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Newiton da Silva Timm

SECAGEM E ARMAZENAMENTO DE GRÃOS DE MILHO DO CENTRO E DAS EXTREMIDADES DA ESPIGA: EFEITOS SOBRE AS PROPRIEDADES FÍSICO-QUÍMICAS DOS GRÃOS E DO AMIDO ISOLADO

Santa Maria, RS
2022

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Tese de doutorado apresentada ao Programa de Pós-Graduação em Engenharia Agrícola, da Universidade Federal de Santa Maria, como requisito para obtenção do título de **Doutor em Engenharia Agrícola**.

Orientador: Prof. Dr. Paulo Carteri Coradi
Coorientador: Prof. Dr. Cristiano Dietrich Ferreira

Santa Maria, RS
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Newiton da Silva Timm

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Deixar de fazê-lo agora seria me desfazer.
(CORTELLA, 2016, p. 55).

RESUMO

SECAGEM E ARMAZENAMENTO DE GRÃOS DE MILHO DO CENTRO E DAS EXTREMIDADES DA ESPIGA: EFEITOS SOBRE AS PROPRIEDADES FÍSICO-QUÍMICAS DOS GRÃOS E DO AMIDO ISOLADO

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Grande parte das cultivares de milho apresentam uma inserção de grãos com dimensões diferentes ao longo de uma espiga, sendo os grãos das extremidades com um formato esférico e os grãos do centro com maior comprimento e menor espessura. Essas diferenças nas dimensões dos grãos podem afetar as propriedades do milho, pois a cinética de secagem pode ser diferente entre os grãos no centro e nas extremidades. Além disso, a consistência do endosperma do milho do centro e das extremidades pode ser diferente, onde os grãos das extremidades apresentam maior presença de endosperma vítreo, o que pode modificar os parâmetros de secagem e os efeitos da operação sobre a qualidade do grão e de seus derivados. Essas diferenças podem afetar as condições de secagem, que pode acarretar em efeitos latentes dessa operação durante o armazenamento do milho. Dessa forma, objetivou-se avaliar os efeitos das condições de secagem e de armazenamento de grãos de milho do centro e das extremidades da espiga sobre as propriedades físico-químicas e tecnológicas dos grãos e do amido isolado. Foram avaliados os efeitos da temperatura de secagem (60, 80 e 100 ºC) sobre a qualidade dos grãos de milho e do amido isolado e os efeitos da temperatura (15 e 25 ºC) e do tempo (0, 3 e 6 meses) de armazenamento sobre a qualidade dos grãos de milho do centro e das extremidades da espiga, separados antes e depois das etapas de pós-colheita. A cinética de secagem foi quantificada pelo tempo de secagem, taxa de secagem e difusividade efetiva de umidade. A qualidade dos grãos foi mensurada pela classificação dos grãos e pela avaliação de propriedades do amido, das proteínas e dos lipídeos do milho. Nas temperaturas de secagem mais altas (80 e 100 ºC), a taxa de secagem e a difusividade efetiva de umidade dos grãos do centro da espiga são maiores em relação aos grãos das extremidades. Foram observadas alterações significativas nas propriedades das proteínas dos grãos, principalmente a redução da solubilidade e inativação da enzima lipase, e a redução dos teores de luteína e β-caroteno nos grãos do centro, separados após a secagem. O aumento da temperatura de secagem resultou em uma redução do rendimento e pureza da extração e aumentou a resistência térmica do amido. Os resultados mostraram que a separação industrial de grãos com diferentes dimensões pode aumentar o rendimento da extração do amido em 35 – 40%. A separação dos grãos do centro e das extremidades da espiga de milho durante as fases de pós-colheita pode aumentar a quantidade de grãos sadios em mais de 2% após 6 meses de armazenamento a 25 ºC. Após este estudo, algumas lacunas de pesquisa foram encontradas: a) estudos de melhoramento para busca de novos genótipos com maior uniformidade de grãos ao longo da espiga de milho, e b) adição de uma etapa de separação de grãos com dimensões diferentes antes da secagem e armazenamento.

Palavras-chaves: Taxa de secagem. Difusividade efetiva de umidade. Proteína solúvel. Extração de amido. Classificação de milho.

ABSTRACT

DRYING AND STORAGE OF CORN GRAINS FROM THE CENTER AND EXTREMITIES OF CORNCOB: EFFECTS ON THE PHYSICO-CHEMICAL PROPERTIES OF GRAINS AND ISOLATED STARCH

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Most corn cultivars have an insertion of grains with different dimensions along a corncob, with the grains from the extremities with a spherical shape and the grains from the center with higher length and lower thickness. These differences in grain dimensions can affect corn properties, as drying kinetics may be different between grains from the center and extremities. In addition, the consistency of the corn endosperm may be different, where the corn from the extremities has a higher presence of vitreous endosperm, which can modify the drying parameters and the effects of the operation on the quality of the grains. These differences can affect drying conditions, which can lead to latent effects of this operation during corn storage. Thus, the objective was to evaluate the effects of drying and storage conditions of corn from the center and extremities of the corncob on the physicochemical and technological properties of the grains and isolated starch. The effects of drying temperature (60, 80, and 100 ºC) on the quality of corn grains and isolated starch, and the effects of storage temperature (15 and 25 ºC) and storage time (0, 3, and 6 months) on the quality of corn from the center and extremities, separated before and after the post-harvest stages were evaluated. Drying kinetics were quantified by drying time, drying rate, and effective moisture diffusivity. Grain quality was measured by grain classification and evaluation of corn starch, protein, and lipid properties. At higher drying temperatures (80 and 100 ºC), the drying rate and the effective moisture diffusivity of the grains from the center were higher concerning the grains from the extremities. Significant changes were observed in the protein properties of the grains, mainly the reduction of the solubility and inactivation of the lipase enzyme, and the reduction of the lutein and β-carotene contents in the grains from the center, separated after drying. The increase in drying temperature resulted in a reduction in the yield and purity of the extraction and increased the thermal resistance of the starch. The results showed that industrial separation of grains with different dimensions can increase the starch extraction yield by 35 – 40%. The separation of grains from the center and extremities of the corncob during the post-harvest phases can increase the amount of not defective grains by more than 2% after 6 months of storage at 25 °C. After this study, some research gaps were found: a) breeding studies to search for new genotypes with higher uniformity of grains along the corncob, and b) addition of a stage of separation of corn grains with different dimensions before drying/storage.

Keywords: Drying rate. Effective moisture diffusivity. Soluble protein. Starch extraction. Corn classification.

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1 INTRODUÇÃO

Na pós-colheita, os grãos de milho (*Zea mays* L.) são submetidos a uma série operações agroindustrias como, limpeza, secagem, armazenamento e processamento. Inicialmente, os grãos passam por uma classificação com o objetivo de se conhecer as características da massa de grãos que será processada. A limpeza dos grãos pode ser dividida em duas etapas, uma antes da secagem, reduzindo para 2 – 4% o teor de matérias estranhas e impurezas (pré-limpeza) e outra após a secagem, reduzindo o teor de impurezas para níveis inferiores a 1%.

O milho quando colhido com teor de água elevado (18-30%) deve ser submetido a uma etapa de secagem, que é conduzida até que os grãos atinjam teores de água seguros (12-14%) para conservar as características físico-químicas e tecnológicas iniciais ao longo das etapas de pós-colheita. Na secagem, devem ser monitorados e controlados uma série de parâmetros técnicos, destacando-se a temperatura do ar de secagem. Posteriormente, os grãos de milho limpos e secos são conduzidos ao armazenamento, que ocorrerá até que os mesmos sejam destinados ao processamento. No armazenamento também devem ser controlados e monitorados alguns parâmetros, destacando-se a temperatura e o teor de água dos grãos.

Nas indústrias de alimentos, o processamento do milho ocorre pelas chamadas via seca e via úmida. Na via seca ocorre a separação do endosperma, do pericarpo e do gérmen. Assim, o endosperma é destinado para a produção de canjicas e farinhas de diferentes granulometrias, o pericarpo é destinado para a produção de farinha com elevado teor de fibras e, o gérmen é destinado para a extração do óleo, que resulta no farelo desengordurado. Além disso, os grãos de milho podem ser moídos sem esta separação, originando farinhas integrais. Já a via úmida é destinada prioritariamente para a extração do amido, havendo também a possibilidade de extração do óleo do gérmen e utilização do restante do material como farelo, destinado principalmente à ração animal.

O mercado consumidor de grãos de milho vem crescendo ao longo dos anos, promovendo aumento de área cultivada e de produtividade. De 1961 a 2022 houve um aumento de aproximadamente 450% na produtividade do milho. Esse incremento de produtividade dessa cultura foi resultado de pesquisas, principalmente devido ao melhoramento genético, com o uso de variedades de polinização aberta, introdução de híbridos, uso de híbridos simples e híbridos simples modificados, visando a resistência de plantas contra patógenos e técnicas avançadas de manejo nas lavouras.

Por mais que os diversos cultivares de milho apresentem características genéticas desejáveis, como alta produtividade e resistência a doenças, alguns problemas podem ser observados. A inserção de grãos ao longo de uma espiga origina grãos com dimensões diferentes, sendo os grãos das extremidades da espiga de formato esférico e os grãos do centro com maior comprimento e menor espessura. Essas diferenças nas dimensões dos grãos podem afetar as propriedades do milho, pois a cinética de secagem pode ser diferente entre os grãos no centro e nas extremidades. Além disso, a consistência do endosperma do milho do centro e das extremidades pode ser diferente, onde os grãos das extremidades apresentam maior presença de endosperma vítreo, o que pode modificar os parâmetros de secagem e os efeitos da operação sobre a qualidade do grão e de seus derivados. Essas diferenças podem afetar as condições de secagem, que pode acarretar em efeitos latentes dessa operação durante o armazenamento do milho.

Dessa forma, o trabalho foi divido em três estudos com o objetivo de (1) avaliar os efeitos da temperatura de secagem de grãos de milho do centro e das extremidades da espiga sobre os parâmetros de secagem, as propriedades proteicas e amiláceas e perfil de carotenoides; (2) avaliar os efeitos da temperatura de secagem de grãos de milho do centro e das extremidades da espiga sobre a morfologia e sobre as propriedades tecnológicas, térmicas e de pasta do amido isolado; e (3) avaliar os efeitos da temperatura e do tempo de armazenamento de grãos de milho do centro e das extremidades da espiga sobre parâmetros de qualidade.

1.1 Hipóteses

1.1.1 Os grãos do centro da espiga apresentam maior difusividade de umidade e menor tempo de secagem em relação aos grãos de milho das extremidades da espiga.

1.1.2 Em uma secagem executada com grãos do centro e das extremidades da espiga juntos, os grãos do centro apresentam menor proteína solúvel e conteúdo de carotenoides.

1.1.3 Em uma secagem executada com grãos do centro e das extremidades da espiga juntos, resulta em maior estresse térmico ao amido extraído dos grãos do centro.

1.1.4 Após a secagem e armazenamento executados com grãos do centro e das extremidades da espiga juntos, os grãos do centro apresentam menor solubilidade proteica e maior acidez, atividade de lipase e teor de defeitos.

1.2 Objetivos

1.2.1 Objetivo geral

Avaliar os efeitos das condições de secagem e de armazenamento de grãos de milho do centro e das extremidades da espiga sobre as propriedades físico-químicas e tecnológicas dos grãos e do amido isolado.

1.2.2 Objetivos específicos

1.2.2.1. Avaliar os efeitos da temperatura de secagem (60, 80 e 100 ºC) de grãos de milho do centro e das extremidades da espiga sobre os parâmetros de secagem, as propriedades proteicas e amiláceas e perfil de carotenoides.

1.2.2.2. Avaliar os efeitos da temperatura de secagem (60, 80 e 100 ºC) de grãos de milho do centro e das extremidades da espiga sobre a morfologia e sobre as propriedades tecnológicas, térmicas e de pasta do amido isolado.

1.2.2.3. Avaliar os efeitos da temperatura (15 e 25 ºC) e do tempo de armazenamento (0, 3 e 6 meses) de grãos de milho do centro e das extremidades da espiga sobre parâmetros de qualidade.

CHAPTER 1 – EFFECTS OF CORN DRYING AND STORAGE CONDITIONS ON FLOUR, STARCH, FEED, AND ETHANOL PRODUCTION – A REVIEW

Abstract

The objective was to carry out a systematic review of the effects of the drying and storage conditions of corn on the physical-chemical quality in the processing of starch and flour, in the production of animal feed, and the industrialization of ethanol. Initially, the review presented an overview of the post-harvest stages of corn grains, highlighting drying and storage. The main drying and storage methods used for corn grains were presented. Among the drying conditions, the air temperature was the main factor that affected the properties of starch, flour, feed, and ethanol produced from corn. It was verified that the corn grains submitted to drying at temperatures below 60 ºC obtained better results in the industry. In storage, in addition to the storage time, factors such as temperature and moisture content of the grains affected the physical-chemical quality of the processed products. In this stage, the moisture content below 14% and the storage temperature below 25 ºC conserved the physical-chemical quality of the grains and obtained better processing results. Further studies are needed to assess the effects of the drying and storage conditions of corn on the properties of flour, starch, animal feed, and, mainly, on ethanol production.

Keywords: *Protein proprieties; Starch extract yield; Pasting proprieties; Digestibility; Ethanol yield.*

1 Introduction

Corn (*Zea mays* L.) is a plant belonging to the Poaceae family and is the most cultivated cereal in the world. This cereal has applicability in several areas, whether in the use of whole-grain or derivatives of its components, isolated or industrially processed (Trehan et al. 2018; Jalali et al. 2020).

In the post-harvest, the corn is submitted to a series of industrial stages such as reception, cleaning, drying, storage, and processing. In drying, parameters such as air temperature and speed, and grain mass temperature must be monitored and controlled. Some studies show the importance of adapting the drying conditions. Elevated temperatures can affect the pasting, physical-chemical, technological, thermal, and morphological properties of corn starch and flour (Malumba et al. 2009a; Malumba et al. 2014; Timm et al. 2020a; Timm et al. 2020b). Drying conditions can also affect the digestibility properties of corn protein and starch, which alters the yield of this product in animal feed (Huart et al. 2018; Malumba et al. 2014). In addition to their use in human and animal feed, corn is used for ethanol production, which is also affected by drying conditions (Coradi et al. 2016a).

During storage, changes also occur in the physical-chemical and technological properties of corn and its derivatives, such as flour, starch, animal feed, and ethanol. The changes are related to the storage time, associated with the temperature and moisture content of the grains (Coradi et al. 2016a; Paraginski et al. 2014a; Paraginski et al. 2014b; Paraginski et al. 2015; Reed et al. 2007; Rehman et al. 2002). In addition to the effects caused by the storage conditions, some changes in the corn and derivatives may also come from the drying conditions used, worsening in storage (Coradi et al. 2020a; Setiawan et al. 2010).

In the food industries, corn is processed through the called dry and wet-milling. In the dry-milling, the separation of the endosperm, pericarp, and germ occurs. Thus, the endosperm is intended for the production of the flour, the pericarp for the high fiber flours production, and the germ for oil extraction, resulting in defatted bran. Also, corn can be ground without this separation, resulting in whole flours. The wet-milling is primarily intended for starch extraction. In wet-milling, the germ is also separated and destined for the extraction of oil, resulting in the corn bran that is destined for animal feed. (Anderson and Almeida 2019; Marinho et al. 2019; Rausch et al. 2019; Timm et al. 2021).

Among the stages of post-harvest corn presented, drying and storage are those that have the greatest influence on grain processing. Thus, the objective of this paper was to systematically review the effects of drying and storage conditions of corn on the properties of starch, flour, animal feed, and ethanol.

2 Review structure

Over the years, a series of studies have been developed on the post-harvest of corn grains, making it evident that the drying and storage stages are the ones that most affect the physicochemical properties of the grains during industrialization.

Knowing this, this article systematically reviewed the main results on the effects of drying and storage conditions on the quality of processed corn. Therefore, we review the main methods of drying and storing corn grains and the factors that must be controlled by the industry. To guide the review, the main studies referring to the industrialization of corn grains when destined for the production of flour, starch, animal feed, and ethanol were presented. Table 1 shows the main studies on the effects of drying and storage conditions on the quality of corn for the production of flour, starch, feed, and ethanol.

The results of the studies gathered in Table 1 were presented and discussed in detail in this review, which had the following specific objectives:

1. Present and discuss the effects of drying conditions on the production of corn flour, starch, feed, and ethanol.
2. Present and discuss the effects of storage conditions on the production of corn flour, starch, feed, and ethanol.
3. Identify research gaps in corn drying, storage, and industrialization.
4. Present and discuss innovative drying and storage techniques.

Table 1. Main studies on the effects of drying and storage conditions on the quality of corn for the production of flour, starch, feed, and ethanol.

