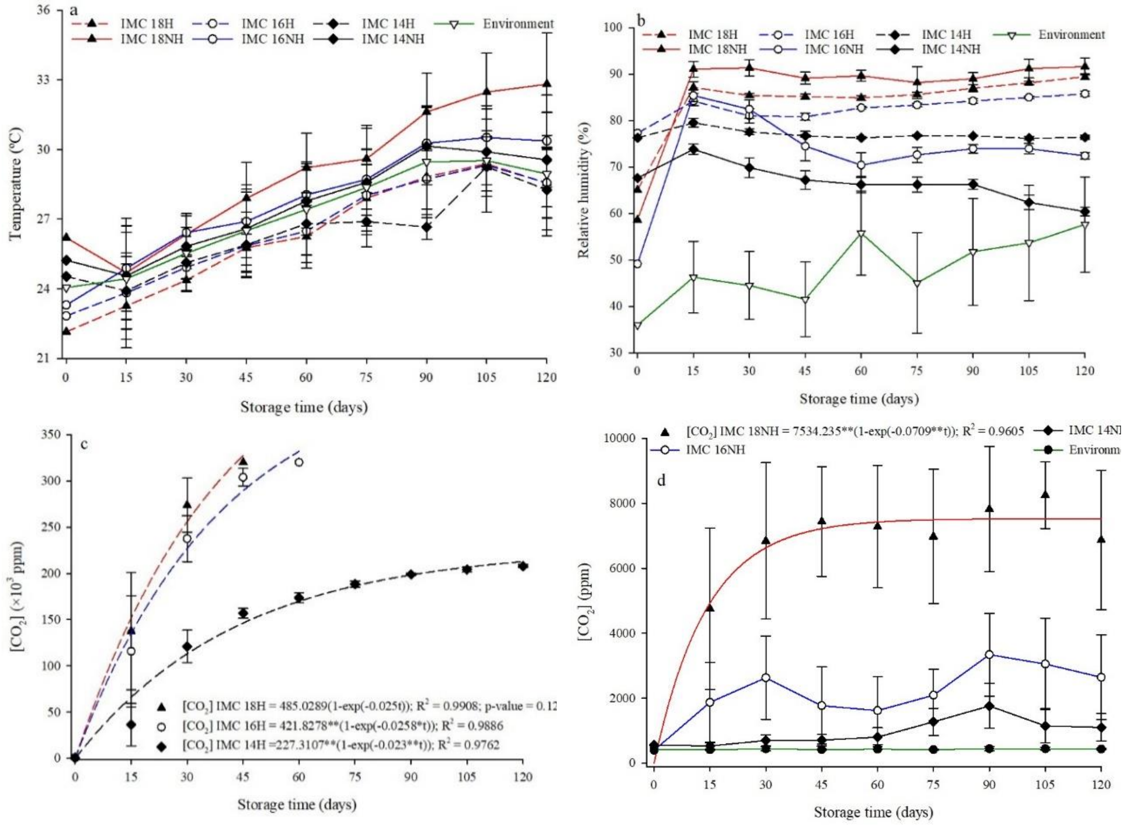
The results were analyzed using means and standard deviations, using a completely randomized design with a 2 × 3 × 5 factorial layout and three repetitions. The treatments were defined based on a combination of storage conditions (H and NH), initial moisture contents (14, 16 and 18% wb) and storage times (0, 30, 60, 90 and 120 days). Data analysis included normality tests, ANOVA, linear regression, and t-tests in RStudio 4.4.2® ($p<0.05$). Regression models were validated by coefficient of determination and coefficient significance. Pearson's correlation and multivariate analysis (PCA and clustering) were also performed.

5.3 Results and discussion

5.3.1. Temperature, relative humidity and CO_2 monitoring

Fig. 1 shows mean temperature (T), relative humidity (RH), and [CO_2] values. Grain temperature increased over time, following environmental trends. In NH, ambient temperature was lower, while the opposite was seen in hermetic storage (Fig. 1a). Higher IMC led to higher temperatures, indicating effects from both factors (SC and IMC). Intergranular RH was consistently higher than ambient air, increasing with IMC. Variations were minimal over time, especially at IMC of 18% wb, reaching around 90%

RH (Fig. 1b). According to Lutz and Coradi (2023), the maintenance or stabilization of RH values in stored grains with higher IMC, combined with higher temperature values, leads to greater respiratory activity in the grain mass and, consequently, a greater risk of deterioration.



* and ** - Significant at $p<0.05$ and $p<0.01$ by t-test; t – storage time

Fig. 1 Mean values of T (a), RH (b) and [CO_2] in hermetic and non-hermetic storage (c, d) recorded during the storage of corn grains in different SC and IMC

The [CO_2] values were higher as the product's IMC increased in both conditions (Fig. 1c-d). In hermetic storage, the values increased exponentially over time for all IMC, and the same was observed in NH only for 18% wb, while IMC of 16 and 14% wb varied, with mean values of 2159.09±886.84 and 954.53±402.93 ppm, respectively. Previous studies have referred [CO_2] above 600 ppm as indicative of early deterioration in NH storage, with 1500–4000 ppm signaling insect and fungal infestation (Aby and Mayer, 2020; Mabasso et al., 2024; Souza et al., 2024). On the other hand, grain mass [CO_2] were consistently higher than the external environment, 429.52±13.59 ppm.

The variation of [CO_2] increased with increasing in the IMC, while external variation remained low due to gas exchange. At IMC of 18% wb, [CO_2] stabilized around

7455.45±119.91 ppm after 60 days, indicating limited but ongoing gas exchange influenced by grain mass conditions. At IMC of 18 and 16% wb, in grains stored hermetically, the maximum [CO_2] (320×10^3 ppm), for the experiment's, was reached in approximately 43 and 55 days, respectively. For IMC of 14% wb, the maximum value reached was 212.92×10^3 ppm, at 120 days of storage.

Lutz and Coradi (2023) state that temperature, as well as the MC of the product, have an impact on the magnitude of the increase in [CO_2]. In their study, they observed a maximum [CO_2] (around 5000 ppm) in 26 days for stored grains with an IMC of 14% and a controlled temperature of 30 ºC. According to Valle et al. (2021), in hermetic storage, metabolic activity is controlled, however, in environments with higher relative humidity or high MC, the presence of some facultative microorganisms can occur, which leads to higher [CO_2], due to a higher respiration rate.

Table S1 shows the ANOVA values for the grains and corn oil quality under different IMC over 120 days. With the exception of *Aspergilus niger* incidence, the other variables were influenced by the combination of SC× IMC×ST. Similar situations, where there was an interaction between the factors studied, were also found by Coradi et al. (2022) and Daba et al. (2024), in a study on assessing grain quality in experimental silo-bags and different packages.