Drying condition		Storage condition			Main results		Reference
Method	Temperature (ºC)	Time (months)	Temperature (ºC)	Moisture content (%)	Evaluation	Result range	
Fluidized-bed	54 – 130	-	-	-	Zein solubility (%)	15.17 – 33.00	Malumba et al. (2008)
Fluidized-bed	54 – 130	-	-	-	Albumin solubility (%)	1.30 – 3.60	Malumba et al. (2008)
Fluidized-bed	54 – 130	-	-	-	Globulin solubility (%)	0.90 – 3.90	Malumba et al. (2008)
Tempering-10	70 – 90	-	-	-	Protein solubility (%)	4.72 – 8.30	Timm et al. (2020a)
Tempering-30	70 – 90	-	-	-	Protein solubility (%)	3.05 – 6.29	Timm et al. (2020a)
Fixed-bed	70 – 90	-	-	-	Protein solubility (%)	8.77 – 11.21	Timm et al. (2020a)
Infrared radiation	70 – 90	-	-	-	Protein solubility (%)	4.83 – 11.24	Timm et al. (2020a)
Fixed-bed	80 – 120	6	10 – 23	12.0	Crude protein (%)	7.29 – 9.00	Coradi et al. (2020a)
Fluidized-bed	54 – 130	-	-	-	Starch extraction yield (%)	44.1 – 61.4	Malumba et al. (2009a)
Fluidized-bed	54 – 130	-	-	-	Starch extraction yield (%)	43.1 – 61.5	Malumba et al. (2009b)
Fluidized-bed	54 – 130	-	-	-	Starch pasting temperature (ºC)	72.6 – 80.8	Malumba et al. (2009b)
Fluidized-bed	54 – 130	-	-	-	Starch peak viscosity (RVU)	269.7 – 351.7	Malumba et al. (2009b)
Fixe-bed	30 – 90	-	-	-	Starch extraction yield (%)	30.32 – 48.98	Timm et al. (2020b)
Fixe-bed	30 – 90	-	-	-	Starch gelatinization enthalpy (J/g)	1.44 – 6.47	Timm et al. (2020b)
Fixe-bed	40 – 100	-	-	-	Starch extraction yield (%)	19.18 – 32.32	Ziegler et al. (2020)
Fixe-bed	40 – 100	-	-	-	Starch pasting temperature (ºC)	75.84 – 80.38	Ziegler et al. (2020)

Fixe-bed	40 – 100	-	-	-	Starch peak viscosity (RVU)	206.67 – 251.67	Ziegler et al. (2020)
Fixe-bed	40 – 100	-	-	-	Starch digestibility (%)	68 – 98	Ziegler et al. (2020)
Fluidized-bed	54 – 130	-	-	-	Protein digestibility (g/kg)	208 – 216	Huart et al. (2018)
Fluidized-bed	54 – 130	-	-	-	Starch digestibility (g/kg)	431 – 484	Huart et al. (2018)
Fluidized-bed	54 – 130	-	-	-	Metabolisable energy (MJ/kg)	14.6 – 14.8	Huart et al. (2018)
Fluidized-bed	54 – 130	-	-	-	Starch digestibility (%)	65 – 95	Malumba et al. (2014)
Fluidized-bed	54 – 130	-	-	-	Protein digestibility (%)	75.08 – 83.32	Odjo et al. (2018)
Fluidized-bed	54 – 130	-	-	-	Starch digestibility (%)	63.37 – 81.10	Odjo et al. (2018)
Fluidized-bed	54 – 130	-	-	-	Glucose (mg/g)	127.1 – 212.3	Odjo et al. (2017)
Fluidized-bed	54 – 130	-	-	-	Maltose (mg/g)	101.8 – 249.8	Odjo et al. (2017)
Fluidized-bed	54 – 130	-	-	-	Total D-glucose solubilized (mg/g)	300.8 – 516.2	Odjo et al. (2017)
Fixe-bed	60 – 140	-	-	-	Metabolisable energy (MJ/kg)	12.13 – 12.86	Kaczmarek et al. (2014)
Fixe-bed	80 – 120	6	10 – 23	12.0	Ethanol yield (L/t)	366.40 – 389.83	Coradi et al. (2016a)
-	25 – 93	-	-	-	Ethanol yield (kg/ha)	31.00 – 79.00	Reicks et al. (2009)
-	35 – 80	6	27	12.5 – 13.1	Starch gelatinization enthalpy (J/g)	27.4 – 31.9	Setiawan et al. (2010)
-	35 – 80	6	27	12.5 – 13.1	Starch pasting temperature (ºC)	72.5 – 75.8	Setiawan et al. (2010)
-	35 – 80	6	27	12.5 – 13.1	Starch peak viscosity (RVU)	128.5 – 160.9	Setiawan et al. (2010)
-	-	2	25	15.0 – 18.0	Free fatty acids (%)	16.97 – 76.60	Reed et al. (2007)
-	-	2	25	15.0 – 18.0	Grains infected by storage molds (%)	0.7 – 70.3	Reed et al. (2007)
Fixe-bed	35	12	5 – 35	14.0	Electric conductivity (µS/cm.g)	14 – 40	Paraginski et al. (2015)

Fixe-bed	35	12	5 – 35	14.0	Protein solubility (%)	28 – 46	Paraginski et al. (2014a)
-	-	6	25 – 35	14.5 – 18.0	Electric conductivity (µS/cm.g)	10 – 50	Costa et al. (2010)
-	-	2	27	14.0 – 20.0	pH	5.7 – 6.4	Suleiman et al. (2018)
Fixe-bed	35	12	5 – 35	14.0	Starch extraction yield (%)	45.99 – 66.94	Paraginski et al. (2014b)
Fixe-bed	35	12	5 – 35	14.0	Starch pasting temperature (ºC)	70.50 – 76.30	Paraginski et al. (2014b)
Fixe-bed	35	12	5 – 35	14.0	Starch peak viscosity (RVU)	284.12 – 352.33	Paraginski et al. (2014b)
Fixe-bed	35	12	5 – 35	14.0	Starch gelatinization enthalpy (J/g)	22.41 – 37.81	Paraginski et al. (2014b)
-	-	6	10 – 45	7.7 – 12.38	Protein digestibility (%)	70.0 – 77.9	Rehman et al. (2002)
-	-	6	10 – 45	7.7 – 12.38	Starch digestibility (%)	49.0 – 57.7	Rehman et al. (2002)
-	-	10	-17.9 – 29.8	14.0	Digestible energy (MJ/kg)	15.5 – 16.1	Zhang et al. (2017)
-	-	10	-17.9 – 29.8	14.0	Metabolisable energy (MJ/kg)	14.9 – 18.8	Zhang et al. (2017)

3.1 Effects of drying conditions on corn processing

3.1.1 Starch and flour

The effects of corn drying conditions on the physical-chemical and technological properties of starch and flour are presented in this review. Among the drying conditions, the most studied factors are the drying temperature and method.

The influence of drying air temperature (54, 80, 110, and 130 ºC) on solubility, purity of isolates, and the molecular weight separation of different classes of corn proteins was studied by Malumba et al. (2008). This study was conducted in a fluidized-bed dryer and a variety of flint corn was used. The solubilities of the albumin, globulin, and zein fractions of corn decreased 63.9, 76.9, and 52.4%, respectively, with an increase in the drying temperature from 54 to 130 ºC. According to Malumba et al. (2008), during drying at high temperatures, new disulfide bonds are formed between proteins, in addition to other mechanisms that still need to be studied. Also, high drying temperatures have resulted in the disappearance of some water-salt-soluble polypeptides, but the molecular weight of the zein has not changed with the drying temperature, even though the solubility of the zein has reduced (Malumba et al. 2008).

The effects of drying temperature (70 and 90 ºC) and of fixed-bed, intermittent (with 10 and 30 min of tempering), and infrared drying methods of floury corn on properties of flour were studied by Timm et al. (2020a). Floury corn presents completely floury endosperm and is a variety with white pericarp, predominantly intended for the production of flour.

The results of this study demonstrated that the reduction in the protein solubility and lipase activity is associated with an increase in the drying temperature and the drying method used. The increase in the drying temperature from 70 to 90 °C reduced 43.13, 51.51, 21.77, and 57.03% the protein solubility in intermittent drying methods with 10 min tempering, intermittent with 30 min tempering, fixed-bed, and by infrared radiation, respectively. The increase in the drying temperature from 70 to 90 ºC reduced 27.60, 28.63, and 70.80% the lipase activity in the intermittent drying methods with 10 min tempering, intermittent with 30 min tempering, and by infrared radiation, respectively, and did not differ fixed-bed drying. Besides, Timm et al. (2020a) reported that the increase in the drying air temperature from 70 to 90 ºC resulted in a reduction in the peak viscosity, breakdown, final viscosity, and setback of white corn flour, regardless of the drying method used.

Although the reduction of lipase activity benefits the maintenance of grain quality during storage, the reduction of soluble protein and changes in the thermal and pasting properties of corn flour can hinder its application in corn-based products, especially when using high drying temperatures (90 ºC). Fixed-bed drying (70 and 90 ºC) resulted in higher soluble protein, lipase activity, peak viscosity, and the breakdown and lower acidity compared to other methods (Timm et al. 2020a). Thus, Timm et al. (2020a) suggested corn drying at 70 °C using the fixed-bed method, to maintain protein solubility and pasting properties of flour. Infrared radiation drying is an alternative method for the industry, mainly due to its potential to inactivate lipases without altering the pasting properties of flour.

In addition to affecting the protein fraction of corn flour, drying conditions also affect industrial performance when corn is used for starch production. Malumba et al. (2009a) studied the influence of the drying air temperature (54, 60, 70, 80, 90, 100, 110, 120, and 130 ºC) on the wet-milling performance and the solubility indices of corn proteins. Malumba et al. (2009a) used a variety of flint corn and a fluidized-bed dryer. These authors reported that the increase in drying temperature from 54 to 130 ºC reduced the extraction yield of starch by 28.18% and increased the residual protein content by 84.06%. Associated with this, the solubility indices of albumin, globulin, and zein continuously decrease with the increase in the drying temperatures of corn, causing difficulties in the protein-starch separation during the wet-milling and this difficulty justifies the reduction extraction yield and increased residual protein in starch (Malumba et al. 2008; Malumba et al. 2009a).

Malumba et al. (2009b) studied the effects of drying temperature (54, 60, 70, 80, 100, 110, 120, and 130 ºC) on the functional properties of corn starch granules extracted from a flint variety and dried in fluidized-bed dried. The increase in the drying air temperature from 54 to 130 ºC reduced the peak viscosity by 23.32% and increased the pasting temperature by 11.29% and the setback by 20.59%. The increase in the drying temperature increased the stiffness of the starch granules, which reduced the swelling capacity, the water binding capacity, and the water solubility (Malumba et al. 2009b).

The ideal drying temperature can vary between different corn genotypes or varieties. Timm et al. (2020b) studied the effects of drying temperature (30, 50, 70, and 90 ºC) and genotype (white floury, yellow floury, and yellow flint corn) on the morphology and on the technological, thermal, and pasting properties of corn starch. These authors reported that there was a reduction in the peak viscosity and the gelatinization enthalpy of the starch of the floury and flint yellow corn according to the increase in the drying temperature, which occurred as a result of the pre-gelatinization of the starch granules during the initial drying steps. The starch extracted from the floury white corn showed higher resistance during the swelling of the granules before the physical collapse, as it was not affected by the increase in the drying temperature, and at 90 °C it presented the higher breakdown and energy necessary for gelatinization. Timm et al. (2020b) recommended drying temperatures below 50 °C as indicated for drying all studied corn genotypes.

The drying temperature also affects the properties of starch isolated from popcorn grains. Ziegler et al. (2020) studied the effects of drying temperature (40, 70, and 100 ºC) on the morphology and the technological and digestibility properties of the starch extracted from red popcorn. The extraction yield of red popcorn starch decreased from 32.32% to 19.18%, with the drying temperature increasing from 40 to 100 °C. Drying at 100 °C increases the internal compaction between the starch granules and the protein, in addition to causing deformation in the starch granules. Drying at 100 °C increases the thermal resistance of the starch, evidenced by the increase in the pasting temperature, peak gelatinization temperature, and gelatinization enthalpy (energy required to gelatinize the starch). Also, increasing the drying temperature from 40 to 100 ºC reduced the in vitro digestibility of popcorn starch. The drying of red popcorn at 40 °C promoted lower changes in the structural and technological properties of starch (Ziegler et al. 2020).

The negative influence of the increase in drying temperature on the quality parameters of the flour and corn starch was evident, mainly due to the denaturation of proteins, resulting in their higher interaction with the starch granules, resulting in lower solubility of proteins in the flour and starch extraction yield. The food industry must pay more attention during drying, seeking a form of operation that allows the use of lower temperatures and, thus, the maintenance of the quality of corn derivatives.

3.1.2 Feed

As feed for animal, corn provides most of the metabolizable energy and an appreciable amount of protein. However, when subjected to high drying temperature, the nutritional and energetic value of the corn grain can undergo significant changes. Studies show that during these high drying temperatures, structural changes occur in the main components of corn, including starch and proteins, which can affect their bioavailability.

Huart et al. (2018) evaluated the impact of drying temperature (54, 90, and 130 ° C) and moisture content of the corn grain at harvest (36% and 29%) on in vitro digestibility, growth performance, and ideal digestibility of broiler chickens. These authors reported that in contrast to the results of in vitro digestibility, the apparent ideal digestibility of starch and energy decreased when the drying temperature increased from 54 to 130 °C, and this effect was more pronounced in the corn grain harvested with high initial moisture content (36%). The ideal digestibility of corn protein decreased significantly when dried at an intermediate temperature (90 °C) and with high harvest moisture content (36%). The drying temperature and initial moisture content did not affect the metabolizable energy (Huart et al. 2018).

Although different corn genotypes have similar crude chemical composition, corn starch granules dried at different temperatures differ in their physical-chemical and nutritional value. Malumba et al. (2014) studied the effects of drying temperature (54, 80, 100, and 130 ºC) of corn on the in vitro digestibility of starch, simulating two stages of the pig digestive tract. The high drying temperatures caused a partial gelatinization of the starch granules and produced a favorable substrate for swine pancreatic amylase, which can influence the animal metabolism by modifying the rate and extent of starch digestion in the small intestine and leading to different dynamics of fermentation by the intestinal microbiota. High drying temperature increased the digestibility of corn starch, while the starch extracted from dried grains at a lower temperature produced a greater volume of gas during its in vitro fermentation (Malumba et al. 2014).

Different corn cultivars can present different digestive characteristics about drying conditions. Odjo et al. (2018) studied the influence of variety, date of harvest, and drying temperature on the composition and in vitro digestibility of corn. Two varieties (Belgian flint-flint-dent corn and flint-dent) of corn grains harvested on two different dates after physiological ripening (harvest moisture content: 33.4 and 32.9%) were dried in a fluidized-bed dryer at temperatures between 54 to 130 °C. These authors reported that protein digestibility was influenced by the corn variety and decreased according to the increase in drying temperature and the initial moisture content. However, in vitro digestibility of dry matter and starch increase with increasing drying temperature (Odjo et al. 2018).

The observed differences may be associated with the structural changes that occurred in the corn during drying. With corn grain being used primarily as a source of starch in animal feed, high temperature drying of corn with a high moisture content may be desirable (Odjo et al. 2018). However, it has already been seen that the use of high corn drying temperatures leads to other deficits in the quality of the product, in addition to reduced protein digestibility. The effects of endosperm hardness (soft or vitreous), drying temperature (60, 100, and 140 ° C), and microbial enzyme supplementation (in enzyme or phytase + xylanase) on broiler performance were studied by Kaczmarek et al. (2014). These authors reported that increasing the drying temperature from 60 °C to 140 °C reduced starch digestibility, protein digestibility, and apparent metabolizable energy.

Li et al. (2017) studied the effects of fluidized-bed drying on the structural, functional, and digestive properties of corn grains. The grains were fluidized with air at 160 ° C. These authors reported an increase in the degree of gelatinization of corn starch from 10.79 to 24.60%, reducing the relative crystallinity of the starch from 32.17 to 16.15%. After the heat treatment was applied, the hydrolysis rate of corn starch increased and the slow-digesting starch increased 4.79%. The fast-digesting starch and glycemic index of corn starch increased by 5.13%. Rupture of ordered structures and the lower viscosity of corn starch subjected to 160 ºC helped the enzymes to penetrate the internal structure of the corn and quickly hydrolyze the starch, which explains the higher hydrolysis rate and the increase in the glycemic index. Thus, it is understood that the submission of corn to high temperatures can increase the content of slowly digestible starch and, consequently, the digestibility of corn starch (Li et al. 2017).

The influence of corn variety, drying temperature, and moisture content on the harvest on saccharides released during an in vitro digestion of pepsin-pancreatin was studied by Odjo et al. (2017). These authors found five saccharides, these being glucose, maltose, isomaltose, maltotriose, and glycosyl-maltotriose. After subsequent hydrolysis with amyloglucosidase from the released saccharides, the amount of total glucose recovered increased with an increase in the drying temperature from 54 to 130 ºC and the moisture content in the harvest from 28.8 to 33.4%. By modifying the structural characteristic of the starch granules, the corn grain, and probably the structure of other components around the starch granules, the drying process certainly affects the accessibility of pancreatic α-amylase towards its attack site and results at different rates and profiles of released saccharides. High temperature drying induces the production of saccharides with a higher degree of polymerization. This can have consequences on the digestive physiology in the small intestine of monogastric (Odjo et al. 2017), such as poultry and pigs.

Odjo et al. (2012) studied the influence of drying temperature (60, 80, 100, and 120 ºC) and a hydrothermal treatment in corn on the denaturation of salt-soluble proteins. These authors report that the lower moisture content of the grains resulted in a lower protein denaturation rate. Thus, low temperatures should be used at the beginning of the corn drying, to reduce the corn moisture content without denaturing salt-soluble proteins. The authors also report that during drying, there may be an increase in temperature. High temperature drying also changes the color parameters of the corn, with a tendency to increase the yellow and red color of the grains. These parameters can be used as indirect indicators to detect the use of excessive heat (Odjo et al. 2012).

The results that were gathered show the effects of drying conditions on feed quality, showing that high drying temperatures can affect the digestion of animals that consume corn feed. In these cases, there may be a direct influence on the conversion of feed consumption into foods of animal origin, such as meat, eggs, and milk. Thus, if the drying temperature is high in the drying of corn destined for feed, it will increase the production costs of meat, eggs, and milk, due to the need for higher feed consumption to complement the necessary digestion.

3.1.3 Ethanol

Ethanol is a biodegradable, renewable biofuel, and that can be produced from different biomasses, including corn. According to Manochio et al. (2017), the use of starch-based raw material has higher ethanol yields, placing corn as the higher ethanol-producing biomass in the world. However, the drying conditions of corn must be controlled as they affect ethanol production. Coradi et al. (2016a) studied the effects of the drying air temperature (80, 100, and 120 ºC) of corn on ethanol production. These authors reported that the extraction yield of corn starch is directly related to the yield in ethanol production. The extraction yield of corn starch was 68.22, 66.20, and 64.12%, and the ethanol yield was 389.83, 378.29, and 366.40 L/t of corn dried at 80, 100, and 120 ºC, respectively (Coradi et al. 2016a).

The reduction in the starch extraction yield occurs due to the higher starch-protein binding resulting from the elevation of the drying temperature, reducing the peak viscosity and the swelling power of the starch granules, increasing the pasting temperature and gelatinization enthalpy (Malumba et al. 2009b; Timm et al. 2020b). Coradi et al. (2016a) attributed the reduction in ethanol yield to these changes in corn starch and a reduction in lipid content.

The influence of the corn variety, the amount of nitrogen (N) applied to the crop, the moisture content at harvest, and the drying temperature of the corn (25, 38, 52, 60, 66, 80, and 93 ºC) on the ethanol production was studied by Reicks et al. (2009). These authors reported significant reductions in the concentration of ethanol at the higher (79 kg/ha) and the lower (31 kg/ha) rate of N applied. Also, drying temperatures of 38 and 52 °C produced the higher concentrations of ethanol, regardless of the grain moisture at harvest. Reicks et al. (2009) reported a tendency to reduce the concentration of ethanol at drying temperatures below 38 ºC and above 52 ºC.