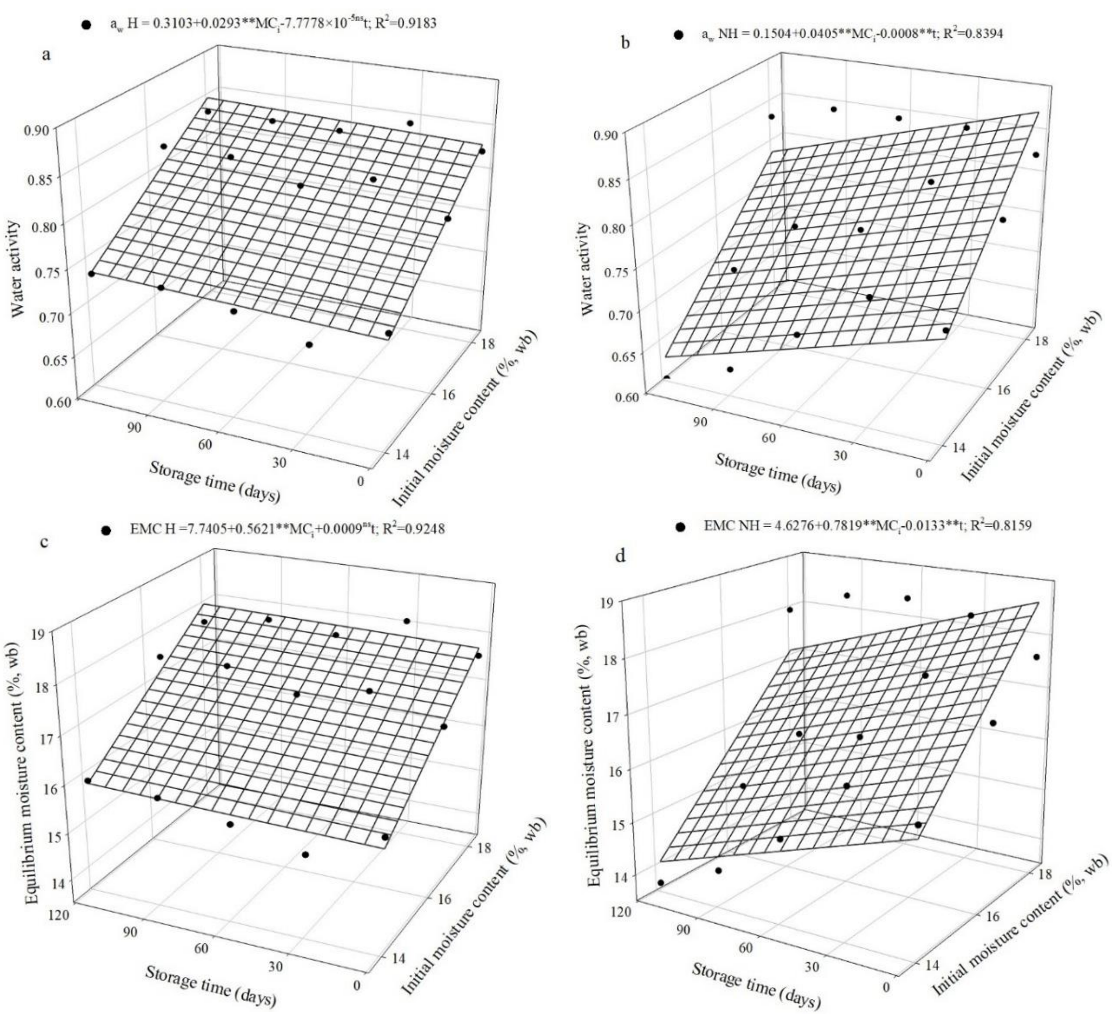
The interaction observed in T, RH, [CO_2] and the IMC has been mentioned in several studies on grain storage, whether in temperature-controlled or non-temperature-controlled environments (Bilhalva et al., 2023; Daba et al., 2024; Mabasso et al., 2024; Souza et al., 2024), with higher rates of respiration in the grain mass being reported as the IMC of the product increased. The relevance of using sensors that combine the measurement of temperature, RH and [CO_2] is also reported in a study carried out by Ramachandran (2022), as an effective tool for monitoring the quality of stored grains, as complementary (Bilhalva et al., 2023; Mabasso et al., 2024; Souza et al., 2024), thus allowing for a better approach to the appropriate management of stored grains.

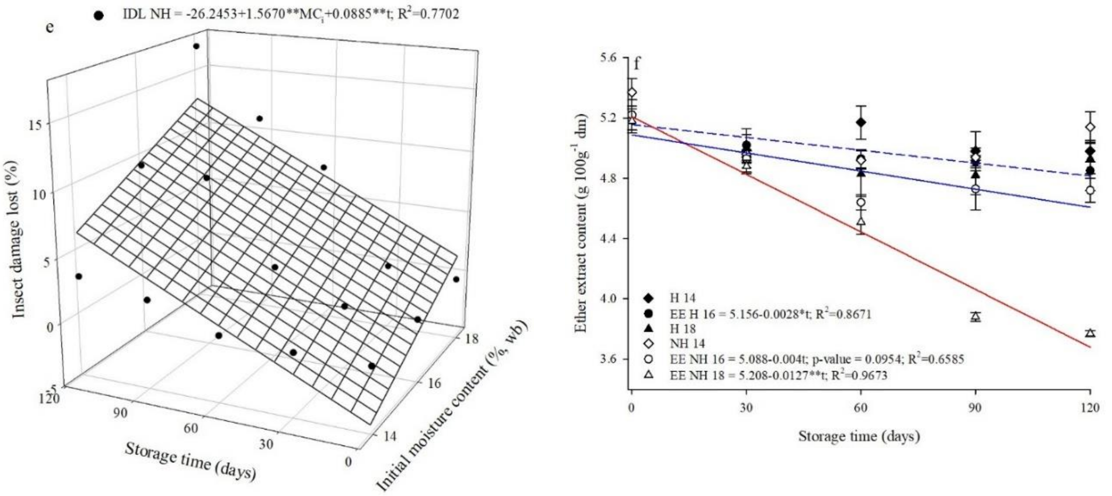
Previous studies reinforce the presence of heating spots in the grain mass as a response to the change in [CO_2] and consequent deterioration of grains, due to its sensitivity when compared to the change in temperature in the grain mass, due to its low thermal conductivity (Valle et al., 2021; Ramachandran, 2022; Bilhalva et al., 2023). The correlation between temperature and [CO_2] has been also reported as weak and positive in some studies (Magan et al., 2020; Leal et al., 2023).

In conventional storage, a continuous oxygen supply sustains metabolic activity. In hermetic systems like SuperGrainBags®, respiration is restricted by oxygen availability and stops once depleted, creating a lethal environment for aerobic organisms (Diarra and Amoah, 2019). This process accelerates in environments with higher grains MC due to facultative microorganisms that develop at aw > 0.85 (Valle et al., 2021).

5.3.2. Water activity and equilibrium moisture content on stored corn grain

Water activity reflects the availability of free water in the grains, making deterioration proportional to MC of the grain and its interaction with dry matter. In this study, a_w in NH storage was significantly affected by both factors (ST and IMC), while in hermetic storage, IMC had a dominant influence over ST (Fig. 2a-b).





* and ** - Significant at $p<0.05$ and $p<0.01$ by t-test; t – storage time; MC_i – initial moisture content

Fig. 2 Mean values of a_w (a, b), EMC (c, d), IDL (e) and EE content (f), as a function of IMC and ST for hermetic and non-hermetic conditions

Hermetic systems help preserve corn quality by reducing metabolic activity, limiting insect and fungal infestations, and slowing the deterioration process (Odjo et al., 2022). Even in hermetic storage, proper grain drying is crucial to prevent fermentative activity in low-oxygen, high-moisture environments, with a $a_w > 0.85$ (Valle et al., 2021; Ngoma et al., 2023).

Similar to a_w, the EMC also followed the same trend, with higher magnitudes recorded for longer ST and IMC (Fig. 2c-d). According to Bilhalva et al. (2023), the EMC serves as an indication of respiratory activity in the grain mass, and is also associated with an increase in the [CO_2] generated in the granular mass, by the conversion of organic matter present into CO_2, as well as other by-products of aerobic respiration.