As the production of ethanol from corn is directly dependent on the quality of the starch, it became clear that raising the drying temperature affects both the production of starch and the production of ethanol.

4.1 Effects of storage conditions on corn processing

4.1.1 Starch and flour

Storage conditions affect the physical-chemical and technological properties of corn. Reed et al. (2007) studied the storage of corn with a moisture content of 15.0, 16.5, and 18%, an initial temperature of 25 ºC, and relative humidity of 85%. The study was conducted for a storage period of 2 months and the presence of molds, respiration rate, and nutrient composition were evaluated.

Reed et al. (2007) reported that regardless of the moisture content, after one week the temperature of the grain mass was above 25 ºC. Corn stored with a moisture content of 18% showed a higher increase in the temperature of the grain mass, reaching approximately 35 ºC, which helps in increasing the amount of grains infected by storage fungi (*Eurotium spp.* and *Aspergillus spp.*), the respiration rate of the grains, and the percentage of free fatty acids in whole flour. The grains stored with a moisture content of 15% showed a lower increase in the temperature of the grain mass, staying on average at 26 ºC, and also the lower infection by storage fungi, the respiration rate of the grains, and percentage of free fatty acids. In addition, Reed et al. (2007) highlight that the appearance of funds in corn grains occurs predominantly in the area of the grain close to the germ, due to the higher lipid concentration.

Increasing the temperature by 1 °C can accelerate the respiration of the grain mass by 2 to 3 times, to a certain extent that respiration ceases at very high temperatures, as a result of the destructive effects of high temperatures on enzymes, causing higher structural damage in the grains (Forti et al. 2010). The increase in the production of free fatty acids in whole corn flours is a preliminary stage of metabolism and lipid degradation and is directly related to the deterioration of the grain by fungi or enzymes, such as lipases (Reed et al. 2007).

Mold activities cause weight loss, increase damaged grains, and reduce the energy content of corn. The speed with which these processes occur and the severity of the damage they produce depends on the moisture content (Coradi et al. 2020b; Reed et al. 2007) and the temperature of the grains (Coradi et al. 2020c; Paraginski et al. 2014b; Paraginski et al. 2015; Rehman et al. 2002; Reed et al. 2007), and the presence of insects in corn (Suleiman et al. 2018).

Nutritional changes of corn stored at different temperatures (10, 25, and 45 ºC) for 6 months were studied by Rehman et al. (2002). These authors reported a reduction in total soluble sugars, total available lysine, and thiamine content of 39.5, 19.9, and 20.4%, respectively, at storage at 45 °C for 6 months. Reductions of 13.7 and 9.3% of total available lysine and thiamine content, respectively, also occurred during the storage of corn grains at 25 °C. No significant changes were observed in any of these nutrients in the storage of corn grains at 10 °C. Thus, Rehman et al. (2002) suggested that corn should not be stored at temperatures above 25 °C to minimize nutrient losses during storage.

The storage of corn at different temperatures (5, 15, 25, and 35 ºC) was also studied by Paraginski et al. (2015), with evaluations performed at 0, 3, 6, 9, and 12 months. These authors reported that it is possible to store corn grains at temperatures of 5, 15, 25, and 35 ° C with a moisture content of 14% for 6 months, without significant changes in the percentage of grain defects. However, after 6 months there is an increase in the percentage of defects in corn at all storage temperatures, except for corn stored at 15 °C. The use of storage temperatures above 15 °C causes increases in the metabolic processes of the grains, identified by the reduction in the germination percentage and increase in the electrical conductivity of the grains (Paraginski et al. 2015).

In a similar study, Paraginski et al. (2014a) evaluated the effects of corn storage temperature (5, 15, 25, and 35 ºC) on the physical-chemical and pasting properties of the flour. The grains were stored at these temperatures for 12 months. Paraginski et al (2014a) reported that the proximate composition of corn was not affected by storage conditions. However, they reported a reduction in pH, protein solubility, and yellow color, and an increase in acidity, percentage of grains infected with visible molds, pasting temperature, setback, and final viscosity during storage.

The reduction in pH and protein solubility in corn flour was higher in the stored grains at 35 ºC (Paraginski et al. 2014a). An increase in disulfide bonds within the protein structure and their interaction with starch and other corn components are responsible for the changes in protein solubility and in the pasting properties. The lower changes in corn during storage are obtained with a temperature of 5 ºC, being able to maintain the grains and flour quality for 12 months (Paraginski et al. 2014a).

The storage of corn grains in a silo-bag was studied by Costa et al. (2010). The grains were stored with different moisture content (14.5 and 18.0%) and temperatures (25, 30, and 35 ºC), and the evaluations were carried out initially and at 30, 60, 90, 135, and 180 days. Costa et al. (2010) reported an increase in the percentage of defects in the corn grain mass under storage conditions with a moisture content of 18% and temperature of 35 ºC. Finally, the authors concluded that it is possible to store corn grains in a silo-bag. Among the levels of factors that were assessed by Costa et al. (2010), storage in a silo-bag for up to 180 days was recommended, with a moisture content of 14.5% and a temperature of 25 to 30 ºC.

The impact of moisture content and the presence of corn weevils on the quality of corn were assessed by Suleiman et al. (2018). The grains were stored for 2 months at 27 ºC and 70% relative humidity, with different moisture contents (14, 16, 18, and 20%). The storage was carried out with and without the presence of insects and in a hermetic and non-hermetic system. Suleiman et al. (2018) reported that corn stored in non-hermetic conditions with weevils at 18 and 20% exhibited high levels of fungal growth and aflatoxin contamination (> 150 ppb). However, very little mold growth was observed in hermetically stored corn, and no aflatoxin was detected at any moisture level.

After 2 months of storage, 100% mortality of *Sitophilus zeamais* was observed next to the grains stored in the hermetic system. However, the number of Sitophilus zeamais increased with increasing moisture content in non-hermetic storage. The pH of the grains varied between 5.7 – 6.4 and showed no difference between treatments. In addition, Suleiman et al. (2018) concluded that hermetic storage can bring benefits to corn storage. In the same sense, Walker et al. (2018) reported that hermetic storage results in less aflatoxin contamination compared to non-hermetic methods.

In inadequate storage conditions, corn may acquire some defects. These defects can affect some properties of the starch extracted from these grains. Paraginski et al. (2019) studied the physical-chemical, pasting, crystallinity, and morphological properties of starch isolated from corn showing different types of defects. Starch was extracted from not detective corn and with the defects broken, fermented, rotten, moldy, germinated, insect-damaged, and shrunken and immature.

Paraginski et al. (2019) reported that the shrunken and immature corn showed lower starch extraction yield. Also, all starches exhibited high purity and similar color. The starch pasting properties of not detective corn and of broken, fermented, rotten, moldy, and insect-damaged corn did not show a significant difference. The starch extracted from rotten and germinated corn showed perforations caused by the attack of enzymes, which probably occurred during the storage of these grains in inadequate storage conditions. Finally, Paraginski et al (2019) reported that starch extracted from moldy grains was safe based on the analysis of mycotoxins, because aflatoxins (B1, B2, G1, and G2), fumonisin B1, ochratoxin A, and deoxynivalenol were not detected in starch isolated.

Products obtained from corn are also affected by grain storage conditions. Paraginski et al. (2014b) studied the characteristics of starch isolated from corn (Flint corn) that were stored at 5, 15, 25, and 35 ºC for 12 months. Paraginski et al. (2014b) reported that the higher pasting temperature was observed in the starch isolated from corn stored at 35 ºC. Also, they reported that the storage of corn at 5 °C resulted in the higher starch peak viscosity, breakdown viscosity, final viscosity, setback, and gelatinization enthalpy. The lower values of breakdown viscosity of the starch isolated from corn stored at 15, 25, and 35 ºC indicate a higher stiffness of the starch granules in these conditions, making the starch granules resistant to breakage and collapse during heating and shearing (Paraginski et al. 2014b).

In addition, Paraginski et al. (2014b) reported that the storage of corn at 35 °C caused a 22.1% reduction in the starch extraction yield and gives the starch a yellowish color, concerning the starch extracted from the freshly harvested grains. This fact makes the starch of the grains stored in these conditions less attractive for applications where the clarity of the paste is important. Regardless of the storage temperature used, starch isolated from grains stored for 12 months reduced the relative crystallinity. This change in relative crystallinity resulted in a more organized rearrangement of the starch chains and promoted interactions with other constituents. This occurred mainly in the starch isolated from corn stored at 35 °C, which increased the energy required for the gelatinization of the starch granules and a lower peak and final viscosity (Paraginski et al. 2014b).

The conditions under which the corn was dried affect their conservability during storage and alter the starch properties. The effects of drying conditions during the storage of corn were evaluated by Setiawan et al. (2010). These authors studied the effects of corn drying in the sun (35 ºC) and with heated air (80 ºC) followed by the corn storage for 6 months at 27 ºC and 85-90% relative humidity on the starch structure and properties.

Sietiawan et al. (2010) reported that the hydrolysis rate of corn starch decreased according to the storage time. Also, the number of damaged starch granules increased and the starch molecular weight and the percentage of long branches of amylopectin decreased according to increased storage time. These changes are associated with starch hydrolysis during corn storage.

After grain storage, starch isolated from sun-dried corn (35 ºC) showed higher levels of enzymatic hydrolysis when compared to dried corn at 80 ºC. The authors attributed this effect to the higher amylase activity remaining in the corn samples after sun-drying (35 ºC) compared to drying at 80 ºC (Sietiawan et al. 2010). This was because the increase in the drying temperature results in a reduction in the enzymatic activity of corn (Timm et al. 2020a).

After corn storage for 6 months, the isolated starch showed a reduction in peak viscosity of 16.25 and 13.45%, in breakdown viscosity of 52.75 and 32.72%, in final viscosity of 2.62 and 19.77%, and in setback of 6.49 and 11.28%, when dried in the sun (30 ºC) and at 80 ºC, respectively. In drying at 35 ºC, the results obtained after storage are associated with high activity of the endogenous enzyme that remained after sun-drying, where it hydrolyzed the starch and reduced the viscosity (Sietiawan et al. 2010). When drying at 80 ºC, changes in pasting properties may be associated with pre-gelatinization of starch during the corn drying (Timm et al. 2020b).

Thus, it was understood that in the post-harvest of corn the effects of drying conditions of the grains can result in latent damages, which are pronounced throughout the storage of the grains. These damages result in the reduction of the quality attributes of the flour and the isolated starch of corn. It was shown that high drying temperatures cause a series of negative effects, which increase if storage conditions present higher temperatures and grain moisture contents.

4.1.2 Feed

The quality of corn intended for animal feed is also affected by storage conditions and can be measured through the digestibility of its constituents. The protein and starch digestibility of corn stored for 6 months at different temperatures (10, 25, and 45 ºC) was presented by Rehman et al. (2002). Protein digestibility ranged from 76.4 to 77.9% and starch digestibility ranged from 56.2 to 57.7% and was not altered during 6 months of storage at 10 ºC. However, protein and starch digestibility decreased when the corn was stored at 25 and 45 ºC. In 6 months of storage, protein digestibility reduced from 77.0 to 73.0% in corn stored at 25 ºC and from 77.0 to 70.0% in corn stored at 45 ºC and starch digestibility reduced from 57.7 to 52.0% in corn stored at 25 ºC and from 57.5 to 49.0% in corn stored at 45 ºC.

The reduced protein and starch digestibility may be the result of Maillard reactions. In this case, free amino acid groups and reducing sugar carbonyl groups form complex intermediate compounds, which interact during storage. These compounds inhibit the activity of proteolytic and amylolytic enzymes, reducing the corn digestibility (Rehman et al. 2002) and their use as feed.

The effects of variety and storage time on the digestibility of nutrients and the digestible and metabolizable energy content of corn fed to growing pigs was studied by Zhang et al. (2017). In this study, four corn varieties were used (LS1 = soft, LS2 = intermediate hardness, LS3 = hard, and LS4 = intermediate hardness). The grains were dried in the sun until reaching a moisture content of 14% and storage was carried out in a warehouse for 0, 3, and 10 months.

When comparing corn varieties, corn with floury endosperm (soft) stands out concerning corn with flint endosperm (hard). Grains with floury endosperm are more suitable for feed production due to higher digestible energy, metabolizable energy, and apparent digestibility of the total tract of nutrients (Li et al. 2014; Zhang et al. 2016; Zhang et al. 2017).

Throughout the storage time, Zhang et al. (2017) reported an increase of 1.9 (0 months) and 20.5% (3 months) of digestible energy and metabolizable energy, respectively. However, there was a reduction of 3.7 and 20.7% in digestible energy and metabolizable energy, respectively, from 3 to 10 months of storage. Also, the authors reported that the differences in the digestible and metabolizable energy of the different varieties of corn during storage were not significant. This indicates that storage conditions can affect all corn varieties and therefore must be monitored and controlled.

The reduction in digestible and metabolizable energy after 3 months of storage is related to the temperature increase in the final period of storage, reaching a maximum temperature of 29.8 ºC (8 months) and in 10 months it was at an average temperature of 15.2 ºC. Also, corn storage alters the activity and properties of endogenous enzymes, such as amylases and phosphatase, which can influence the nutritional composition of the grains. Thus, the alteration of the starch structure and function and the alteration of the enzyme activity and properties helped to the alterations presented (Zhang et al. 2017).

To reduce the cost of pig production, for example, corn that contains higher levels of digestible and metabolizable energy should be used, as long as prices are compatible (Zhang et al. 2016).

4.1.3 Ethanol

It was seen that the corn drying conditions modify the ethanol yield produced. Besides, according to Coradi et al. (2016a), corn storage conditions also interfere with the ethanol yield produced. Corn storage is necessary for industrial ethanol operations to take place throughout the year.

In general, ethanol production is lower during the first month after the corn harvest. Depending on storage conditions, ethanol production may be higher in grains stored for 6-7 months and reduced in grains stored for 12 months or more. The difference between ethanol yields in the second and fourth quarters can be 6.8%. Coradi et al. (2016a) stored the corn under ambient conditions (at 23 ºC and relative humidity of 60%) and refrigeration (at 10 ºC and relative humidity of 40%).

As previously mentioned, the ethanol yield is related to the starch extraction yield and decreases with increasing drying temperature, and further reduces during storage. The ethanol yield decreased from 389.83 to 355.49 L/t, from 378.29 to 344.57 L/t, and from 366.40 to 332.80 L/t for dried corn at 80, 100, and 120 ºC, respectively, and stored for 6 months at 23 ºC. The reduction in ethanol yield after 6 months of storage at 10 ºC was lower. In this storage condition, the ethanol yield decreased from 389.83 to 388.63 L/t, from 378.29 to 377.60 L/t, and from 366.40 to 365.77 L/t for dried corn at 80, 100, and 120 ºC, respectively (Coradi et al. 2016a).

These reductions are associated with changes in the pasting, crystallinity, and thermal properties of the starch. Paraginski et al. (2014b) cited that the increase in the storage temperature of corn increased the energy required for the gelatinization of the starch granules and a lower peak and final viscosity of the starch. These changes in starch properties have a direct influence on the reduction of corn ethanol yield (Coradi et al. 2016a).

4.2 Innovative drying and storage techniques

Innovative drying techniques such as infrared, microwave, vacuum drying, and other combined methods, also called hybrid and assisted drying, are increasingly gaining ground in post-harvest grain. Some studies presented alternative drying methods and reported advantages over conventional methods, combining energy efficiency and maintenance of the initial quality of the dry product.

Infrared drying has advantages over conventional drying such as lower drying times, uniform temperature, superior quality products, high degree of process control, high heat transfer coefficient, space-saving, and lower energy cost. To preserve the initial quality of the product, lower temperatures can be used and with lower drying times when compared to conventional methods (Bualuang et al., 2012; Nourmohamadi-Moghadami et al., 2017).

By combining different processes, Łechtańska et al. (2015) evaluated hybrid drying techniques, optimizing drying quality, kinetics, and energy consumption. The authors used convection, microwave, and infrared drying, separately and in combination. By joining different physical processes, the authors reported lower drying times when combining microwave and infrared radiation convection drying methods, with a reduction of up to 76% in drying time, when compared to drying with hot air flow.

In the microwave convection drying method, there are advantages compared to conventional drying methods, such as lower energy consumption, higher penetration of waves in the grains, and uniformity in the reduction of moisture content.

In the drying process using the microwave, the removal of moisture occurs due to the application of energy. This method only needs 20% and 35% of drying space compared to other methods (Kouchakzadeh & Shafeei, 2010). Drying time can be reduced to 50% or more, although this depends on the grain and drying conditions. In microwave drying, the generation of heat leads to an increase in the internal temperature and pressure of the grain, which accelerate the flow of water to the surface. However, the drying rate is increased (Shen et al., 2020).

Drying corn grains with microwave heating can be an alternative to preserve some parameters of the processed product, such as flour. Microwave-dried corn grains between 6 and 15 min showed lighter flours when compared to the conventional continuous drying method, which may be desirable, depending on the application (Velu et al., 2006). Nair et al. (2011) evaluated the drying of corn grains intermittently and continuously by microwave, varying the intensity of the equipment between 2 and 4 W/g and with a controlled temperature (constant) between 30 and 50 °C. The authors found that continuous microwave drying with fixed power had lower germination rates (0%) when compared to dry grains with constant temperature (99.5%).

Vacuum drying is a technique with potential application for heat-sensitive food products, as it requires lower pressure and temperature in environments with low oxygen content. Usually, this technique is associated with other drying methods, such as microwaves or infrared irradiation. Due to the use of lower pressure, the drying temperature can be reduced, and thus the higher quality product is obtained compared to convective drying using atmospheric pressure (Menon et al., 2020; Wray & Ramaswamy, 2015).

The quality of vacuum-dried grains is higher than in other methods because the boiling point of water is lowered under vacuum, raising the temperature inside the dry particles compared to the surface of the product. This phenomenon increases the partial pressure that takes the water from evaporation to the outer layer. Heat-sensitive materials can be dried under a vacuum because the system temperature is kept below 75 °C (Menon et al., 2020; Wray & Ramaswamy, 2015). Another alternative method of drying can be radiofrequency heating, which involves the transfer of electromagnetic energy directly to the product (Piyasena et al., 2003). Its use in grains occurs in combination with hot air flow to improve heating uniformity, shorter drying time, and greater treatment efficiency (Xie et al., 2020).