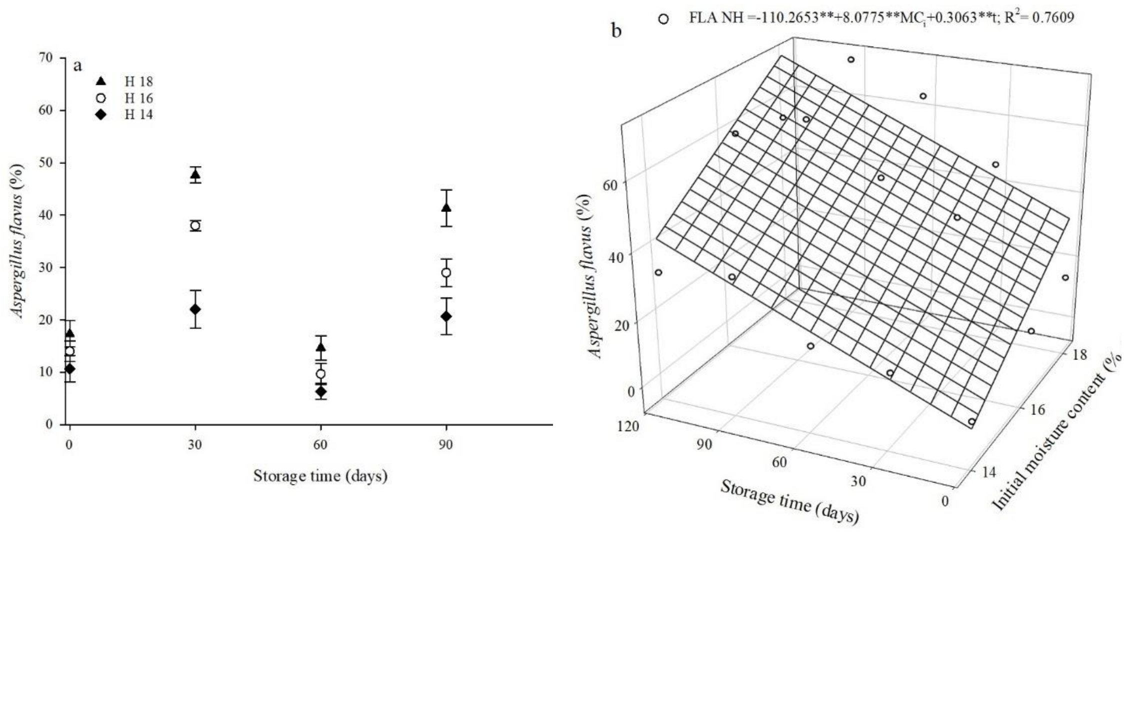
There is a close relationship between T, RH, [CO_2], a_w, and EMC, which can negatively affect grains with higher MC. In such conditions, RH stabilizes at levels favorable to microbiological activity ($a_w > 0.85$) (Valle et al., 2021), leading to higher [CO_2], especially in NH, where limited air renewal amplifies the effect. During storage, a_w and EMC values were lower at 14% wb and higher at 18% wb, remaining similar for both SC (Table S2). For IMC of 16 and 14% wb, NH showed lower values due to water loss in the grain mass, especially toward the end of storage, correlating with reduced RH (Fig. 1b).

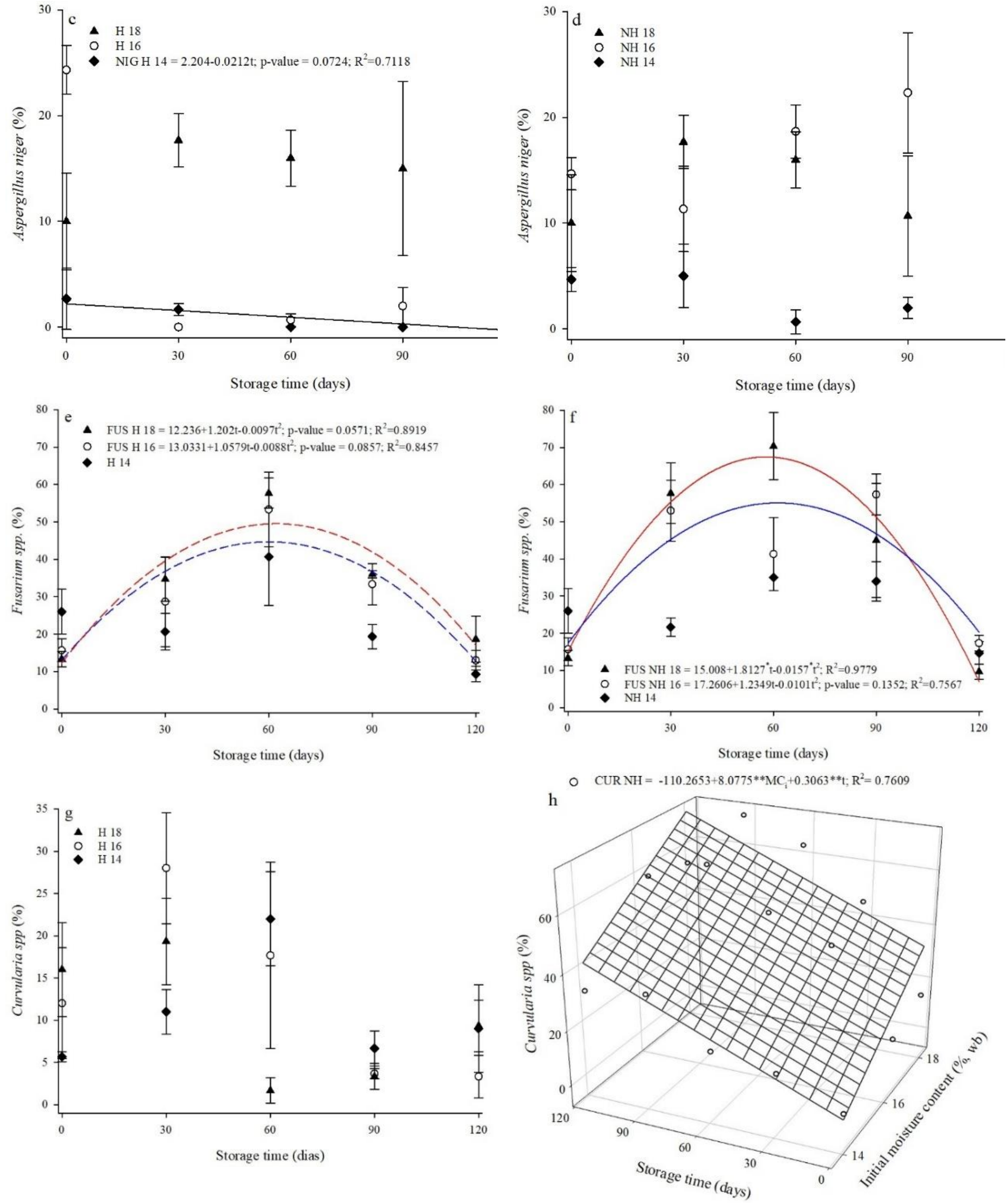
5.3.3. Insect damage loss and incidence of fungi on quality of stored corn grain

Fig. 2e shows that IDL in NH was linked to various stages of insect development and grain damage, while no IDL was observed in hermetic storage. A similar finding was reported by Mabasso et al. (2024), where no insect damage was recorded in an experiment carried out under the same conditions. Kiobia et al. (2020), evaluating different packaging for stored corn grains, also found an absence of live insects in corn grains stored in an hermetic condition, using GrainPro® packaging. The level of IDL increased with the increase in ST and IMC, with the highest rate for the IMC (1.57%). The data presented is also consistent with the increase in [CO_2], T and RH, since the increase in IDL is associated with intensified biological activity.

The mean EE values were generally lower for higher IMC and decreased over time, especially at IMC of 18 and 16% wb in NH (Fig. 2f). Relative values of EE were mostly higher for hermetic storage in all IMC. This behavior was also noted by Daba et al. (2024), with a greater magnitude for the IMC of 15% wb in relation to the MC of 12% wb.

The mean values for fungal incidence were generally higher for the NH condition and the higher MC (Fig. 3). For the *Aspergillus flavus* species, no trend was observed for ST, with the IMC factor prevailing as a conditioning factor for the behavior pattern (Fig. 3a). For NH, the incidence was positively influenced by both factors, with IMC being the most important in the variation, with a rate of 8.08%, while for ST, the rate was 0.31% (Fig. 3b).





* and ** - Significant at $p<0.05$ and $p<0.01$ by t-test; t – storage time; MC_i – initial moisture content

Fig. 3 Mean values of the incidence of *Aspergillus flavus* (a, b), *Aspergillus niger* (c, d), *Fusarium spp*. (e, f) and *Curvularia spp*. (g, h) in corn grains stored at different IMC and under hermetic and non-hermetic conditions

Aspergillus niger (Fig. 3c-d) was equally influenced by the two factors (IMC and ST), with a reduction for the IMC of 14% wb in grains stored hermetically. In the NH, no trends were observed, but higher values were observed as IMC increased. The incidence of *Fusarium spp.* were similar for the both conditions at IMC of 18 and 16% wb, with maximum values of 49.25% (66.78 days) and 44.83% (60.11 days) for hermetic and 67.33% (57.73 days) and 55.01% (61.13 days) for NH at IMC of 18 and 16% wb, respectively (Fig. e-f). As for the MC of 14% wb, the average for the hermetic was 23.20±11.47 and 26.27±8.54% for the NH.

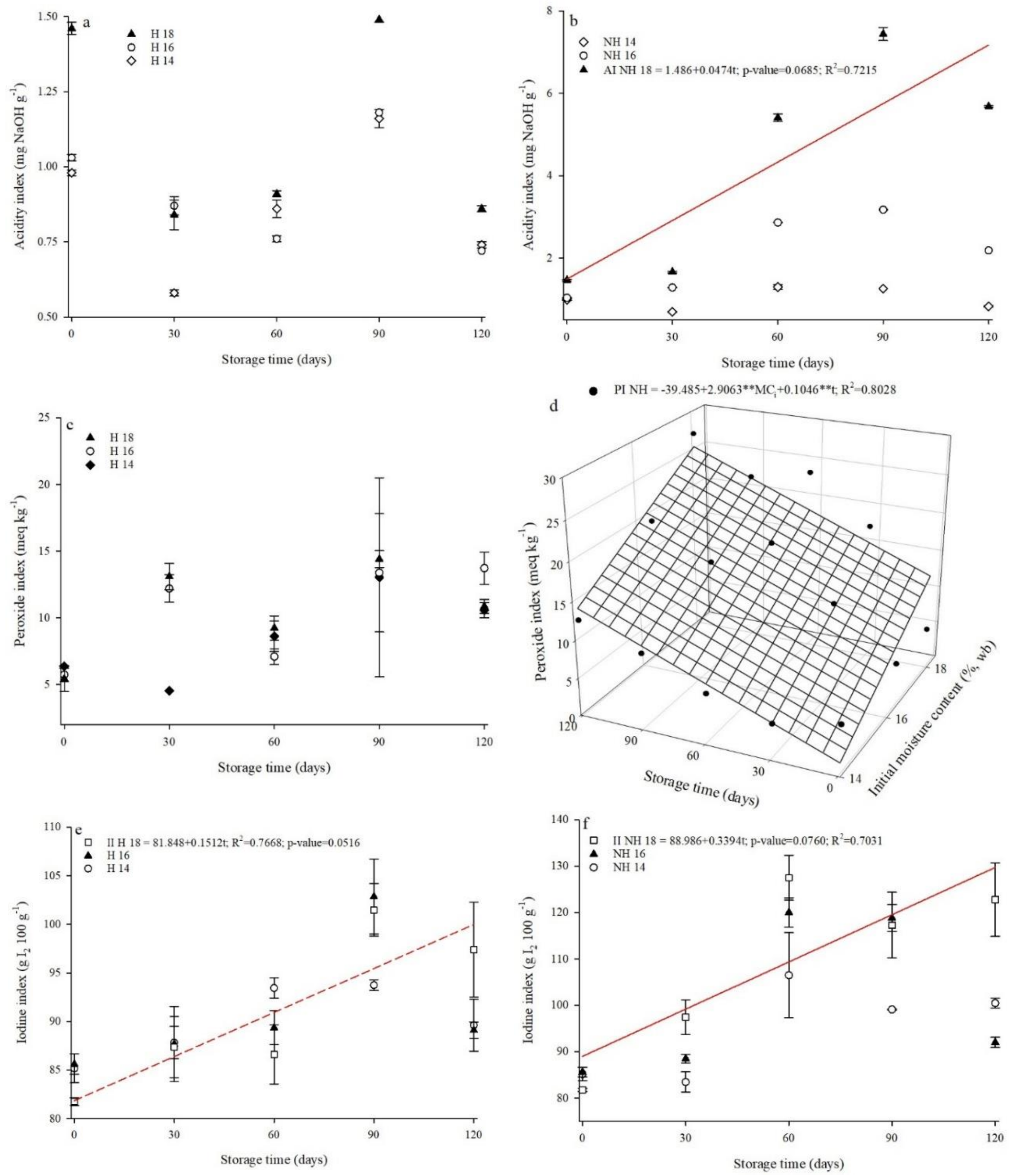
For *Curvalaria spp.* the values followed a random trend over the ST (Fig. 3g-h) for grains stored hermetically. For NH, the values increased with increasing ST and IMC of the product, and were higher than those observed in the hermetic. In overall terms, it can be seen that, in most situations, the levels of fungi were higher for the NH, regardless of the IMC, but for the IMC of 14% wb, there was less difference between the both SC (Table S3). However, the *Aspergillus flavus*, *Curvularia spp*. and *Fusarium spp*. were the species with the highest incidence, and therefore of greatest importance. Globally, the fungal incidence and insect damage correspond to the magnitude of a_w, high [CO_2], T and RH. Values of $a_w > 0.85$ were mainly observed for IMC of 16 and 18% for most fungal species, representing greater microbial growth for both SC.

The highest values of fungi could be found in packaging with a thinner lower layer, which has a lower capacity to contain gas exchange. Therefore, the effectiveness of hermetic conditions depends on the ability of the packaging to promote a carbon dioxide-rich and oxygen-poor environment, which is lethal to aerobic organisms (Ali et al., 2024).

According to Schmidt et al. (2018), if the conditions for the development of fungi are favorable during storage, the spread of an outbreak of infestation, even in small proportions, occurs quickly, and the genus *Aspergillus* is among the most frequent and, can develop in conditions of high [CO_2], above 80%, provided that at least 4% oxygen is present, since, modified atmosphere technology alters SC, improving food preservation, but does not eliminate existing fungi.

5.3.4. Oil quality during the storage of corn grain

The AI values from grains stored hermetically showed an increasing trend in relation to the increase in IMC (Fig. 4a). In NH, the trend was similar for the IMC of 16 and 14% wb, with an increase for the IMC of 18% wb, over time (Fig. 4b). Similar trend was recorded by Bilhalva et al. (2023), with 7.97 mg NaOH g^{-1} being the maximum value obtained. Odjo et al. (2022) also observed an increase in AI to grains stored non-hermetically over time, causing the product to undergo an oxidation process, compared to hermetic storage in which values were random during storage.



* and ** - Significant at $p<0.05$ and $p<0.01$ by t-test; t – storage time; MC_i – initial moisture content

Fig. 4 Mean values of AI (a, b), PI (c, d), II (e, f) in corn grains stored with different IMC in hermetic and non-hermetic conditions

In relation to the data presented in Table S4, it was also found that for NH storage the values were always higher than the hermetic condition in most of the product's storage periods, with less variation for the IMC of 14% wb, where there was only a difference at 60 days of storage.