In a study developed by Hassan et al. (2019), it was verified that the use of radiofrequency (27.12 MHz and 3kW) in corn grains, with temperatures of 50, 55, and 60 °C, did not change the water absorption capacity and increased the absorption capacity of oil, emulsifying capacity, emulsifying activity, and emulsion stability, when the grains were submitted to 55 and 60 °C, concerning grains that were not submitted to the thermal process. The technique also allows for enzymatic stabilization in bran, as reported by Liao et al. (2020). The industrial application of these technologies is still difficult to apply, due to the high cost, compared to other drying methods. However, the reduction in drying time increased energy efficiency, and possible beneficial effects on the product allow the advancement of these methodologies. In this way, the transfer of knowledge to the grain drying industry must be carried out, so that the methods can be applied in an assisted or hybrid way to conventional convection methods.

Some innovative techniques are being used to store corn grains. UV-C radiation (254 nm) was used for the control of weevil (*Sitophilus zeamais Motschulsky*). The study was developed by Ferreira et al. (2018) and it was reported that UV-C radiation can be used as a control of adult weevils, as it presented a lower number of live adult weevils (33.6 counts), reduced grain mass loss (15 g), and lower grains. Damaged content (12.9%). Ferreira et al. (2018) highlighted that UV-C radiation was effective for the control of adult insects and that this technology is free of chemical residues, allowing the processing of grains at any time. In addition to insect control, UV-C radiation is an alternative for controlling fungi and reducing mycotoxins in stored grains (Ferreira et al., 2021).

5 Conclusion

For the drying step to be operationally efficient and for minimal changes to occur in protein solubility, starch extraction yield, pasting properties, and gelatinization enthalpy of starch and flour it is indicated that the drying of the corn is carried out at a temperature below 60 ºC. During storage, the moisture content must be less than 14% and it is indicated that the storage temperature is below 25 ºC. Thus, there will be less proliferation of storage fungi, less content of free fatty acids and acidity of the flour, and less gelatinization enthalpy of starch granules. Also, favorable storage conditions result in higher solubility of sugars, lysine, thiamine, and protein solubility of flour and higher extraction yield of starch. The same indications are valid for corn intended for the production of animal feed.

The ethanol yield decreases as the drying temperature of the corn increases. During storage, ethanol yield is reduced, but storage of grains under refrigeration (10 °C) is indicated.

Further studies are needed to assess the effects of the drying and storage conditions of corn on the properties of flour, starch, animal feed, and, mainly, on ethanol production. On drying, studies are needed to evaluate factors such as the drying method, grain temperature, and air on a real scale. On storage, in addition to evaluating the factors mentioned in this review (temperature, moisture content, and time), new studies should present the interactions between factors such as the presence of insects in the grain mass, cleaning of silos before storage, and aeration time of the grains. All of these factors can affect the quality of products generated from corn.

References

Anderson B, Almeida H (2019). Corn Dry Milling: Processes, Products, and Applications. In: Serna-Saldivar SO (ed) Corn Chemistry and Technology. Elsevier, pp. 405-433. https://doi.org/10.1016/B978-0-12-811971-6.00015-2

Bualuang O, Tirawanichakul Y, Tirawanichakul S (2012) Comparative study between hot air and infrared drying of parboiled rice: Kinetics and qualities aspects. J. Food Process. Preserv. 37:1119–1132. https://doi.org/10.1111/j.1745-4549.2012.00813.x

Coradi PC, Milane LV, Camilo LJ, Andrade MGO (2016a) Drying and storage of corn grains for ethanol production in Brazil. Bioscience J. 32(5):1175-1190. https://doi.org/10.14393/BJ-v32n5a2016-32754

Coradi PC, Maldaner V, Lutz E, Daí PVS, Teodoro PE (2020a) Influences of drying temperature and storage conditions for preserving the quality of maize postharvest on laboratory and field scales. Sci. Rep. 10:e22006. https://doi.org/10.1038/s41598-020-78914-x

Coradi PC, Lima RE, Padia CL, Alves CZ, Teodoro PE, Cândido ACS (2020b) Soybean seed storage: Packaging technologies and conditions of storage environments. J. Stored Prod. Res. 89:101709. https://doi.org/10.1016/j.jspr.2020.101709

Coradi PC, Oliveira MB, Carneiro LO, Souza GAC, Cardoso MC, Brackmann A, Teodoro PE (2020c) Technological and sustainable strategies for reducing losses and maintaining the quality of soybean grains in real production scale storage units. J. Stored Prod. Res. 87:101624. https://doi.org/10.1016/j.jspr.2020.101624

Costa, A.R., Faroni, L.R.D., Alencar, E.R., Carvalho, M.C.S, Ferreira, L.G., 2010. Quality of corn grains stored in bag silos. Rev. Ciên. Agron. 41(2), 200-207. https://doi.org/10.1590/S1806-66902010000200005

Ferreira CD, Lang GH, Lindemann IS, Timm NS, Hoffmann JF, Ziegler V Oliveira M (2021) Postharvest UV-C irradiation for fungal control and reduction of mycotoxins in brown, black, and red rice during long-term storage. Food Chemistry 339:127810. https://doi.org/10.1016/j.foodchem.2020.127810

Ferreira CD, Ziegler V, Goebel JTS, Lang GH, Elias MC, Oliveira M (2018) Quality of grain and oil of maize subjected to UV-C radiation (254 nm) for the control of weevil (Sitophilus zeamais Motschulsky). Journal of Food Processing and Preservation 42: e13453. https://doi.org/10.1111/jfpp.13453

Forti VA, Cícero SM, Pinto TLF (2010) Evaluation of the evolution of 'moisture' damage and reduced vigor in soybean seeds, cultivate TMG 113-RR, during storage, using X-ray images and physiological potential tests. Rev. Bras. Sem. 32(3):123-133. http://dx.doi.org/10.1590/S0101-31222010000300014

Hassan AB, von Hoersten D, Mohamed Ahmed IA (2019) Effect of radio frequency heat treatment on protein profile and functional properties of maize grain. Food Chemistry, 27:142–147. https://doi.org/10.1016/j.foodchem.2018.07.190

Huart F, Malumba P, Odjo S, Al-Izzi W, Béra F, Beckers Y (2018) In vitro and in vivo assessment of the effect of initial moisture content and drying temperature on the feeding value of maize grain. J. British Poult. Sci. 59:452-462. https://doi.org/10.1080/00071668.2018.1477253

Jalali M, Sheikholeslami Z, Elhamirad AH, Khodaparas, MHH, Karimi, M (2020) The effect of the ultrasound process and pre-gelatinization of the corn flour on the textural, visual, and sensory properties in gluten-free pan bread. J Food Sci Technol 57:993–1002. https://doi.org/10.1007/s13197-019-04132-7

Kaczmarek SA, Cowieson AJ, Józefiak D, Rutkowski A (2014) Effect of maize endosperm hardness, drying temperature and microbial enzyme supplementation on the performance of broiler chickens. Animal Prod. Sci. 54(7):956-965. https://doi.org/10.1071/AN13113

Kouchakzadeh A, Shafeei S (2010) Modeling of microwave-convective drying of pistachios. Energy Conversion and Management 51(10):2012–2015. https://doi.org/10.1016/j.enconman.2010.02.034

Łechtańska JM, Szadzińska J, Kowalski SJ (2015) Microwave- and infrared-assisted convective drying of green pepper: Quality and energy considerations. Chemical Engineering and Processing: Process Intensification. 98:155–164. https://doi.org/10.1016/j.cep.2015.10.001

Li Q, Shi M, Shi C, Liu D, Piao X, Li D, Lai C (2014) Effect of variety and drying method on the nutritive value of corn for growing pigs. J. Animal Sci. Biotechn. 5(1):18-24. https://doi.org/10.1186/2049-1891-5-18

Li Y, Duan R, Shi F, Wang L, Chen Z (2017) Effects of High-Temperature Air Fluidization (HTAF) on the Structural, Functional, and in Vitro Digestive Properties of Corn. Starch, 69:1–8. https://doi.org/10.1002/star.201600137

Liao M, Damayanti W, Xu Y, Zhao Y, Xu X, Zheng Y, Jiao S (2020) Hot air-assisted radio frequency heating for stabilization of rice bran: Enzyme activity, phenolic content, antioxidant activity and microstructure. Lwt, 131:109754. https://doi.org/10.1016/j.lwt.2020.109754

Malumba P, Vanderghem C, Deroanne C, Béra F (2008) Influence of drying temperature on the solubility, the purity of isolates and the electrophoretic patterns of corn proteins. Food Chem. 111:564-572. https://doi.org/10.1016/j.foodchem.2008.04.030

Malumba P, Janas J, Masimango T, Sindic M, Deroanne C, Béra F (2009a) Influence of drying temperature on the wet-milling performance and the proteins solubility indexes of corn kernels. J. Food Eng. 95:393-399. https://doi.org/10.1016/j.jfoodeng.2009.05.022

Malumba P, Massaux C, Deroanne C, Masimango T, Béra F (2009b) Influence of drying temperature on functional properties of wet-milled starch granules. Carbohydr. Polym. 75:299-306. https://doi.org/10.1016/j.carbpol.2008.07.027

Malumba P, Odjo S, Boudry C, Danthine S, Bindelle J, Beckers Y, François B (2014) Physicochemical Characterization and in Vitro Assessment of the Nutritive Value of Starch Yield from Corn Dried at Different Temperatures. Starch. 66:738–748. https://doi.org/10.1002/star.201400012

Manochio C, Andrade BR, Rodriguez RP, Moraes BS (2017) Ethanol from biomass: A comparative overview. Ren. Sustain. Energ. Rev. 80:743-755. http://doi.org/10.1016/j.rser.2017.05.063

Marinho CM, Lemos COT, Arvelos S, Barrozo MAS, Hori CE, Watanabe EO (2019) Extraction of corn germ oil with supercritical CO2 and cosolvents. J Food Sci Technol 56:4448–4456. https://doi.org/10.1007/s13197-019-03923-2

Menon A, Stojceska V, Tassou SA (2020) A systematic review on the recent advances of the energy efficiency improvements in non-conventional food drying technologies. Trends in Food Science and Technology. 100: 67–76. https://doi.org/10.1016/j.tifs.2020.03.014

Nair GR, Li Z, Gariepy Y, Raghavan V (2011) Microwave drying of corn (Zea mays L. ssp.) for the seed industry. Drying Technology. 29(11):1291–1296. https://doi.org/10.1080/07373937.2011.591715

Nourmohamadi-Moghadami A, Rahmanian-Koushkaki H, Zare D, Karimi G (2017) Experimental and theoretical investigation of hot air- infrared thin layer drying of corn in a fixed and vibratory bed dryer. Eng. Agr. Environ. Food. 10(3):191-197. https://doi.org/10.1016/j.eaef.2017.01.004

Odjo S, Malumba P, Dossou J, Janas S, François B (2012) Influence of Drying and Hydrothermal Treatment of Corn on the Denaturation of Salt-Soluble Proteins and Color Parameters. J. Food Eng. 109:561–570. https://doi.org/10.1016/j.jfoodeng.2011.10.023

Odjo S, Huart F, Béra F, Jacquet N, Richel A, Blecker C, Malumba P (2017) Influence of Corn Variety, Drying Temperature, and Moisture Content at Harvest on the Saccharides Released during an in Vitro Pepsin-Pancreatin Digestion. Starch 69:e1600292. https://doi.org/10.1002/star.201600292

Odjo S, Béra F, Beckers Y, Foucart G, Malumba P (2018) Influence of variety, harvesting date and drying temperature on the composition and the in vitro digestibility of corn grain. J. Cereal Sci. 79:218-225. https://doi.org/10.1016/j.jcs.2017.10.008

Paraginski RT, Vanier NL, Berrios JJ, Oliveira M, Elias MC (2014a) Physicochemical and pasting properties of maize as affected by storage temperature. J. Stored Prod. Res. 59:209-214. https://doi.org/10.1016/j.jspr.2014.02.010

Paraginski RT, Vanier NL, Moomand K, Oliveira M, Zavareze ER, Silva RM, Ferreira CD, Elias MC (2014b) Characteristics of starch isolated from maize as a function of grain storage temperature. Carbohydr. Polym. 102:88-94. https://doi.org/10.1016/j.carbpol.2013.11.019

Paraginski1 RT, Rockenbach BA, Santos RF, Elias MC, Oliveira M (2015) Quality of corn kernels stored at different temperatures. Rev. Bras. Eng. Agr. Amb. 19(4):358–363. https://doi.org/10.1590/1807-1929/agriambi.v19n4p358-363

Paraginski RT, Colussi R, Dias AG, Zavareze E, Elias MC, Vanier NL (2019) Physicochemical, pasting, crystallinity, and morphological properties of starches isolated from maize kernels exhibiting different types of defects. Food Chem. 274:330-336. https://doi.org/10.1016/j.foodchem.2018.09.026

Piyasena P, Dussault C, Koutchma T, Ramaswamy HS, Awuah GB (2003) Radio Frequency Heating of Foods: Principles, Applications and Related Properties - A Review. Critical Reviews in Food Science and Nutrition. 43(6):587–606. https://doi.org/10.1080/10408690390251129

Rausch KD, Hummel D, Johnson LA, May JB (2019) Wet Milling: The Basis for Corn Biorefineries. In: Serna-Saldivar SO (ed) Corn Chemistry and Technology. Elsevier, pp. 501-535. https://doi.org/10.1016/B978-0-12-811971-6.00018-8

Reed C, Doyungan S, Ioerger B, Getchell A (2007) Response of storage molds to different initial moisture contents of maize (corn) stored at 25 °C, and effect on respiration rate and nutrient composition. J. Stored Prod. Res. 43:443–458. https://doi.org/10.1016/j.jspr.2006.12.006

Rehman ZU, Habib F, Zafar SI (2002) Nutritional changes in maize (Zea mays) during storage at three temperatures. Food Chem. 77:197-201. https://doi.org/10.1016/S0308-8146(01)00337-5

Reicks G, Woodard HJ, Bly A (2009) Improving the fermentation characteristics of corn through agronomic and processing practices. Agron. J. 101:201–206. https://doi.org/10.2134/agronj2007.0398

Setiawan S, Widjaja H, Rakphongphairoj V, Jane J (2010) Effects of Drying Conditions of Corn Kernels and Storage at an Elevated Humidity on Starch Structures and Properties. J. Agr. Food Chem. 58:12260–12267. http://doi.org/10.1021 / jf102838j

Shen L, Wang L, Zheng C, Liu C, Zhu Y, Liu H, Liu C, Shi Y, Zheng X, Xu H (2020). Continuous microwave drying of germinated brown rice: Effects of drying conditions on fissure and color, and modeling of moisture content and stress inside kernel. Drying Technology, 669-697. https://doi.org/10.1080/07373937.2019.1705331

Suleiman R, Bern CJ, Brumm TJ, Rosentrater KA (2018) Impact of moisture content and maize weevils on maize quality during hermetic and non-hermetic storage. J. Stored Prod. Res. 78:1-10. https://doi.org/10.1016/j.jspr.2018.05.007

Timm NS, Lang GH, Ramos AH, Pohndorf RS, Ferreira CD, Oliveira M (2020a) Effects of drying methods and temperatures on protein, pasting, and thermal properties of white floury corn. J. Food Proc. Preserv. 44:e14767. https://doi.org/10.1111/jfpp.14767

Timm NS, Ramos AH, Ferreira CD, Biduski B, Eicholz ED, Oliveira M (2020b) Effects of drying temperature and genotype on morphology and technological, thermal, and pasting properties of corn starch. Intern. J. Biol. Macrom. 165:354-364. https://doi.org/10.1016/j.ijbiomac.2020.09.197

Timm NS, Ramos AH, Ferreira CD, Rios AO, Zambiazi R, Oliveira M (2021) Influence of germ storage from different corn genotypes on technological properties and fatty acid, tocopherol, and carotenoid profiles of oil. Eur Food Res Technol 247:1449–1460. https://doi.org/10.1007/s00217-021-03723-z

Trehan S, Singh N, Kaur A (2018) Characteristics of white, yellow, purple corn accessions: phenolic profile, textural, rheological properties and muffin making potential. J Food Sci Technol 55:2334–2343. https://doi.org/10.1007/s13197-018-3171-5

Velu V, Nagender A, Prabhakara Rao PG, Rao DG (2006) Dry milling characteristics of microwave dried maize grains (Zea mays L.). Journal of Food Engineering 74(1):30–36. https://doi.org/10.1016/j.jfoodeng.2005.02.014

Walker S, Jaime R, Kagot V, Probst C (2014) Comparative effects of hermetic and traditional storage devices on maize grain: mycotoxin development, insect infestation and grain quality. J. Stored Prod. Res. 77:34-44. https://doi.org/10.1016/j.jspr.2018.02.002

Wray D, Ramaswamy HS (2015) Novel Concepts in Microwave Drying of Foods. Drying Technology. 33(7):769–783. https://doi.org/10.1080/07373937.2014.985793

Xie Y, Zhang Y, Xie Y, Li X, Liu Y, Gao Z (2020). Radio frequency treatment accelerates drying rates and improves vigor of corn seeds. Food Chemistry, 319:126597. https://doi.org/10.1016/j.foodchem.2020.126597

Zhang L, Li YK, Li ZC, Li QF, Lyu MB, Li DF, Lai CH (2016) The Nutritive Values in Different Varieties of Corn Planted in One Location Fed to Growing Pigs over

Three Consecutive Years. Asian-Australasian J. Animal Sci. 29(12):1768-1773. https://10.5713/ajas.16.0052

Zhang L, Liu L, Li D, Li Q, Piao X, Tracker PA, Brown MA, Lai C (2017) Effects of variety and storage duration on the nutrient digestibility and the digestible and metabolisable energy content of maize fed to growing pigs. Arch. Anim. Nutr. 71:67-80. https://doi.org/10.1080/1745039X.2016.1226034

Ziegler V, Timm NS, Ferreira CD, Goebel JT, Pohndorf RS, Oliveira M (2020) Effects of drying temperature of red popcorn grains on the morphology, technological, and digestibility properties of starch. Intern. J. Biol. Macrom. 145:568-574. https://doi.org/10.1016/j.ijbiomac.2019.12.198

CHAPTER 2 – EFFECTS OF DRYING TEMPERATURE OF CORN FROM THE CENTER AND EXTREMITIES OF THE CORNCOB ON DRYING PARAMETERS, PROTEIN AND STARCH PROPERTIES, AND CAROTENOID PROFILE

Abstract

The corn grains from the extremities of corncob are known to have a spherical shape and the grains from the center of corncob have higher length and less thickness. It is understood that these differences in grain dimensions can affect post-harvest processes and the properties of the grains. Therefore, the objective was to evaluate the effects of drying temperature (60, 80, and 100 ºC) of corn from the center and extremities of corncob on drying parameters, protein and starch properties, and carotenoid profile. At 60 ºC, the drying rate and effective moisture diffusivity of corn from the center and extremities of the corncob did not differ. However, at 80 and 100 ºC these parameters were higher in the corn from the center. Corncob part and separation did not significantly affect corn pasting properties. However, they caused significant changes in the properties of the grain proteins, mainly the reduction of the solubility and inactivation of the lipase enzyme, and the reduction of the lutein and β-carotene contents in the grains from the center and separated after drying. The results of this research show the need to evaluate the effects of these drying conditions during grain storage. In addition, the implementation of an industrial separation step and/or the development of new corn cultivars with more homogeneous grains should be studied.