The PI of corn oil followed a similar trend to AI in hermetic storage, with the highest values at IMC of 18% wb (Fig. 4c). In NH, PI increased with both ST and IMC (Fig. 4d), remaining higher than in hermetic storage, except for IMC of 14% wb at 90 days (Table S4). PI is an indicator of the primary phase of lipid oxidation, in which lipid radicals are oxidized by oxygen to formulate lipid hydroperoxides (Winkler-Moser and Breyer, 2011). And the oxidative stability of oils is affected by many factors, including the composition of fatty acids, the concentration and stability of antioxidants in the oil, so higher PI values are indicative of a more degraded product, and greater demand in refining processes (Winkler-Moser and Breyer, 2011; Barrera-Arellano et al., 2019).

The trend observed for loss of quality or increase in AI and PI values in relation to IMC was also observed in studies carried out by Zheng et al. (2018), in which, evaluating the effect of MC and heat treatment of corn germ, they recorded an increase in values in relation to MC of 15 and 25% wb, ranging from 3.53±0.6 to 4.01±0.23 mg KOH g^{-1} and 0.72±0.05 to 1.05±0.10 meq kg^{-1}, for AI and PI, respectively. Increased lipid acidity is linked to greater grain deterioration (Bilhalva et al., 2023).

The II values were higher for IMC of 16% wb compared to 14% wb in both SC. At IMC of 18% wb, II increased with ST, with the highest rate for NH (0.3394) and a lower rate for hermetic storage (0.1512 g I_2 100 g^{-1} oil per day) from 0 to 120 days (Fig. 4e-f). Overall, NH consistently showed equal or higher values than hermetic storage (Table S4).

5.3.5. Correlation matrix of quality parameters

Fig. 5 presents the correlation matrix between grain quality variables and oil extracted from grains stored at different IMC, ST, and SC. IDL, EE, and CUR showed the strongest correlations. EE, which indicates oil extracted, had a strong negative correlation with IDL, as the corn germ, where insects feed, is also where the lipid fraction is concentrated (Bakhtavar et al., 2019). IDL showed a positive correlation with FLA and CUR, but weak correlations with NIG and FUS. Mabasso et al. (2024) observed similar results, noting increased weevil-damaged and mold damage grains under similar conditions of this study ($r=0.632$; $p<0.05$). This, along with increased respiration rate, temperature, and insect presence, promotes microorganism growth and mycotoxin production, with a positive correlation between insect infestation and [CO_2] (Ramachandran, 2022).

Diarra and Amoah (2019) found that temperatures between 25 and 45 ºC promote insect and microorganism growth, with the optimal range being 25 to 35 ºC, aligning with the temperatures, especially in NH. A strong negative correlation was also observed between IDL and CUR with AI, PI, and II (Fig. 5), which are quality indicators for the oil.

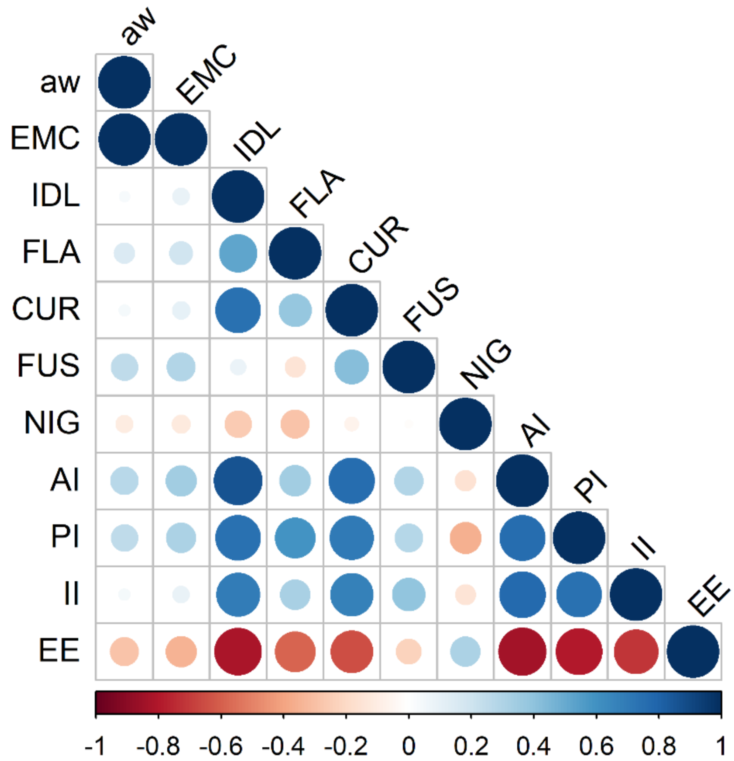


Fig. 5 Correlation matrix between grain quality variables and extracted oil as a function of different IMC (14, 16 and 18% wb) and ST (0, 30, 60, 90 and 120 days)

The correlations between the PI, AI and II variables were also strong and positive, showing consistency in their interpretation, as well as coherence in relation to the behavior and differences between the SC and the IMC, where, despite some variations, higher values prevailed for the higher MC and for NH storage. In relation to the incidence of fungi, FLA, CUR and FUS are the most important variables, and their interaction is generally positive with the variables related to the physical aspect, showing that the higher the values relating to the incidence of fungi in stored grain, the higher the values relating to the parameters associated with the quality of the extracted oil, and therefore the greater the level of deterioration.

5.3.6. Fatty acid profile of corn oil

Table S5 shows the fatty acid profile of oil extracted from corn grains before and after 120 days of storage under H and NH at three IMC. Oleic acid (C18:1) and linoleic acid (C18:2) were the most prominent, along with other unsaturated fatty acids (UFA). Linoleic acid, an essential fatty acid not synthesized by the human body, plays a crucial role in biological processes (Sanjeev et al., 2014).

Greater differences in absolute values were observed for palmitic acid (C16:0) and elaidic acid (C18:0), both saturated fatty acids (SFA), showing a slight reduction in oil from hermetic storage. Barrera-Arellano et al. (2019) reported that corn oil typically has low levels of SFA, with palmitic acid (11.6%) and stearic acid (1.8%) remaining stable over storage, though slightly lower in NH at 18 and 16% wb compared to initial levels, for palmitic acid.

For the other fatty acids, the variation was low and there was no clear trend as function of IMC and SC. The results of this study reinforce the stability of corn oil, due to the presence of a high content of UFA, since, in addition to having a high level of antioxidant compounds and various phenolic compounds, it has a low level of linolenic acid (<1.0%), which is sensitive to the oxidation process (Barrera-Arellano et al., 2019; Wang and White, 2019). The stability of vegetable oil depends on the degree of tolerance to oxidative processes during processing and storage (Barrera-Arellano et al., 2019). Naghshineh et al. (2010) reported that high level of oleic and linoleic acids, as characteristic for corn oil, are associated to an improved oil stability.

SFA, unlike UFA ones such as linoleic and oleic, are associated with greater potential for increasing cholesterol levels, compared to the reducing effect observed with polyunsaturated fatty acids (Sanjeev et al., 2014). The quality of edible oil is generally associated with a higher ratio of UFA/SFA, that varied between 5.67 and 6.17, thus conferring greater stability during storage and cooking (Singh et al., 2014). Alshehri et al. (2024) reported heating process as one of the reasons for UFA degradation, with reduction on UFA/SFA.

5.3.7. Multivariate statistical analysis of quality parameters of stored corn grains

Table S6 presents the summary data from the multivariate analysis, including variance, eigenvalues, and correlation for the three dimensions considered. These dimensions, selected based on eigenvalues greater than one, account for 79.42% of the cumulative explanatory variance. The reduction in individual variance and eigenvalues below one indicates a decrease in their relevance, as principal components.

The first principal component (Dim1) showed strong correlations with most variables, especially IDL, FLA, CUR, AI, PI, and II, with lower values for EE. For the second (Dim2) and third (Dim3) components, the number of correlated variables and their magnitude decreased, reflecting their reduced relevance. Dim2 was characterized by higher values for a_w and EMC, while Dim3 was associated with higher values for FUS.