Keywords: *Zea mays L.; molecular weight of proteins; lutein; pasting temperature.*

1 Introduction

Corn (*Zea mays* L.) is the most produced cereal in the world and is used in several areas, whether in the use of whole grains or derivatives of their components, isolated or industrially processed (Jalali, Sheikholeslami, Elhamirad, Khodaparas, & Karimi, 2020; Trehan, Singh, & Kaur, 2018). Corn grains are normally harvested at 18-30% moisture content, making it necessary to dry these grains to 12-14% moisture content for safe grain storage. Drying stands out as one of the main operations in the post-harvest stages of corn (Coradi, Maldaner, Lutz, Dai, & Teodoro, 2020).

During drying, the temperature of the drying air and grain mass, the initial and final grain moisture, the air and grain flow in the dryer, and the ambient air conditions must be monitored and controlled (Coradi, Nunes, Bellochio, Camilo, & Teodoro, 2021; Nunes et al., 2021). Among these drying parameters, the temperature of the drying air is the main one. Some studies have reported that, as the drying temperature of corn grains increases, there is a reduction in the total solubility of proteins (Timm et al., 2020a) and the fractions of zeins, albumins, and globulins (Malumba, Vanderghem, Deroanne, & Bera, 2008).

In the same way that the properties of the proteins are affected according to the increase in the drying temperature of the corn, the quality of the flour and the starch isolated from these grains also change. In this case, there is mainly a reduction in the starch extraction yield and a reduction in the peak viscosity, and an increase in the pasting temperature of the flour and the starch (Malumba, Massaux, Deroanne, Masimango, & Béra, 2009; Malumba et al., 2009b; Timm et al., 2020a; Timm et al., 2020b). Drying conditions can also affect the digestibility properties of corn protein and starch, which alters the yield of this product in animal feed (Huart et al. 2018; Malumba et al. 2014). In addition to its use in human and animal feed, corn is used for ethanol production, which is also affected by drying conditions (Coradi, Milane, Camilo, & Andrade, 2016).

All these studies considered the corn grains to be homogeneous in the total grain mass. However, the insertion of grains along a corncob originates grains with different dimensions, with the grains from the extremities of the corncob having a spherical shape and the grains from the center having a higher length and less thickness. These differences in grain dimensions can affect the properties of the corn as the drying kinetics may be different between grains at the center and the extremities. In addition, the consistency of the endosperm of the corn from the center and extremities can be different, where the grains from the extremities present a higher presence of vitreous endosperm, which can modify the drying parameters and the effects of the operation on the quality of the grains (Muthukumarappan & Gunasekaran, 1994).

Therefore, the objective was to evaluate the effects of drying temperature (60, 80, and 100 ºC) of corn from the center and extremities of corncob on drying parameters, protein and starch properties, and carotenoid profile.

2 Material and methods

2.1 Material

Yellow flint corn (Pioneer P3016 VYHR) was used, harvested in Canguçu, the Rio Grande do Sul, Brazil, in the crop year 2019/2020. Immediately after harvesting, grains were packed in plastic bags and transported to the Laboratory of Postharvest (LAPOS) at Federal University of Santa Maria (UFSM), Campus Cachoeira do Sul, where drying experiments were carried out.

Table 1 presents the physical properties and chemical composition of corn from the center and extremities of the corncob. The physical properties were determined according to Mohsenin (1986) and the chemical properties were determined using the NIRS equipment (Near Infrared Reflectance Spectroscopy, DS2500, FOSS, Brazil). The grains from the center and extremities of the corncob were manually separated. This separation was standardized by defining corncob areas. Therefore, the grain area at the center of the corncob and the areas of the grain at the extremities of the corncob were defined, as illustrated in Supplementary Material 1.

Table 1. Physical properties and chemical composition of corn from the center and extremities of the corncob.

Corncob part	Extremities corn	Center corn
	Physical properties	
Length (mm)	11.94	13.06
Width (mm)	9.15	9.06
Thickness (mm)	5.81	5.23
Bulk density (kg/m^3)	702.33	712.33
Unit mass (g)	0.35	0.38
Volume (mm^3)	276.67	296.67
Equivalent radium (mm)	4.30	4.26
Sphericity	0.72	0.65
	Chemical composition	
Protein (%)	8.63	9.24
Fat (%)	3.92	4.03
Fiber (%)	2.58	2.45
Ash (%)	1.43	1.36
Starch (%)	83.44	82.92

Figure 1 shows a graphic summary of the sample preparation for the experiment. Initially, the grains were threshed into three groups: (1) grains from the center of the corncob (10 kg), (2) grains from the extremities of the corncob (10 kg), and (3) grains from the center and extremities together (20 kg). The threshed corn was then cleaned and the initial moisture content of the grains was measured in an oven at 140 ºC for 3 h (ASAE, 2000).

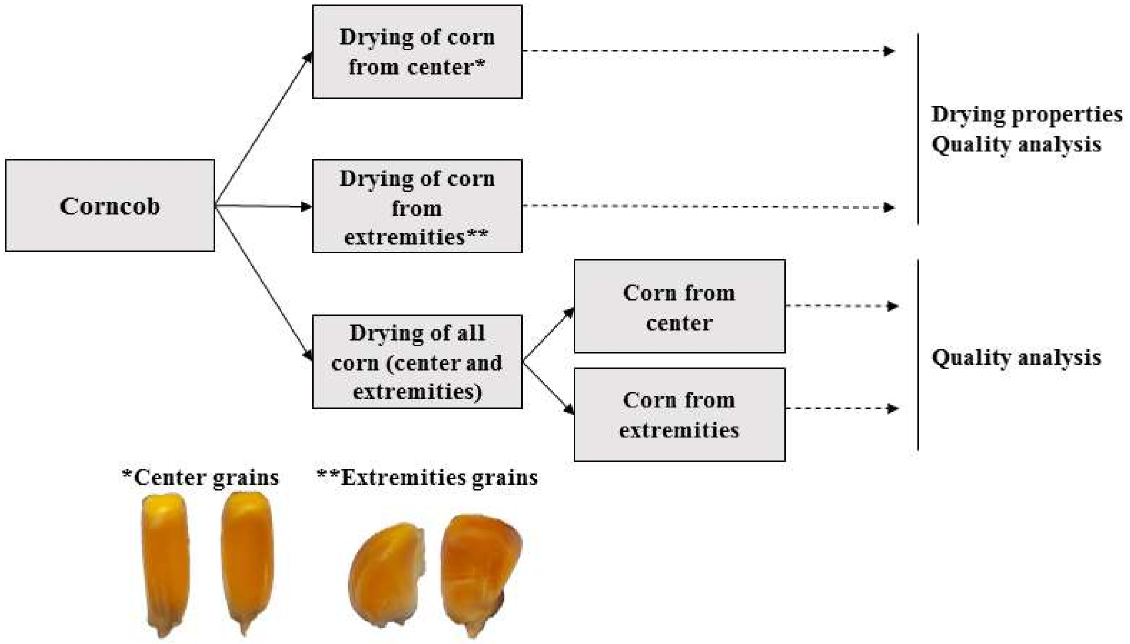


Figure 1. Graphical summary of the preparation of corn samples for experimenting.

The drying was carried out in these three groups of samples, being the group 1 and the group 2 denominated as separate corn before drying, where the grains from the center and extremities were dried and evaluated separately. Group 3, which consists of grains from the center and extremities together, was subjected to drying in this way. After drying, the grains from the center and extremities of the corncob were separated and analyses were performed. This group was called separation after drying. The separation of the corn from the center and extremities of group 3 was performed using a digital caliper, according to the grain dimensions shown in Table 1.

2.2 Drying conditions, moisture ratio, drying rate, and moisture diffusivity

The grains with an initial moisture content of 31.90±0.20% were dried at different temperatures (60, 80, and 100 ºC) in an experimental fixed bed dryer, with an airflow rate of 0.5 m s^{-1}, until reaching a water content of 13.00±0.20%. In all treatments the water content was monitored by the difference in mass, following Eq. 1, where wf is the final weight of the sample (g), wi is the initial weight of the sample (g), mi is the initial moisture (g g^{-1}), and mf the final moisture (g g^{-1}).

$$wf = wi \times \left(\frac{100-}{100-mf}\right) \quad (1)$$

For each treatment, the parameters of moisture ratio, drying rate, and moisture diffusivity were calculated. The moisture ratio was calculated based on the equilibrium moisture content of the grains at each drying temperature using the modified Henderson equation (Eq. 2), considering the parameters of air humidity and temperature collected during drying. The equilibrium moisture (Xe) is calculated by the relative humidity of the drying air (RH), the temperature of the drying air (T), and the parameters a = -0.00003074, b = 273.15, and c = 1.8156 previously stipulated for corn grains according to ASAE D245.5 (ASAE, 1995).

$$X_e = \frac{(0.01*(ln(1-RH))}{(a*(T+b))^{(1/c)}} \qquad (2)$$

The dimensionless moisture ratio was calculated through Eq. (3), where X is the moisture content at each instant, Xe is the calculated equilibrium moisture, and X_0 is the initial grain moisture, before drying.

$$MR = \frac{(X-X_e)}{(X_0-X_e)} \qquad (3)$$

To investigate the kinetic behavior of the corn drying the mathematical model represented by the Brooker equation (Eq. 4) was used. This equation is suitable for cereals, especially for drying corn grains (Brooker, Bakker-Arkem, & Hall, 1974), where k drying constant (m m^{-1}), t is the drying time (min), and C is the model coefficient.

$$MR = C\exp(-kt) \qquad (4)$$

The drying rate was calculated by Eq. 5, where t is the drying time (min), X is the moisture content in t, X_i is the initial grain moisture in time t_i, and X_{i+1} is the moisture content at time t_{i+1}.

$$\frac{dX}{dt} = \frac{(X_{i+1}-X_i)}{(t_{i+1}-t_i)} \qquad (5)$$

Corn moisture diffusivities were estimated by the diffusion equation (Fick's law) and the slope method. Corn grains were considered spherical particles and the moisture diffusion mechanism was represented by Eq.6, suitable for corn (Brooker, Bakker-Arkem, & Hall, 1974).

$$\frac{\partial X}{\partial t} = D_{eff}\left(\frac{\partial^2 X}{\partial r^2} + \frac{2}{r}\frac{\partial X}{\partial r}\right) \qquad (6)$$

According to Crank (1975), an analytical solution of Eq. 6 can be obtained assuming some conditions: (a) moisture content should be uniformly distributed throughout the mass of the grain; (b) the mass transfer is symmetric from the center of the sphere; (c) at the beginning of drying, the surface of the grains reaches the equilibrium moisture content; (d) negligible surface resistance for mass transfer; (e) mass transfer occurs by diffusive mechanism; (f) shrinkage of the grains is negligible and the diffusion coefficient is constant during drying. With these assumptions, the initial and boundary conditions are used and the moisture diffusion model of spherical bodies can be solved by Eq. 7 (Crank, 1975), where Deff is the moisture diffusivity ($m^2 s^{-1}$), MR is the moisture ratio (dimensionless), and R is the corn equivalent radius (m).

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(-n^2\pi^2\frac{D_{eff}}{R^2}t\right) \tag{7}$$

2.3 Acidity

Acidity (mg NaOH $100g^{-1}$) was determined according to as described in the AACC method 02-01A (AACC, 2000). The acidity was expressed as the mg of sodium hydroxide required to neutralize the acids in 100 g of sample, using phenolphthalein solution as an indicator.

2.4 Lipase activity

The lipase activity (%) was measured according to Kaur, Ramamurthy, and Kothari (1993) and expressed in the lipolysis percentage (%), based on the saponification index of the substrate.

2.5 Soluble protein

The soluble protein in water was determined according to Liu, McWatters, and Phillips (1992). The nitrogen content was determined by the Kjeldahl method and the resulted nitrogen value was converted to protein using factor 6.25. The soluble protein (%) was expressed in the percentage of total protein content on corn.

2.6 Molecular weight distribution of proteins

The molecular weight distribution of corn proteins was performed according to the methodology described by Buggenhout, Brijs, and Delcour (2013), using liquid chromatography (Prominence UFLC system, Shimadzu, Japan) according to Silva et al. (2017). Determination of molecular weight distribution of proteins was determined at a wavelength of 214 nm using the following chromatographic patterns: phosphorylase b (Molecular weight = 97 kDa/ Retention time = 6.17 min/ region I), bovine serum albumin

(Molecular weight = 66 kDa/ Retention time = 7.00 min/ region II), and pepsin (Molecular weight = 34 kDa/ Retention time = 9.68 min/ region III).

2.7 Carotenoids profile

Individual carotenoids (µg g^{-1}) content was determined according to Mercadante, Rodriguez-Amaya, and Britton (1997) by extracting pigments with acetone and saponifying in a 35% KOH solution (in methanol) overnight at room temperature. The extract was concentrated by rotary evaporation (Heidolph, Laborota Model 4000, Kelheim, Bavaria, Germany) at 25 ºC and stored at 18 ºC for quantification by high performance liquid chromatography (HPLC).

The HPLC analysis was conducted according to Reis et al. (2015). The extract was diluted with methyl tert-butyl ether (MTBE-JT Baker, 99.96% of purity), sonicated (Unique, model USC 1400) for 30 s, and filtered (Millex LCR 0.45 mm, 13 mm) for injection into an Agilent 1100 Series HPLC (Santa Clara, CA, USA) equipped with a quaternary system and a UV detector. The column used was a 250 4.6 mm ID, 3 mm, C30 polymeric reverse phase column (YMC, model CT99SO3-2546WT). The mobile phase gradient (water:methanol:MTBE) (JT Baker, 99.96% of purity) commenced at 5:90:5, reaching 0:95:5 at 12 min, 0:89:11 at 25 min, 0:75:25 at 40 min, and finally 00:50:50 at 60 min. The flow rate was 1 mL.min-1 at 33 ºC. Spectra were obtained between 250 and 600 nm (or at a fixed wavelength of 450 nm for carotenoids).

Compounds were identified by comparing the sample retention times with the retention times obtained for controls. For quantification, a standard curve was constructed for carotenoids over the following ranges: lutein 1-65 µg mL^{-1} (95% of purity, Sigma-Aldrich); zeaxanthin 1-40 µg mL^{-1} (95% of purity, Sigma-Aldrich); cryptoxanthin 4-100 µg mL^{-1} (97% of purity, Sigma-Aldrich); and β-carotene 5-50 µg mL^{-1} (97% of purity, Sigma-Aldrich). The limits of detection (LOD) were as follows. Lutein: 0.037 µg g^{-1}; zeaxanthin: 0,0654 µg g^{-1}; cryptoxanthin: 0.026 µg g^{-1}; and β-carotene: 0.066 µg g^{-1}.

2.8 Pasting properties

The corn grains were grounded in a laboratory mill (Perten 3100, Perten Instruments, Huddinge, Sweden) equipped with 35-mesh sieves to obtain flour samples with uniform particle sizes. The pasting properties of the corn flour (4 g, 14% moisture basis) were determined with a Rapid Visco Analyser (RVA-4; Newport Scientific, Warriewood, Australia) using the RVA profile Standard Analysis 1. The sample was held at 50 ºC for 1 min, heated to 95 ºC for 3.5 min, and held at 95 ºC for 2.5 min. The sample was then cooled to 50 ºC for 4 min and held at 50 ºC for 2 min. The rotating speed was held at 960 rpm for 10 s and then maintained at 160 rpm during the process. The parameters determined were pasting temperature (ºC), peak viscosity (RVU), breakdown (RVU), final viscosity (RVU), and setback (RVU).

2.9 Statistical analysis

The experiment was performed in triplicate, except for the molecular weight distribution of proteins, which was performed only once. The results of the three determinations were submitted to analysis of variance (ANOVA) with 95% reliability. When the independent variables (drying temperature, time of separation, and corncob part) showed significant effects, the splitting into simple effects was performed. Simple effects were observed by t-test (between corn separation and corncob part) and Tukey's test (between drying temperature) with 95% reliability.

3 Results and discussion

3.1 Moisture ratio, drying rate, and moisture diffusivity

In Figure 2 the moisture ratio and the drying rate are presented and in Figure 3 the effective moisture diffusivity is presented. A reduction in drying time (Figure 2A) and an increase in drying rate (Figure 2B) and effective moisture diffusivity (Figure 3) were observed by the increase in drying temperature. Doymaz and Pala (2003) studied the drying characteristics of thin-layer corn at temperatures of 55, 65, and 75 °C. These authors reported a reduction in drying time from 135 min to 70 min with an increase in drying temperature from 55 to 75 ºC. In addition, Doymaz and Pala (2003) reported that increasing the drying temperature from 55 to 75 °C resulted in an increase in moisture diffusivity from 9.488×10^{-11} m² s^{-1} to 17.68×10^{-11} m² s^{-1}. Lang et al. (2018) studied the diffusivity of black rice grains during drying at different temperatures (20-100 °C). Lang et al. (2018) reported an increase in diffusivity from 1.00×10^{-11} m² s^{-1} (20 °C) to 13.00×10^{-11} m² s^{-1} (100 °C), which also resulted in a reduction in drying time.