Fig. 6 shows the main components and how each of the variables and factors relate to Dim1 and Dim 2. According to the clusters, there was a clear difference between the grains stored hermetically and those stored non-hermetically, with the hermetic system being defined by higher EE values, while for the NH there was a greater predominance of higher values, especially for IDL, CUR, II, PI, AI and FLA (Fig. 6a). The same behavior was observed in relation to the IMC, with IMC 18 characterized by higher values for a_w, EMC and FUS, IMC 14 identified by higher values for EE, IMC 16 was in the intermediate region, but closer to IMC 16 when compared to IMC 14 (Fig. 6b).

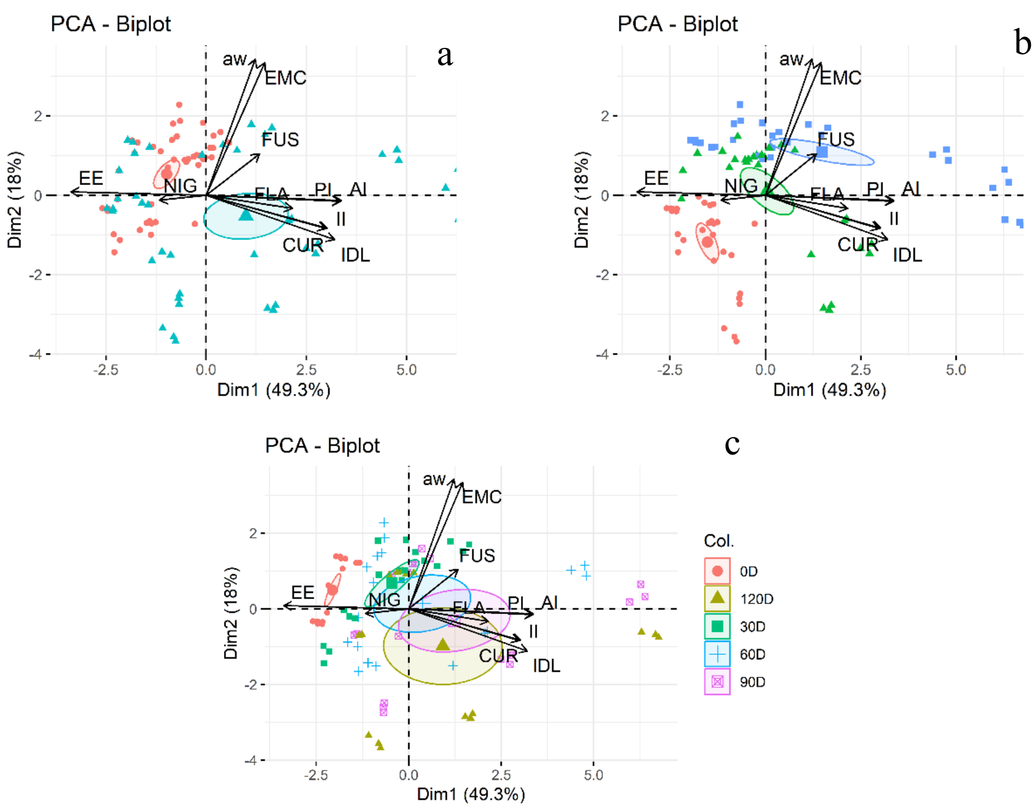


Fig. 6 Principal component analysis map (a-c) for Dim1 and Dim2 from the variables analyzed. IMC 14, IMC 16 and IMC 18 - initial moisture content of 14, 16 and 18% wb

For ST, a difference was observed between the grains before storage and those at later times, though the differences became less pronounced over longer ST. The ellipses for 60-, 90-, and 120-day storage overlapped, indicating similar characteristics. These clusters were associated with higher values of IDL, CUR, PI, AI, FLA, a_w, EMC, and FUS, which contribute to greater grain and corn oil deterioration (Fig. 6c).

The data showed a greater deterioration trend for grains stored non-hermetically with higher IMC (18 and 16% wb), with the deterioration process intensifying over 60, 90, and 120 days, as seen in the overlapping clusters. This was consistent with variables indicating higher deterioration levels compared to grains stored at IMC of 14% wb or for ST of 0 and 30 days. Climatic conditions and packaging type contributed to a negative effect on corn grain quality and nutritional composition (Daba et al., 2024) and, Bartosik et al. (2023) highlight that in hermetic storage systems (e.g., silo-bags) and temperature plays a crucial role, especially with higher grain MC, which promotes microbial activity, particularly during summer, which can limit the effectiveness of hermetic systems when grains are stored under conditions with high IMC.

The quality of corn grains is influenced by factors like temperature, IMC, and SC, where any one factor, if not properly managed, can compromise grain quality. Ziegler et al. (2021) emphasize that the ideal IMC for preservation depends on the grain type and ST, while considering other factors that affect metabolic activity in the grain mass. Mabasso et al. (2024) observed an increase in weevil-damage and moldy grains with an increase in IMC. Coradi et al. (2022) noted higher infestation of *Aspergillus spp.* and *Rhizopus spp.* with increased temperature and MC in hermetic silo-type storage, particularly between 13 and 18% wb. Lutz and Coradi (2023) also found greater fungal infestation over time, with temperature having a stronger effect, in corn grains stored in silo-bags at MC of 13% wb.

5.4 Conclusion

Hermetic storage with IMC of 14% wb effectively maintained the corn grain and oil quality over 120 days. In addition, for better quality, grains stored with IMC of 16 and 18% wb should be limited to 30 days, regardless of the SC, and the deterioration effect is minor.

Corn grain and oil quality depend on IMC, SC, and ST. Longer storage at higher MC reduces quality, with 14% wb recommended as maximum for both conditions. Key quality loss indicators include increased IDL, 1.96 to 12.58% for IMC of 18% wb in NH storage, CUR, PI, AI, FLA, a_w, EMC, and FUS, and decreased EE in 28.86 and 9.43% for IMC of 18 and 16% wb in grains stored in NH storage, where respiration intensified even in grains stored hermetically.

Temperature, RH, and [CO_2] varied by IMC and SC over 120 days, increasing with time and IMC. Intergranular temperature and RH followed external conditions, with higher values in the NH; only RH was higher in the hermetic system. [CO_2] stayed above ambient, peaking in NH due to limited gas exchange. Increasing in IMC (16–18% wb), particularly under NH storage, led to pronounced degradation of grain and corn oil after 60 days. While fatty acid profiles showed minimal variation, the corn oil stability factor impacted significantly with the UFA/SFA from 5.67 to 6.17.

Supplementary Information The manuscript contains supplementary material available.

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Authorship contribution G. A. Mabasso: conceptualization, data curation, formal analysis, investigation, methodology, project administration, writing-original draft, writing-review and editing. O. Resende: Supervision, conceptualization, funding acquisition, investigation, methodology, project administration, review–original draft, writing-review and editing. D. G. Souza: conceptualization, investigation, methodology, review–original draft, writing-review and editing. A. B. de Almeida, V. C. Siqueira, D. E. C. de Oliveira, W. D. Quequeto: investigation, methodology, writing-review and editing. É. R. de Freitas: methodology and research.

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Data availability The data will be made available upon request.

Declaration

Competing interest The authors declare that there are no known competing financial interests or personal relationships that may have impacted the work reported in this manuscript.