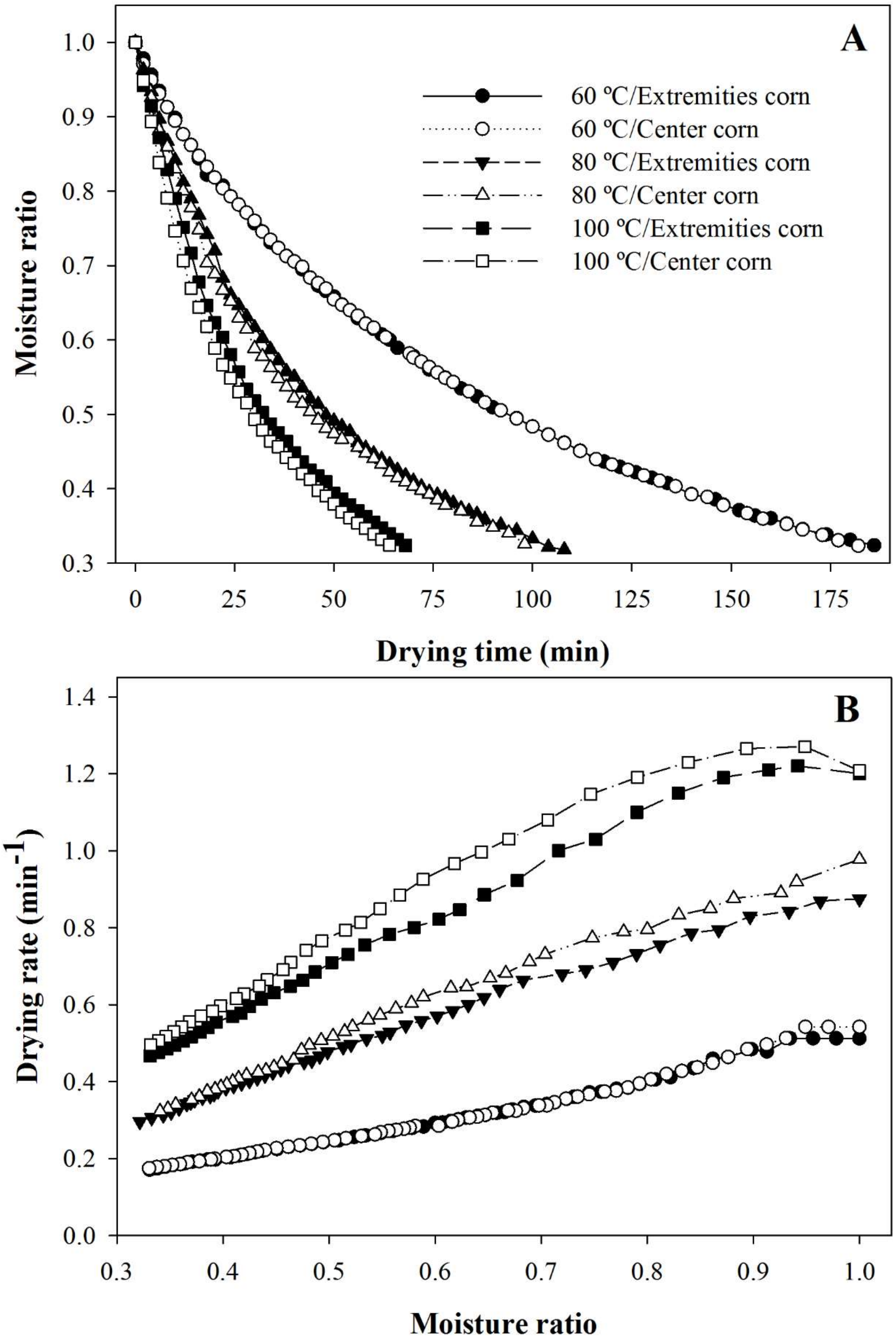


Figure 2. Dimensionless moisture ratio (A) and drying rate (B) of corn grains from center and extremities of corncob subjected to different drying temperatures.

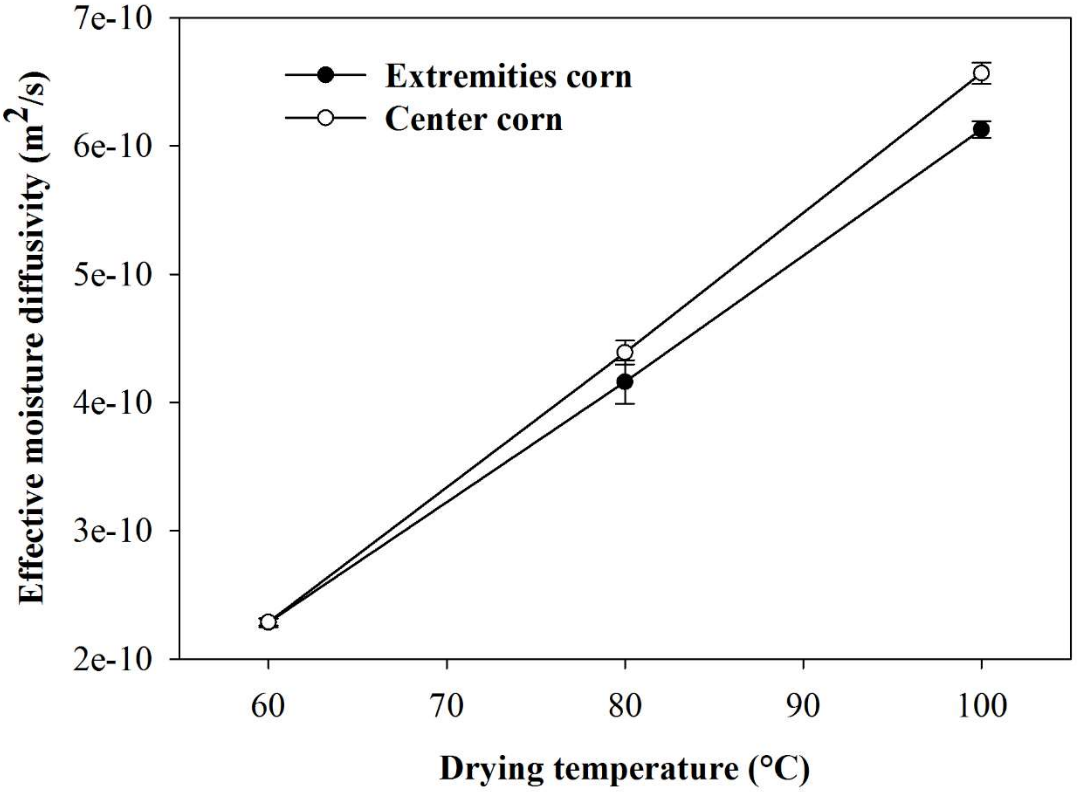


Figure 3. Effective moisture diffusivity of corn grains from center and extremities of corncob subjected to different drying temperatures.

At 60 ºC, drying time, drying rate, and effective moisture diffusivity showed no difference between the grains from the center and extremities of the corncob (Figures 1 and 2). However, when the grains were dried at 80 and 100 ºC, a higher drying rate and effective moisture diffusivity were observed in the grains from the center. These results were due to the lower thickness, equivalent radius, and sphericity of the corn from the center of the corncob (Table 1). Inside the grains, water tends to diffuse through the shortest distance between the interior and the periphery of the grain, thus, in the direction of thickness. In this way, the lower the grain thickness, the easier it will be for water to move from the interior to the periphery and the higher the effective moisture diffusivity, resulting in the acceleration of the drying process of the grains from the center concerning the grains from extremities. These results are in agreement with Tohidi, Sadeghi, and Torki-Harchegani (2017), who reported that the physical structure of grains and the chemical composition of the products can affect the effective moisture diffusivity.

Effective moisture diffusivity corresponds to the magnitude of drying rates affected by drying temperature. Thus, the higher the drying rate (Figure 2B), the higher the effective moisture diffusivity (Figure 3) (Lang et al., 2018; Maldaner et al., 2021; Tohidi et al., 2017). Another characteristic that justifies the higher diffusivity of the grains from the center of the corncob may be related to the consistency of the endosperm of these grains, where the floury endosperm predominates. On the other hand, the grains from the extremities have a higher presence of vitreous endosperm. According to Muthukumarappan and Gunasekaran (1994), the diffusivity of the floury endosperm can be 75 to 79% higher than the diffusivity of the vitreous endosperm.

3.2 Acidity

Analysis of variance showed significant effects ($P < 0.05$) of separation, temperature, and interaction between the variables evaluated on corn acidity. No effects ($P \geq 0.05$) of the corncob part on corn acidity were observed (Supplementary material 2). A tendency of acidity reduction was observed according to the increase in the drying temperature of the grains from the center of the corncob. At 60 and 100 ºC, the grains from the center separated after drying showed higher acidity than the grains separated before drying. No differences were observed in grain acidity at the extremities (Table 2).

These results are in agreement with Coradi et al. (2020), who studied the drying of corn grains at different temperatures (80 – 120 ºC). Coradi et al. (2020) reported that drying at 120 °C resulted in a 26.8% lower acidity index compared to grains dried at 80 °C. The higher acidity index in drying at lower temperatures can be explained by the longer exposure time of the grains to heat (Figure 2A). Thus, the process of hydrolysis of triacylglycerols into free fatty acids is accelerated (Stewart, Ragha, Orsat, & Golden, 2003), which can cause grain fermentation and increase acidity (Coradi et al., 2020).

Table 2. Acidity, lipase activity, and soluble protein of the corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Grains separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
			*Acidity (mg NaOH $100g^{-1}$)**			
Extremities grains	1.70 ± 0.08 aAα	1.79 ± 0.03 aAα	1.55 ± 0.11 aAα	1.53 ± 0.06 aAα	1.60 ± 0.01 aAα	1.55 ± 0.14 aAα
Center grains	1.68 ± 0.00 aAβ	1.81 ± 0.03 aAα	1.55 ± 0.01 bAα	1.62 ± 0.00 bAα	1.38 ± 0.04 cAβ	1.55 ± 0.02 bAα
			*Lipase activity (% of lipolysis)**			
Extremities grains	27.76 ± 0.24 aAα	22.54 ± 0.95 aAβ	18.67 ± 1.19 bAα	19.52 ± 0.00 bAα	14.97 ± 1.19 cAα	14.13 ± 0.48 cAα
Center grains	23.89 ± 0.95 aBα	16.15 ± 0.48 aBβ	19.52 ± 3.33 aAα	14.80 ± 0.95 bBβ	16.15 ± 0.00 bAα	14.22 ± 0.36 bAα
			*Soluble protein (%)**			
Extremities grains	12.93 ± 0.41 aAα	12.59 ± 2.53 aAα	11.70 ± 1.19 aAα	11.35 ± 1.66 aAα	10.31 ± 0.02 aAα	10.64 ± 0.45 aAα
Center grains	11.91 ± 1.84 aAα	11.16 ± 0.12 aAα	10.62 ± 0.16 aAα	7.34 ± 0.36 bBβ	10.16 ± 0.90 aAα	7.16 ± 0.03 bBβ

**Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.3 Molecular weight distribution of proteins, lipase activity, and soluble protein

The molecular weight distribution of proteins is shown in Figure 4. Analysis of variance showed significant effects ($P < 0.05$) of all variables studied on lipase activity and soluble protein (Supplementary material 2).

In the molecular weight distribution of proteins, regions I and II contain proteins with molecular weight (MW) of 97 and 66 kDa, respectively, corresponding to dimmers, trimmer, and polymerized forms of corn proteins. Region III corresponds to the β-glutelin fraction with a molecular weight of 34 kDa. The regions I, II, and III were confirmed with chromatographic patterns. The region with a retention time of 8 min refers to the α-glutelin with a molecular weight of 34 kDa and the region with a retention time higher than 12 min refers to the presence of low molecular weight proteins, globulins, and/or prolamin (Figure 4) (Timm et al., 2020a).

In the grains separated before drying, in regions I, II, and III the higher absorbance was observed in the grains from the center of the corncob dried at 80 °C, followed by the grains from the center dried at 60 °C. In the low molecular weight fractions (between 12 and 14 min) the higher absorbance was observed in the grains from the center dried at 100 ºC and the lower absorbance in the grains from the extremities dried at 60 ºC (Figure 4A). In the grains separated after drying, in regions I, II, and III the higher absorbance was observed in the grains from the center and extremities dried at 60 ºC. In the low molecular weight fractions (between 12 and 14 min) the higher absorbance was observed in the grains at the center dried at 100 ºC and the lower absorbance in the grains from the extremities dried at 60 ºC (Figure 4B).

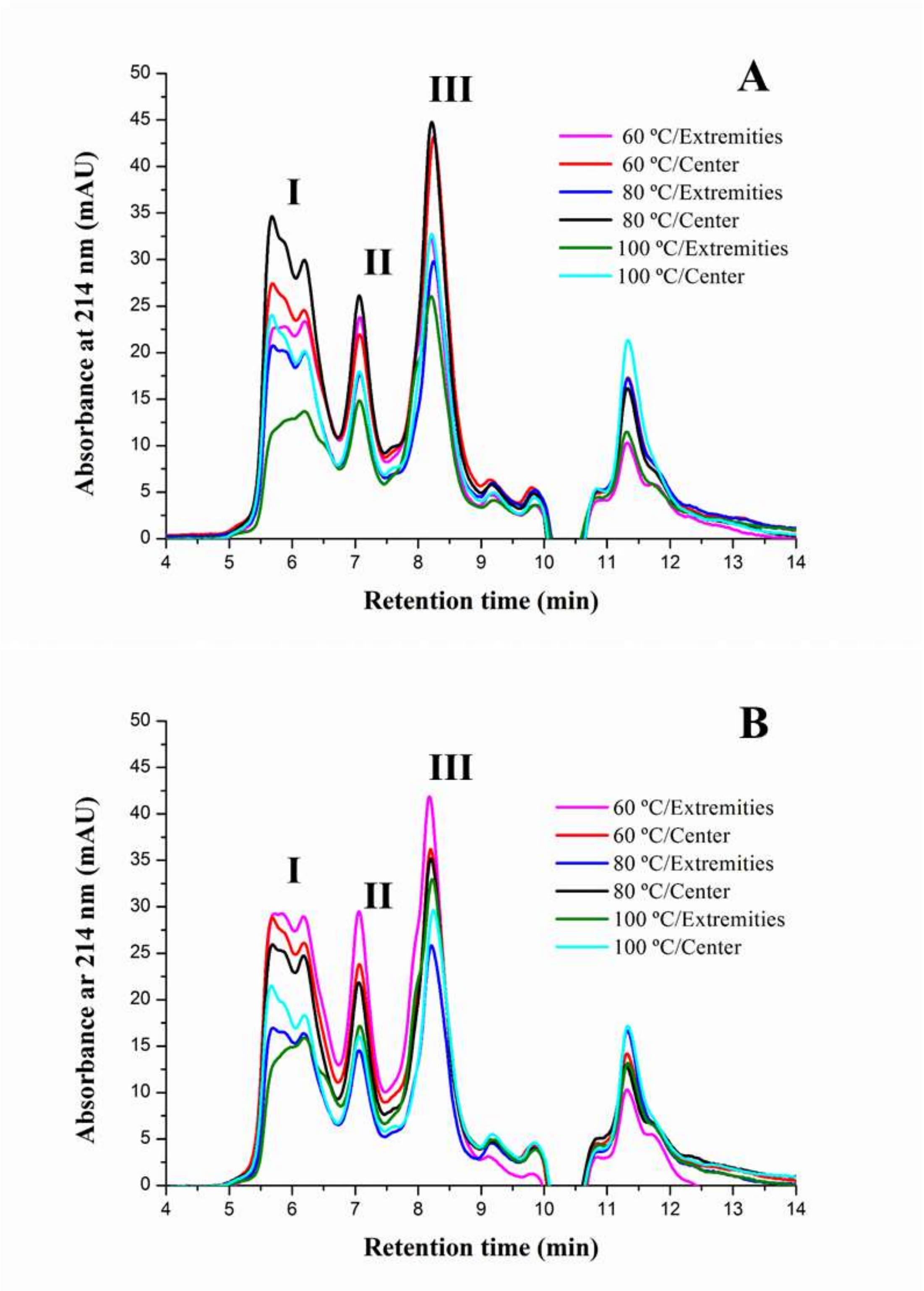


Figure 4. Molecular weight protein distribution of corn grains from center and extremities of corncob separated before drying (A) and after drying (B), prepared with sodium phosphate buffer containing 2.0% sodium dodecyl sulfate (SDS). MW = 97 Da/ RT = 6.17 min (Region I), MW = 66 Da/ RT = 7.0 min (Region II), and MW = 34 Da/ RT = 9.68 min (Region III).

A tendency of reduction of the lipase activity and soluble protein was observed according to the increase in the drying temperature. At 60 ºC, lipase activity was lower in the corn from the center and for soluble protein, no difference was observed between treatments. At the same temperature, when comparing the time of corn separation, lower lipase activity was observed in the separated grains after drying. At 80 ºC, lower lipase activity and soluble protein were observed in the grains from the center, separated after drying. At 100 ºC, no difference was observed between treatments for lipase activity, and the lower soluble protein was observed in the grains from the center, separated after drying. (Table 2).

The reduction of lipase activity and soluble protein at higher drying temperatures occurred because under these conditions a higher starch-protein interaction occurs (Malumba et al. 2009b). The lower values of lipase activity and soluble protein were observed in the grains from the center and separated after drying at 100 ºC, thus occurring a higher denaturation of lower molecular weight proteins, which can be confirmed by the reduction of peaks in the fraction with time retention higher than 12 min (Figure 4B).

Even though the effects of increased drying temperature on starch-protein interactions have already been clarified in studies carried out by Malumba et al. (2009a), Malumba et al. (2009b), and Timm et al. (2020b), this research it was observed that the effect of drying temperature can be intensified when we have a mass of corn grains with non-uniform dimensions, as is the case of drying grains from the center and extremities together (separation after drying).

As the grains from the center of the corncob are thinner (Table 1), water tends to diffuse at a higher speed in these grains, when compared to the grains from the extremities that are more spherical (Figure 3). Thus, when the drying of grains from the center and extremities occurred together, the effect of drying temperature was more intensified in the center grains, promoting enzyme denaturation and higher starch-protein and protein-protein interaction, through disulfide bonds (Kaczmarek, Cowieson, Józefiak, & Rutkowski, 2014; Malumba et al., 2008; Timm et al. 2020a). According to Malumba et al. (2008), high temperatures denature corn proteins, mainly due to changes in the structure of zein, such as hydrophobic interactions, chain folding, and covalent bonds with other compounds and, in addition, the enzymatic proteins present in corn grains are the most readily heat-denatured protein.

3.4 Carotenoids profile

The carotenoids lutein, zeaxanthin, cryptoxanthin, and β-carotene were identified in the evaluated corn grains, which are the main carotenoids found in corn grains (Muzhingi et al., 2016). This identification is in agreement with the results obtained by Timm et al. (2021), who evaluated the carotenoid profile of the oil extracted from the germ of different corn genotypes.

Analysis of variance showed significant effects ($P < 0.05$) of all variables analyzed on lutein, zeaxanthin, cryptoxanthin, and β-carotene (Supplementary material 3). A tendency to decrease lutein, zeaxanthin, and β-carotene and a tendency to increase cryptoxanthin with increasing drying temperature was observed (Table 3).

At 60 ºC, a lower content of lutein, zeaxanthin, and cryptoxanthin was observed in the grains from the center of the corncob, separated after drying. At 60 ºC, a difference in β-carotene content was observed only between the corncob part, being higher in the grains from the extremities. At 80 ºC and 100 ºC, a lower content of lutein and β-carotene was observed in the grains from the center, separated after drying. The reduction of carotenoids occurs due to the sensitivity that these compounds have to the increase in temperature, in addition to the presence of light and changes in pH (Parra, Saldivar, & Liu, 2007), which justifies the reduction of lutein and β-carotene contents as the drying temperature increases. In this sense, when the grains from the center of the corncob were separated after drying, there was an intensification of the effects of the drying temperature at 80 and 100 ºC, further reducing the content of lutein (2.24 μg g-1) and β-carotene (0.86 μg g-1) in this condition (Table 3).

At 100 ºC, the higher zeaxanthin and cryptoxanthin contents were observed in the grains from the center of the corncob, separated after drying. In this case, the high drying temperature inactivated the enzymes responsible for the degradation of phytochemicals, and softened the plant tissues, thus increasing the bioaccessibility to carotenoids in the grain (Multari, Marsol-Vall, Keskitalo, Yang, & Suomela, 2018). Carotenoids are present in the cell wall, serving as photosynthetic and photoprotective agents. The elevation of the drying temperature promoted the disruption of the cell wall, intensified the grains from the center, and separated after drying. This cellular disruption facilitated the release of carotenoids, mainly by disrupting carotenoid-protein complexes and softening cellular tissues (Gómez, Ramos, Zhu, Belloso, & Fortuny., 2017), increasing the amount of carotenoids extracted.

Table 3. Carotenoids profile of the corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
*Lutein (µg g^{-1})**						
Extremities grains	4.62 ± 0.29 aBα	4.40 ± 0.11 aAα	4.37 ± 0.14 aAα	4.37 ± 0.04 aAα	3.31 ± 0.10 bBα	3.11 ± 0.02 bAα
Center grains	5.20 ± 0.41 aAα	4.27 ± 0.11 aAβ	4.17 ± 0.49 aAα	2.72 ± 0.05 bBβ	4.12 ± 0.24 aAα	2.24 ± 0.04 cBβ
*Zeaxanthin (µg g^{-1})**						
Extremities grains	0.29 ± 0.00 aAα	0.30 ± 0.01 aAα	0.26 ± 0.02 aAα	0.20 ± 0.01 bAβ	0.24 ± 0.02 aAα	0.15 ± 0.01 bBβ
Center grains	0.31 ± 0.04 aAα	0.13 ± 0.00 cBβ	0.23 ± 0.02 abAα	0.20 ± 0.02 bAα	0.20 ± 0.00 bBβ	0.26 ± 0.01 aAα
*Cryptoxanthin (µg g^{-1})**						
Extremities grains	0.49 ± 0.02 bAα	0.44 ± 0.01 aAα	0.39 ± 0.01 bAα	0.22 ± 0.01 cAβ	1.44 ± 0.14 aAα	0.32 ± 0.03 bBβ
Center grains	0.51 ± 0.04 aAα	0.19 ± 0.01 bBβ	0.45 ± 0.03 aAα	0.32 ± 0.03 bAβ	0.48 ± 0.02 aBβ	1.31 ± 0.06 aAα
*β-carotene (µg g^{-1})**						
Extremities grains	1.82 ± 0.03 aAα	1.75 ± 0.04 aAα	1.58 ± 0.01 bAα	1.64 ± 0.01 aAα	1.52 ± 0.07 bAα	1.02 ± 0.05 bAβ
Center grains	1.36 ± 0.01 aBα	1.40 ± 0.05 aBα	1.31 ± 0.08 aBα	0.81 ± 0.00 bBβ	1.14 ± 0.08 aBα	0.86 ± 0.02 bBβ

**Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.5 Pasting properties

The analysis of variance showed a significant effect of the corncob part on pasting temperature, peak viscosity, breakdown, and setback, of the corn separation only on peak viscosity, and of storage temperature on pasting temperature, peak viscosity, breakdown, final viscosity, and setback (Supplementary material 4). A tendency to increase pasting temperature and a reduction of the peak viscosity, breakdown, final viscosity, and setback were observed according to the increase in corn drying temperature. At 60 and 80 ºC, differences in pasting temperature were not observed when compared to the corncob part and separation step. At 100 ºC, a lower pasting temperature was observed in the grains from the center of the corncob (Table 4).

These changes observed in the pasting properties showed that gelatinization was hampered by the increase in temperature, which also resulted in a reduction in soluble protein (Table 2), a higher amylose-lipid interaction, and/or due to the strengthening of intermolecular bonds of starch (Timm et al., 2020a; Timm et al., 2020b). The denatured protein matrix decreases the swelling power and breakdown of starch granules during heating (Yang et al., 2019; Ziegler et al., 2017), leading to higher gelatinization temperature values (Table 4) and the lower peak viscosity and breakdown values (Table 4). Probably, the higher starch-lipid and/or starch-protein interaction resulted in lower final viscosity and setback values (Timm et al. 2020a; Timm et al., 2020b; Yang et al., 2019).

Table 4. Pasting properties of flour from corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
			*Pasting temperature (ºC)**			
Extremities grains	76.60 ± 0.07 cAα	77.38 ± 0.04 cAα	79.50 ± 0.49 bAα	79.48 ± 0.67 bAα	83.58 ± 0.46 aAα	83.93 ± 0.04 aAα
Center grains	77.10 ± 0.71 cAα	76.68 ± 0.04 cAα	79.15 ± 0.00 bAα	78.65 ± 0.64 bAα	81.90 ± 0.49 aBα	82.80 ± 0.49 aBα
			*Peak viscosity (RVU)**			
Extremities grains	226.92 ± 1.18 aBβ	244.50 ± 1.17 aAα	170.21 ± 0.41 bBα	174.96 ± 5.71 bBα	124.30 ± 0.88 cAα	122.71 ± 9.14 cBα
Center grains	236.17 ± 6.84 aAα	237.75 ± 5.06 aAα	187.46 ± 10.08 bAα	184.17 ± 1.06 bAα	128.42 ± 1.18 cAα	132.63 ± 1.00 cAα
			*Breakdown (RVU)**			
Extremities grains	73.71 ± 0.76 aBα	78.58 ± 7.42 aAα	22.92 ± 2.24 bBα	21.42 ± 2.83 bAα	9.63 ± 1.83 cAα	12.54 ± 1.82 cAα
Center grains	87.59 ± 6.13 aAα	86.50 ± 2.47 aAα	32.54 ± 2.88 bAα	26.92 ± 3.89 bAα	9.30 ± 1.82 cAα	6.21 ± 3.13 cAα
			*Final viscosity (RVU)**			
Extremities grains	437.54 ± 5.01 aAα	464.96 ± 6.31 aAα	361.92 ± 0.94 bAα	370.17 ± 5.07 bAα	265.54 ± 3.48 cAα	249.63 ± 15.49 cAα
Center grains	418.58 ± 8.49 aAα	431.84 ± 4.12 aAα	382.00 ± 18.03 bAα	368.63 ± 5.24 bAα	249.42 ± 3.89 cAα	261.92 ± 4.72 cAα
			*Setback (RVU)**			
Extremities grains	284.33 ± 4.60 aAα	299.05 ± 15.55 aAα	214.63 ± 2.76 bAα	216.63 ± 3.47 bAα	150.88 ± 0.77 cAα	139.46 ± 8.19 cAα
Center grains	270.00 ± 7.78 aAα	280.59 ± 1.53 aBα	227.09 ± 10.84 bAα	211.38 ± 8.07 bAα	130.29 ± 3.24 cBα	135.50 ± 8.84 cAα

**Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

4 Conclusion

At the higher drying temperatures (80 and 100 ºC), the drying rate and effective moisture diffusivity of corn from the center of the corncob are higher than from the extremities. Corncob part and grain separation did not significantly affect corn pasting properties. However, they caused significant changes in the properties of the grain proteins, mainly the reduction of the solubility and inactivation of the lipase enzyme, and the reduction of the lutein and β-carotene contents in the grains from the center, separated after drying. Among the temperatures evaluated, 60 ºC is the most suitable temperature for drying corn grains at high temperatures. However, the latent effects of this drying condition must be studied throughout the grains storage. In addition, the implementation of an industrial separation step and/or the development of new corn cultivars with more homogeneous grains should be studied.

References

AACC, 2000. Fat acidity e general method. Method 02-01A. In: Approved Methods of the American Association of Cereal Chemists. American Association of Cereal Chemists, Inc, St. Paul, MN, USA.

ASAE, American Society of Agricultural Engineers. Moisture measurement- unground grain and seeds, in: Standards ASAE, Saint Joseph, 2000, pp. 563.

ASAE, American Society of Agricultural Engineers. Moisture relationship of plant-based agricultural products. ASAE Standard D245.5. St. Joseph, MI: ASAE, 1995.

Buggenhout, J., Brijs, K., & Delcour, J. A. (2013). Impact of processing conditions on the extractability and molecular weight distribution of proteins in parboiled brown rice. Journal of Cereal Science, 58(1), 8–14. https://doi.org/10.1016/j.jcs.2013.05.002

Coradi, P.C., Maldaner, V., Lutz, E., Daí, P.V.S., & Teodoro, P.R (2020). Influences of drying temperature and storage conditions for preserving the quality of maize postharvest on laboratory and field scales. Scientific Reports, 10, e22006. https://doi.org/10.1038/s41598-020-78914-x

Coradi, P.C., Milane, L.V., Camilo, L.J., & Andrade, M.G.O. (2016). Drying and storage of corn grains for ethanol production in Brazil. Bioscience J. 32(5), 1175-1190. https://doi.org/10.14393/BJ-v32n5a2016-32754

Coradi, P.C., Nunes, M.T., Bellochio, S.D.C., Camilo, L.J., & Teodoro, P.E (2021). Effects of drying temperatures and storage conditions on the levels of lipids and starches in corn grains for yield ethanol industry. Biofuels, 1-10. https://doi.org/10.1080/17597269.2021.1904674

Crank, J. The mathematics of diffusion (2nd ed.). Oxford, UK: Oxford University Press, 1975.

D.B. Brooker, A. F. W. Bakker-Arkem, C.W. Hall. Drying cereal grains. Westport, AVI Publishing, 265p. 1974.

Doymaz, I., & Pala, M (2003). The thin-layer drying characteristics of corn. Journal of Food Engineering, 60, 125-130. https://doi.org/10.1016/S0260-8774(03)00025-6

Gómez, J. D., Ramos, A. J., Zhu, C., Belloso, O. M., & Fortuny, R. S. (2017). Influence of Cooking Conditions on Carotenoid Content and Stability in Porridges Prepared from High-Carotenoid Maize. Plant Foods for Human Nutrition, 72, 113–119. https://doi.org/10.1007/s11130-017-0604-7

Huart, F., Malumba, P., Odjo, S., Al-Izzi, W., Béra, F., & Beckers, Y. (2018). In vitro and in vivo assessment of the effect of initial moisture content and drying temperature on the feeding value of maize grain. J. British Poult. Sci. 59, 452-462. https://doi.org/10.1080/00071668.2018.1477253

Jalali, M., Sheikholeslami, Z., Elhamirad, A. H., Khodaparas, M. H. H., & Karimi, M. (2020), The effect of the ultrasound process and pre-gelatinization of the corn flour on the textural, visual, and sensory properties in gluten-free pan bread. J Food Sci Technol, 57, 993–1002. https://doi.org/10.1007/s13197-019-04132-7

Kaczmarek, S.A., Cowieson, A.J., Józefiak, D., & Rutkowski. A. (2014). Effect of maize endosperm hardness, drying temperature and microbial enzyme supplementation on the performance of broiler chickens. Animal Production Science, 54, 956–965. https://doi.org/10.1071/AN13113

Kaur, J., Ramamurthy, V., & Kothari, R. M. (1993). Characterization of oat lipase for lipase for lipolysis of rice bran oil. Biotechnology Letters, 15, 257-262. https://doi.org/10.1007/BF00128315

Lang, G. H., Lindemann, I. S., Ferreira, C. D., Pohndorf, R. S., Vanier, N. L., & Oliveira, M. (2018). Influence of drying temperature on the structural and cooking quality properties of black rice. Cereal Chemistry, 95 (4), 564-574. https://doi.org/10.1002/cche.10060

Liu, K., McWatters, K. H., & Phillips, R. D. (1992). Protein insolubilization and termal destabilization during storage as related to hard-to-cook defect in cowpeas. Journal of Agricultural and Food Chemistry, 40(12), 2483-2487. https://doi.org/10.1021/jf00024a028

Maldaner, V., Coradi, P. C., Nunes, M. T., Müller, A., Carneiro, L. O., Teodoro, P. E., Bressiani, J., Anschau, K. F., & Müller, E. I. (2021). Effects of intermittent drying on physicochemical and morphological quality of rice and endosperm of milled brown rice. LWT, 152, 112334. https://doi.org/10.1016/j.lwt.2021.112334

Malumba, P., Janas, J., Masimango, T., Sindic, M., Deroanne, C., & Béra. F. (2009b). Influence of drying temperature on the wet-milling performance and the proteins solubility indexes of corn kernels. J. Food Eng. 95, 393-399. https://doi.org/10.1016/j.jfoodeng.2009.05.022

Malumba, P., Massaux, C., Deroanne, C., Masimango, T., & Béra, F. (2009a). Influence of drying temperature on functional properties of wet-milled starch granules. Carbohydr. Polym. 75, 299-306. https://doi.org/10.1016/j.carbpol.2008.07.027

Malumba, P., Odjo, S., Boudry, C., Danthine, S., Bindelle, J., Beckers, Y., & François, B. (2014). Physicochemical Characterization and in Vitro Assessment of the Nutritive Value of Starch Yield from Corn Dried at Different Temperatures. Starch, 66, 738–748. https://doi.org/10.1002/star.201400012

Malumba, P., Vanderghem, C., Deroanne, C., & Béra, F. (2008). Influence of drying temperature on the solubility, the purity of isolates and the electrophoretic patterns of corn proteins. Food Chem. 111, 564-572. https://doi.org/10.1016/j.foodchem.2008.04.030

Mohsenin, N. N. Physical properties of plant and animal materials. New York: Gordon and Breach Publishers, 1986. 841p.

Multari, S., Marsol-Vall, A., Keskitalo, M., Yang, B., & Suomela, J. P (2018). Effects of different drying temperatures on the content of phenolic compounds and carotenoids in quinoa seeds (Chenopodium quinoa) from Finland. Journal of Food Composition and Analysis, 72, 75-82. https://doi.org/10.1016/j.jfca.2018.06.008

Muthukumarappan, K., & Gunasekaran, S. (1994). Moisture Diffusivity of Corn Kernel Components During Adsorption Part III: Soft and Hard Endosperms. Transactions of the ASAE, 37, 1275–1280. doi:10.13031/2013.28207

Muzhingi, T., Rojas, N. P., Miranda, A., Cabrera, M. L., Yeum, K. J., & Tang, G. (2016). Genetic variation of carotenoids, vitamin E and phenolic compounds in

Provitamin A biofortified maize. Journal of the Science of Food and Agriculture, 97, 793-801. https://doi.org/10.1002/jsfa.7798

Nunes, M.T., Coradi, P.C., Müller, A., Carneiro, L.O., Steinhaus, J.I., Anschau, K.F.. Souza, G.A.C., Muller, E.I., Teodoro, P.E., & Dutra, A.P (2022). Stationary rice drying: influence of initial moisture and impurities contents in the mass grains on the physicochemical and morphological rice quality. Journal of Food Processing and Preservation, 1, 1-10. https://doi.org/10.1111/jfpp.16558

Parra, C., Serna-Saldivar, S., & Liu, R.H. (2007) Effect of processing on the phytochemical profiles and antioxidant activity of corn for production of masa, tortillas, and tortilla chips. Journal of Agricultural and Food Chemistry, 55, 4177-4183. https://doi.org/10.1021/jf063487p

Rajarammanna, R., Jayas, D. S., & White, N. D. G. (2010) Comparison of deterioration of rye under two different storage regimes. Journal of Stored Products Research, 46, 87-92. https://doi.org/10.1016/j.jspr.2009.10.005

Reis, L. C. R, Oliveira, V. R., Hagen, M. E. K., Jablonski, A., Flôres, S. H., & Rios, A. O. (2015) Carotenoids, flavonoids, chlorophylls, phenolic compounds and antioxidant activity in fresh and cooked broccoli (Brassica oleracea var. Avenger) and cauliflower (Brassica oleracea var. Alphina F1). LWT – Food Science and Technology, 63, 177-183. https://doi.org/10.1016/j.lwt.2015.03.089

Silva, W., M., F., Biduski, B., Lima, K. O., Pinto, V. Z., Hoffmann, J. F., Vanier, N. L., & Dias, A. R. G. (2017). Starch digestibility and molecular weight distribution of proteins in rice grains subjected to heat-moisture treatment. Food Chemistry, 219, 260–267. https://doi.org/10.1016/j.foodchem.2016.09.134

Stewart, O. J., Ragha, G. S. V, Orsat, V., & Golden, K. D. (2003). The effect of drying on unsaturated fatty acids and trypsin inhibitor activity in soybean. Process Biochemistry, 39, 483-489. https://doi.org/10.1016/S0032-9592(03)00130-4