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SUPPLEMENTARY MATERIAL (CHAPTER III)

Concentration of CO_2 in hermetic and non-hermetic storage and effect on incidence of insect, fungi and oil quality of corn grain with different moisture contents

Journal: **Journal of Food Process Engineering**

Fig. S1 Illustrative image of the hermetic packaging (a) and experimental silo (b) used for storing corn grains

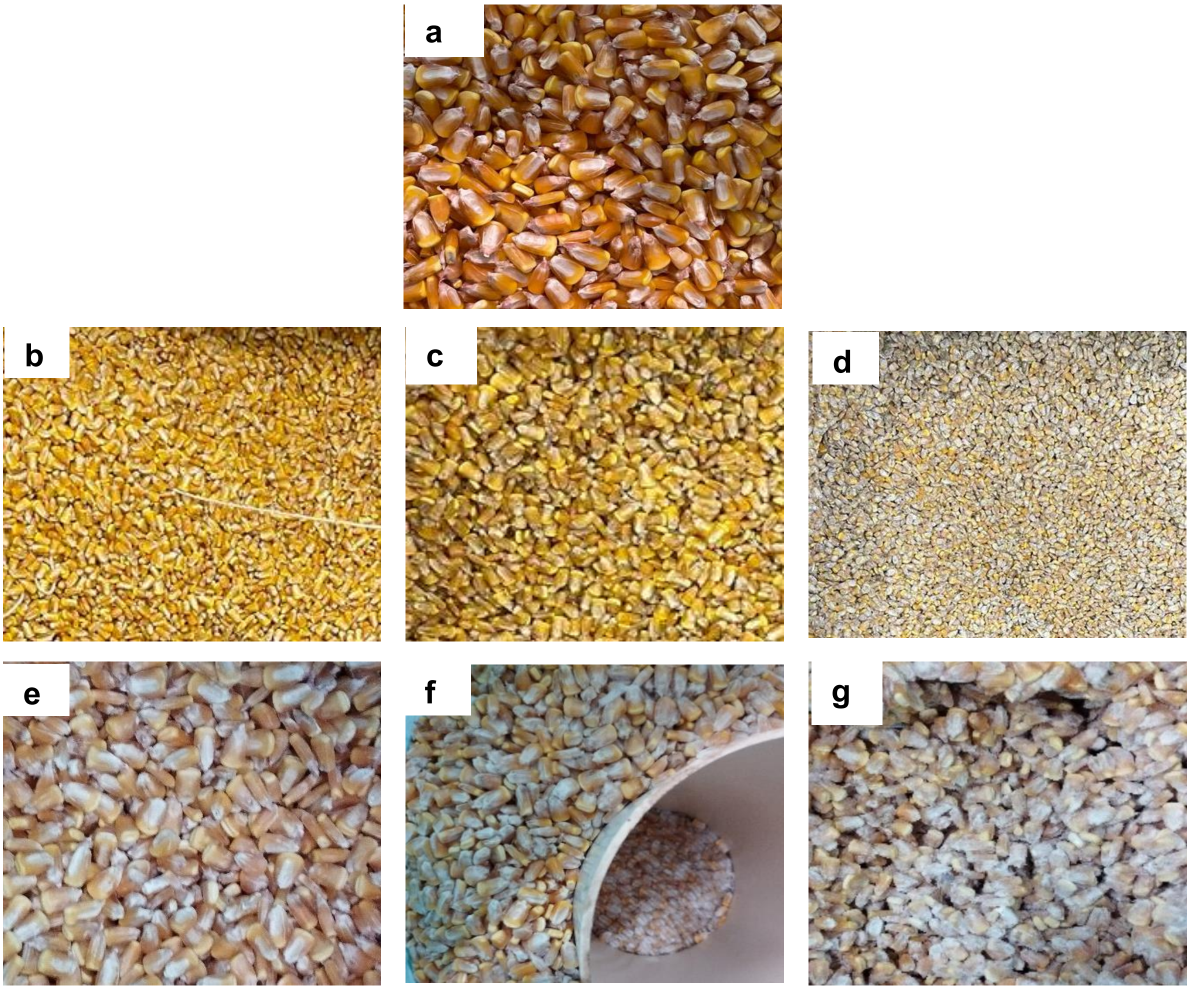

Fig. S2 Illustrative image of the grain before storage (a), after 120 days of storage in non-hermetic (b, c and d) and hermetic packaging (e, f and g) for initial moisture content of 14, 16 and 18% wb

Table S1 Summary of the analysis of variance for the quality of corn grains and oil stored under different conditions and initial moisture contents

SV	a_w	EMC	IDL	EE	FLA	CUR
SC	532.73**	168.09**	1789.51**	136.48**	140.06**	425.13**
IMC	4431.67**	2971.52**	129.04**	132.89**	134.05**	55.12**
ST	273.86**	154.67**	287.87**	108.83**	363.56**	27.69**
SC × IMC	262.28**	183.95**	142.50**	58.14**	8.60**	54.65**
SC × ST	324.72**	166.92**	301.05**	17.88**	15.87**	46.28**
IMC × ST	53.77**	34.24**	23.34**	17.67**	19.73**	1.42^{ns}
SC × IMC × ST	93.17**	58.95**	19.46**	18.24**	4.19**	7.33**
CV (%)	0.54	0.56	22.09	1.85	11.24	25.19
FV	FUS	NIG	AI	PI	II	
SC	19.24**	12.09**	33898.80**	64.24**	216.04**	
IMC	22.05**	7.58**	10860.11**	113.54**	37.37**	
ST	90.18**	32.63**	5162.55**	132.62**	108.17**	
SC × IMC	1.24^{ns}	1.44^{ns}	14353.31**	29.77**	28.64**	
SC × ST	8.45**	12.59**	4293.57**	11.91**	43.71**	
IMC × ST	11.34**	2.18*	2167.08**	25.28**	13.67**	
SC × IMC × ST	3.62**	1.07^{ns}	1861.23**	6.86**	5.88**	
CV (%)	21.27	55.14	2.27	4.81	8.07	

SV: source of variation; SC: storage condition (H, NH); IMC: initial moisture content (%, wb); ST: storage time (days); CV: coefficient of variation (%); a_w: water activity; EMC: equilibrium moisture content (%, wb); IDL: insect damage loss (%); EE: ether extract content (g $100g^{-1}$ dm); FLA: *Aspergillus flavus*; CUR: *Curvularia spp.*; FUS: *Fusarium spp.*; NIG: *Aspergillus niger*; AI: acidity index; PI: peroxide index, II: iodine index. * and ** -Significant at $p<0.05$ and $p<0.01$ by F-test and; ns: not significant

Table S2 Mean values of water activity and equilibrium moisture content of corn grains stored in hermetic and non-hermetic conditions with different initial moisture contents

		Water activity (%)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	0.832a	0.832a	0.850a	0.852a	0.830b	0.854a	0.834a	0.548a	0.827a	0.834a
	16	0.792a	0.792a	0.815a	0.821a	0.802^{a}	0.751b	0.817a	0.735b	0.817a	0.665b
	14	0.733a	0.733a	0.702b	0.754a	0.717^{a}	0.690b	0.633b	0.729a	0.733a	0.595b
		Equilibrium moisture content (%, wb)									
	18	17.70a	17.70a	18.20a	18.30a	17.70b	18.47a	17.82b	18.37a	17.57a	17.93a
	16	16.90a	16.90a	17.37a	17.55a	16.19b	17.06a	17.42a	16.02b	17.39a	14.72b
	14	18.88a	18.88a	15.20b	16.28a	15.51^{a}	15.06b	15.75a	14.17b	15.38a	13.62b

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the t-test.

Table S3 Mean values of mass incidence of *Aspergillus flavus*, *Curvularia spp.*, *Fusarium spp.* and *Aspergillus niger* in corn grains stored in hermetic and non-hermetic conditions with different initial moisture contents

		Aspergillus flavus (%)									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
	18	17.33a	17.33a	47.67a	44.33a	14.67b	20.67a	41.33a	47.00a	60.00b	78.33a
	16	14.00a	14.00a	38.00b	47.33a	9.67b	26.33a	29.00a	31.67a	44.00b	56.33a
	14	10.67a	10.67a	22.00b	42.00a	6.33b	27.33a	20.67b	27.00a	28.33b	45.00a
		Curvularia spp. (%)									
	18	16.00a	16.67a	19.33b	48.00a	1.67b	65.33a	3.33b	73.33a	9.33b	52.67a
	16	12.00a	12.00a	28.00b	42.00a	17.67b	50.00a	3.67b	63.67a	3.33b	56.33a
	14	5.67a	5.67a	11.00a	14.67a	22.00a	17.67a	6.67b	33.33a	9.00b	25.33a
IMC		*Fusarium spp.* (%)									
	18	13.33a	13.33a	34.67b	57.67a	57.67b	70.33a	36.00a	45.00a	18.67a	9.67a
	16	15.67a	15.67a	28.67b	53.00a	53.33b	41.33a	33.33b	57.33a	13.00a	17.33a
	14	26.00a	26.00a	20.67a	21.67a	40.67a	35.00a	19.33b	34.00a	9.33a	14.67a
		Aspergillus niger (%)									
	18	10.00a	10.00a	15.00a	10.67a	0.00b	11.33a	2.00a	0.67a	0.00a	0.67a
	16	17.67a	17.67a	7.00a	11.33a	0.67b	18.67a	2.67a	4.67a	0.00a	2.00a
	14	16.00a	16.00a	24.33a	14.67a	2.00b	22.33a	1.67a	5.00a	0.33a	4.00a

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the t-test.

Table S4 Mean values of the acidity index, peroxide index and iodine index of corn oil obtained from stored grains as a function of different initial moisture contents, storage conditions and storage time

		Acidity index (mg NaOH g^{-1})									
ST		0		30		60		90		120	
SC		H	NH	H	NH	H	NH	H	NH	H	NH
IMC	18	1.46a	1.46a	0.84b	1.66a	0.91b	5.41a	1.49b	7.44a	0.86b	5.68a
	16	1.03a	1.03a	0.87b	1.28a	0.76b	2.86a	1.18b	3.17a	0.72b	2.18a
	14	0.98a	0.98a	0.58a	0.69a	0.86b	1.29a	1.16a	1.25a	0.74a	0.82a
		Peroxide index (meq kg^{-1})									
	18	5.43a	5.43a	13.10b	18.18a	9.23b	24.13a	14.40b	22.41a	10.86b	27.13a
	16	5.73a	5.73a	12.19a	12.14a	7.09b	18.62a	13.38a	14.73a	13.72b	18.89a
	14	6.38a	6.38a	4.52a	4.49a	8.61a	6.47a	13.04a	9.88b	10.57a	12.49a
		Iodine index (g I_2 100 g^{-1})									
	18	81.76a	81.76a	87.36b	97.46a	86.62b	127.50a	101.48b	117.27a	97.38b	122.77a
	16	85.60a	85.60a	87.68a	88.49a	89.34b	120.02a	102.86b	118.82a	89.10a	92.00a
	14	85.16a	85.16a	87.82a	83.45a	93.44b	106.48a	93.74a	99.08a	89.61b	100.46a

Values following by different superscript small letters in the row for each storage time and initial moisture content indicate significant difference at $p<0.05$ by the t-test.

Table S5 Profile of fatty acids obtained in corn oil stored according to different conditions of initial moisture content and storage conditions at the beginning and after 120 d

ST × SC	Total fatty acid composition (% m m^{-1})								
	Time 0			120 d					
Fatty acids	18	16	14	H18	H16	H14	NH18	NH16	NH14
Myristic C14:0	0.06	0.05	0.15	-	0.07	-	0.04	0.05	-
Palmitic C16:0	12.00	12.00	12.24	12.23	12.14	11.91	11.57	11.77	11.99
Palmitoleic C16:1	0.11	0.07	0.13	0.09	0.10	0.08	0.08	0.08	0.07
Heptadecanoic C17:0	0.06	0.05	0.12	0.07	0.08	0.06	0.08	0.06	0.06
Stearic C18:0	1.99	2.02	2.19	2.03	2.09	2.02	2.00	1.96	1.98
Elaidic C18:1 trans	-	0.06	0.16	-	0.06	0.04	0.02	-	-
Oleic C18:1 (9)	43.04	43.16	43.45	43.07	43.18	43.18	43.73	43.17	42.96
Linoleic C18:2 (9,12)	41.49	41.33	40.31	41.17	41.01	41.47	41.29	41.67	41.74
Arachidic C:20:0	0.13	0.13	0.12	0.15	0.14	0.13	0.13	0.13	0.13
Linolenic C18:3 (3)	0.99	0.99	1.00	1.04	1.00	1.00	0.94	0.99	0.95
Behenic C22:0	0.13	0.14	0.13	0.15	0.13	0.11	0.12	0.12	0.12
Saturated	14.37	14.39	14.95	14.63	14.65	14.23	13.94	14.09	14.28
Mono-unsaturated	43.15	43.29	43.74	43.16	43.34	43.30	43.83	43.25	43.03
Poli-unsaturated	42.48	42.32	41.31	42.21	42.01	42.47	42.23	42.66	42.69
UFA/SFA	5.96	5.95	5.69	5.84	5.83	6.03	6.17	6.10	6.00

H14, H16 e H18 – initial moisture content of 14, 16 and 18% for hermetic conditions at 120 days; NH14, NH16 e NH18 – initial moisture content of 14, 16 and 18% for non-hermetic conditions at 120 days; UFA/SFA – Unsaturated fatty acids/Saturated fatty acids.

Table S6 Eigenvalues, variance and correlation analysis between the variables analyzed and the principal components (Dim 1, Dim 2 and Dim3) in corn grains stored with different initial moisture contents and conditions

Variable	Dim 1	Dim 2	Dim 3
Eigenvalues	5.40	1.98	1.35
Individual variance	49.13	18.00	12.31
Cumulative variance	49.13	67.13	79.43
a_w	0.322^{**}	0.933^{**}	-0.072^{ns}
EMC	0.386^{**}	0.910^{**}	-0.059^{ns}
IDL	0.873^{**}	-0.297^{**}	-0.095^{ns}
FLA	0.582^{**}	-0.075^{ns}	-0.596^{**}
CUR	0.813^{**}	-0.222^{*}	0.288^{**}
FUS	0.361^{**}	0.283^{**}	0.700^{**}
NIG	-0.315^{**}	-0.044^{ns}	0.538^{**}
AI	0.903^{**}	-0.071^{ns}	0.168^{ns}
PI	0.910^{**}	-0.031^{ns}	-0.092^{ns}
II	0.821^{**}	-0.220^{*}	0.254^{*}
EE	-0.918^{**}	0.013^{ns}	0.130^{ns}

*Statistically significant at p<0.05, **Statistically significant at p<0.01 and ns Statistically not significant by *t-test*

6 GENERAL CONCLUSION

The temperature, relative humidity and CO_2 concentration generated in mass grain were influenced by the environmental air condition, as well as the storage conditions, initial moisture content and storage time. Corn grains stored under non-hermetic conditions tended to have increased metabolic activity, especially those stored with initial moisture contents of 18 and 16% wb.

Grains stored with a moisture content of 14% wb presented better preservation quality up to 120 days of storage, with hermetic conditions being more favorable. Hermetic packaging proved to be more effective in controlling insects, a crucial factor in limiting metabolic activity. Thus, it represents a viable alternative for small-scale farmers, who often lack the resources to adopt more robust storage systems, such as vertical silos, mainly in regions of high postharvest losses.

In general, as previous studies have shown, the use of CO_2 sensors is an important tool to complement the use of thermometry in the management of stored corn grain, especially with the integration of real-time monitoring, thus allowing decisions to be made in advance, thereby reducing the deterioration levels of stored grain.