Timm, N. S., Lang, G. H., Ramos, A. H., Pohndorf, R. S., Ferreira, C. D., & Oliveira, M. (2020a). Effects of drying methods and temperatures on protein, pasting, and thermal properties of white floury corn. J. Food Proc. Preserv. 44, e14767. https://doi.org/10.1111/jfpp.14767

Timm, N. S., Ramos, A. H., Ferreira, C. D., Biduski, B., Eicholz, E. D., & Oliveira, M. (2020b). Effects of drying temperature and genotype on morphology and technological, thermal, and pasting properties of corn starch. Intern. J. Biol. Macrom. 165, 354-364. https://doi.org/10.1016/j.ijbiomac.2020.09.197

Timm, N. S., Ramos, A. H., Ferreira, C. D., Rios, A. O., Zambiazi, R. C., & Oliveira, M. (2021). Influence of germ storage from different corn genotypes on technological properties and fatty acid, tocopherol, and carotenoid profiles of oil. European Food Research and Technology, 247, 1449–1460. https://doi.org/10.1007/s00217-021-03723-z

Tohidi, M., Sadeghi, M., & Torki-Harchegani, M. (2017). Energy and quality aspects for fixed deep bed drying of paddy. Renewable and Sustainable Energy Reviews, 70, 519–528. https://doi.org/10.1016/j.rser.2016.11.196

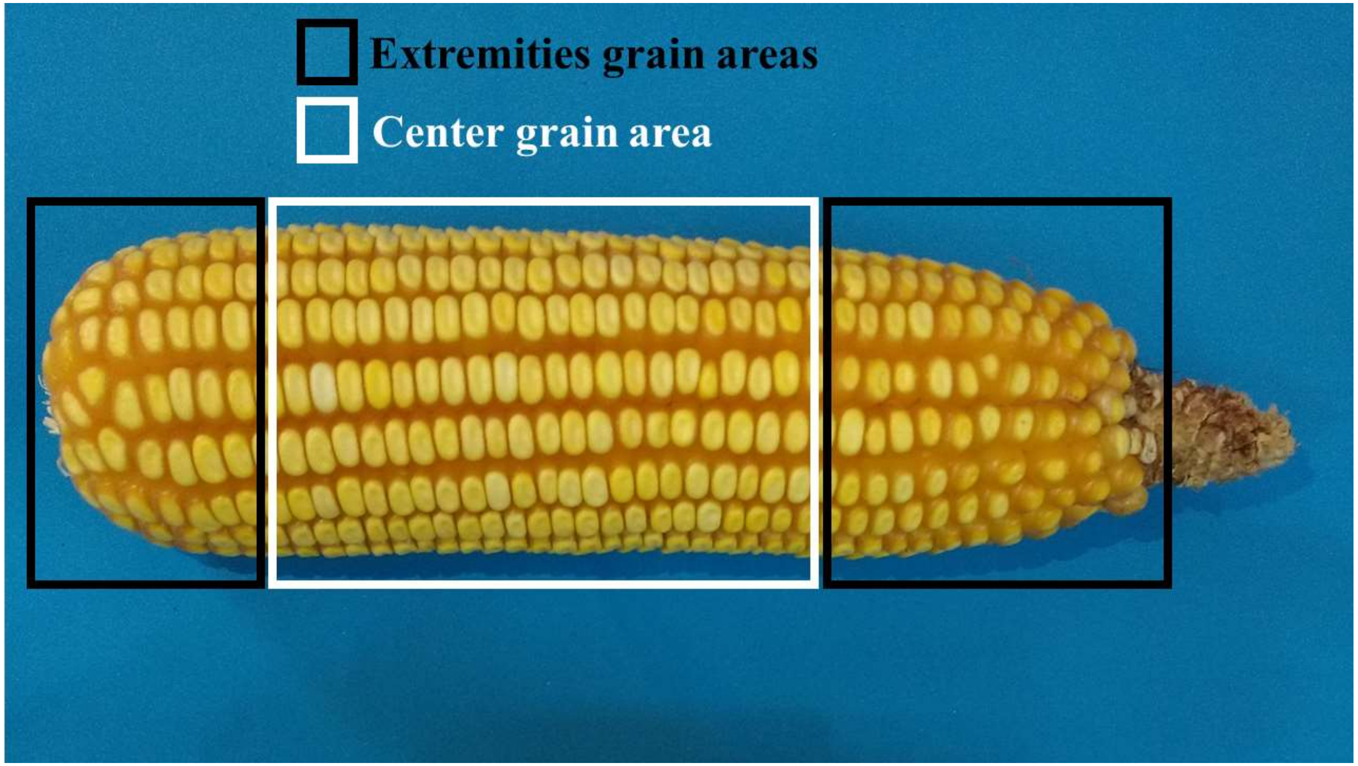
Trehan, S., Singh, N., & Kaur, A. (2018) Characteristics of white, yellow, purple corn accessions: phenolic profile, textural, rheological properties and muffin making potential. J Food Sci Technol, 55, 2334–2343. https://doi.org/10.1007/s13197-018-3171-5

Yang, Y., Wang, L., Li, Y., Qian, H. F., Zhang, H., Wu, G. C., & Qi, X. G. (2019). Investigation the molecular degradation, starch-lipid complexes formation and pasting properties of wheat starch in instant noodles during deep-frying treatment. Food Chemistry, 283, 287–293. https://doi.org/10.1016/j.foodc hem.2019.01.034

Ziegler, V., Ferreira, C. D., Goebel, J. T. S., El Halal, S. L. M., Santetti, G. S., Gutkoski, L. C., … & Elias, M. C. (2017). Changes in properties of starch isolated from whole rice grains with brown, black, and red pericarp after storage at different temperatures. Food Chemistry, 216, 194– 200. https://doi.org/10.1016/j.foodc hem.2016.08.045

Supplementary materials

Supplementary material 1. The standard definition of the grains from the center area of the corncob and the grains from the extremities areas of the corncob.



Supplementary material 2. Analysis of variance for acidity, lipase activity, and soluble protein.

Main effects	DF	Mean Square		
		Acidity	Lipase activity	Soluble protein
Corncob part	1	0.00259448^{NS}	27.6066697*	20.82221569*
Separation	1	0.02538116*	64.0240287*	9.08241961*
Corncob part × separation	1	0.02068856*	14.0114846*	7.43740007*
Temperature	2	0.11468064*	120.0888361*	14.32138459*
Corncob part × temperature	2	0.01191483*	16.6673101*	0.87687352^{NS}
Separation × temperature	2	0.00329420^{NS}	15.6106406*	0.81382143^{NS}
Corncob part × separation × temperature	2	0.00528871*	2.5909630^{NS}	1.24304075^{NS}
Repetition	2	0.01876908^{NS}	0.5200795^{NS}	0.56514244^{NS}
CV (%)		3.052062	6.662304	10.86514
Error		0.02651426	16.7592970	14.74212498

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 3. Analysis of variance for carotenoids profile.

Main effects	DF	Mean Square			
		Lutein	Zeaxanthin	Cryptoxanthin	β-carotene
Corncob part	1	0.35996544*	0.00206870*	0.00013440*	0.99784429*
Separation	1	3.67284518*	0.01402478*	0.15427698*	0.25503468*
Corncob part × separation	1	2.43808310*	0.00003365^{NS}	0.49337968*	0.00825331^{NS}
Temperature	2	4.05163647*	0.00419430*	0.70858365*	0.40060942*
Corncob part × temperature	2	0.72569337*	0.00526972*	0.02024841*	0.04076707*
Separation × temperature	2	0.11216359^{NS}	0.00277889*	0.00097230^{NS}	0.07025729*
Corncob part × separation × temperature	2	0.12902950^{NS}	0.01565641*	0.73151075*	0.08817179*
Repetition	2	0.00466045^{NS}	0.00011572^{NS}	0.00600065^{NS}	0.00000156^{NS}
CV (%)		6.001510	7.582925	8.644706	3.521823
Error		0.60509943	0.00333653	0.02454197	0.02487793

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 4. Analysis of variance for pasting properties.

Main effects	DF	Mean Square				
		Pasting temperature	Peak viscosity	Breakdown	Final viscosity	Setback
Corncob part	1	2.9051042*	308.02335*	152.61127*	232.7528^{NS}	418.75260*
Separation	1	0.1926042^{NS}	90.17127*	2.04167^{NS}	172.0562^{NS}	4.83304^{NS}
Corncob part × separation	1	0.2109375^{NS}	55.44960^{NS}	43.09440^{NS}	9.0774^{NS}	4.53270^{NS}
Temperature	2	76.4319792*	23918.58166*	11438.74575*	67401.2665*	41838.07516*
Corncob part × temperature	2	0.8626042*	71.76289*	110.73018*	651.4819*	223.03000*
Separation × temperature	2	0.3938542^{NS}	49.04580^{NS}	15.22375^{NS}	337.0763*	214.22251^{NS}
Corncob part × separation × temperature	2	0.3865625^{NS}	60.81101^{NS}	0.57221^{NS}	364.3153*	149.50655^{NS}
Repetition	2	0.0026042^{NS}	113.36107^{NS}	1.18815^{NS}	121.8603^{NS}	0.48450^{NS}
CV (%)		0.574614	2.260897	9.516977	2.247027	3.461008
Error		2.3086458	183.89903	151.43385	700.6452	599.57825

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

CHAPTER 3 – EFFECTS OF DRYING TEMPERATURE OF CORN FROM THE CENTER AND EXTREMITIES OF THE CORNCOB ON MORPHOLOGY AND TECHNOLOGICAL, THERMAL, AND PASTING PROPERTIES OF ISOLATED STARCH

Abstract

The corn grains from the extremities of corncob are known to have a spherical shape and the grains from the center of corncob have higher length and less thickness. It is understood that these differences in grain dimensions can affect post-harvest processes and the properties of the starch isolated from these grains. Therefore, the objective was to evaluate the effects of drying temperature (60, 80, and 100 ºC) of corn from the center and extremities of corncob on morphology and technological, thermal, and pasting properties of isolated starch. Increasing the drying temperature results in reduced extraction yield and purity, and increases the thermal resistance of the starch. When the grains from the center and extremities were separated after drying at 80 and 100 ºC, there was an intensification of these changes in the starch isolated from the corn from the center of the corncob. This condition results in a higher reduction in extraction yield, purity, and water-binding capacity. The results showed that the industrial separation of corn grains with different dimensions can increase the extraction yield by 35 to 40%.

Keywords: *Effective moisture diffusivity; Extraction yield; Starch purity; Thermal resistance of starch.*

1 Introduction

Starch is made up of amylose and amylopectin molecules and is widely applied as a thickener, gelling agent, bulking agent, and water retention agent in food preparation. In addition, starch is used in non-food industries, such as in the manufacture of bioethanol, paper, fabrics, plaster, adhesives, bioplastics, and fiberglass. Among the raw materials for the extraction of starch, corn grains correspond to more than 85% of the starch produced in the world (Choi et al., 2018; Zhang et al., 2021).

Before the starch is extracted through wet-milling, the corn goes through a series of post-harvest operations. Drying is the main operation as it is directly related to success in the later stages of storage and processing. Thus, according to Coradi et al. (2020) the drying must be carried out properly so as not to affect the properties of the grains and their derivatives, mainly controlling the drying air temperature (Maldaner et al., 2021) and the grain mass temperature (Nunes et al., 2022).

The influence of drying temperature (54 – 130 ºC) on wet-milling performance and corn protein solubility indices was studied by Malumba et al. (2009a). These authors reported that increasing the drying temperature from 54 to 130 ºC reduced the starch extraction yield by 28.18% and increased the residual protein content by 84.06%. Malumba et al. (2009b) evaluated the effects of drying temperature (54 – 130 ºC) on the functional properties of isolated starch. According to Malumba et al. (2009a), high drying temperatures cause structural changes to the starch granules, which affect the pasting properties of corn starch, reducing peak viscosity and breakdown, increasing pasting temperature and setback.

The effects of drying temperature (30 – 90 ºC) and corn genotype (yellow floury, white floury, and yellow flint) on the morphology and on the technological, thermal, and pasting properties of corn starch were evaluated by Timm et al. (2020). These authors reported that there was a reduction in the peak viscosity and the gelatinization enthalpy of starch of the yellow floury and yellow flint corn according to the increase in drying temperature, which occurred as a result of the pre-gelatinization of the starch granules during the initial drying steps.

All these studies considered the corn grains to be homogeneous in the total grain mass. However, the insertion of grains along a corncob originates grains with different dimensions, with the grains from the extremities of the corncob having a spherical shape and the grains from the center having a higher length and less thickness. These differences in grain dimensions can affect the properties of the isolated starch as the drying kinetics may be different between grains at the center and the extremities. Therefore, the objective was to evaluate the effects of drying temperature (60, 80, and 100 ºC) of corn from the center and extremities of corncob on morphology and technological, thermal, and pasting properties of isolated starch.

2 Material and methods

2.1 Material and sample preparation

Yellow flint corn (Pioneer P3016 VYHR) was used, harvested in Canguçu, the Rio Grande do Sul, Brazil, in the crop year 2019/2020. Immediately after harvesting, grains were packed in plastic bags and transported to the Laboratory of Postharvest (LAPOS) at Federal University of Santa Maria (UFSM), Campus Cachoeira do Sul, where drying experiments were carried out.

Table 1 presents the physical properties and chemical composition of corn from the center and extremities of the corncob. The physical properties were determined according to Mohsenin (1986) and the chemical properties were determined using the NIRS equipment (Near Infrared Reflectance Spectroscopy, DS2500, FOSS, Brazil). The grains from the center and extremities of the corncob were manually separated. This separation was standardized by defining corncob areas. Therefore, the grain area at the center of the corncob and the areas of the grain at the extremities of the corncob were defined, as illustrated in Supplementary Material 1.

Table 1. Physical properties and chemical composition of corn from the center and extremities of the corncob.

Corncob part	Extremities corn	Center corn
	Physical properties	
Length (mm)	11.94	13.06
Width (mm)	9.15	9.06
Thickness (mm)	5.81	5.23
Bulk density (kg/m^3)	702.33	712.33
Unit mass (g)	0.35	0.38
Volume (mm^3)	276.67	296.67
Equivalent radium (mm)	4.30	4.26
Sphericity	0.72	0.65
	Chemical composition	
Protein (%)	8.63	9.24
Fat (%)	3.92	4.03
Fiber (%)	2.58	2.45
Ash (%)	1.43	1.36
Starch (%)	83.44	82.92

Figure 1 shows a graphic summary of the sample preparation for the experiment. Initially, the grains were threshed into three groups: (1) grains from the center of the corncob (10 kg), (2) grains from the extremities of the corncob (10 kg), and (3) grains from the center and extremities together (20 kg). The threshed corn was then cleaned and the initial moisture content of the grains was measured in an oven at 140 ºC for 3 h (ASAE, 2000).

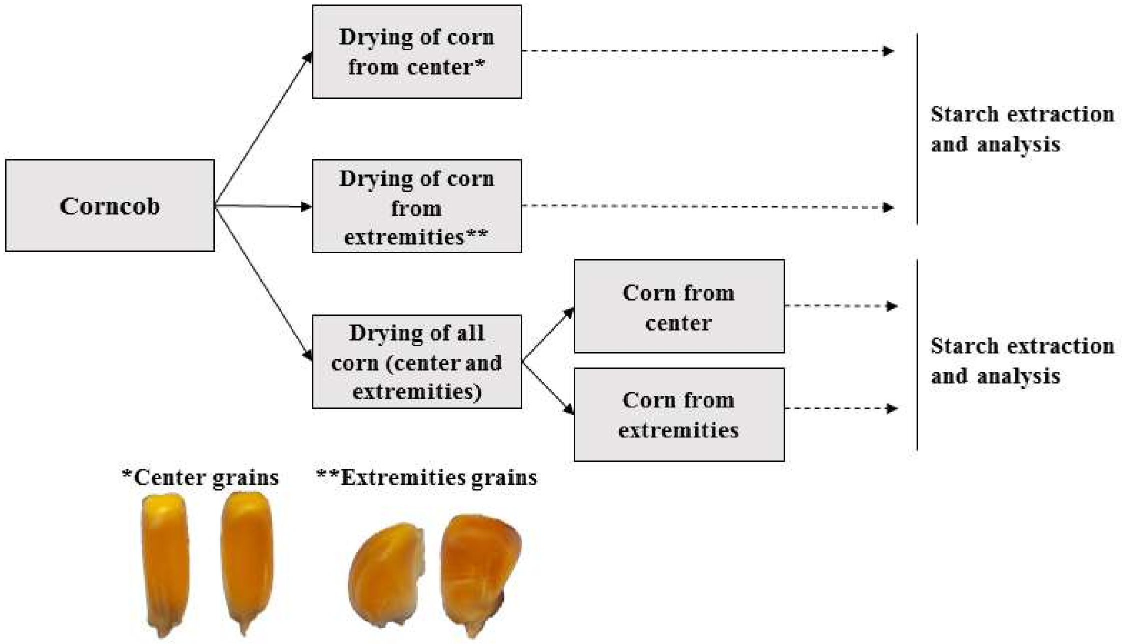


Figure 1. Graphical summary of the preparation of corn samples for experimenting.

The drying was carried out in these three groups of samples, being the group 1 and the group 2 denominated as separate corn before drying, where the grains from the center and extremities were dried and evaluated separately. Group 3, which consists of grains from the center and extremities together, was subjected to drying in this way. After drying, the grains from the center and extremities of the corncob were separated and starch extraction and analysis were performed. This group was called separation after drying. The separation of the corn from the center and extremities of group 3 was performed using a digital caliper, according to the grain dimensions shown in Table 1.

2.2 Drying conditions, moisture ratio, drying rate, and moisture diffusivity

The grains with an initial moisture content of 31.90±0.20% were dried at different temperatures (60, 80, and 100 ºC) in an experimental fixed bed dryer, with an airflow rate of 0.5 m s^{-1}, until reaching a water content of 13.00±0.20%. In all treatments the water content was monitored by the difference in mass, following Eq. 1, where wf is the final weight of the sample (g), wi is the initial weight of the sample (g), mi is the initial moisture (g g^{-1}), and mf the final moisture (g g^{-1}).

$$\mathrm{wf} = \mathrm{wi} \times \left(\frac{100-\mathrm{mi}}{100-\mathrm{mf}}\right) \tag{1}$$

For each treatment, the parameters of moisture ratio, drying rate, and moisture diffusivity were calculated. The moisture ratio was calculated based on the equilibrium moisture content of the grains at each drying temperature using the modified Henderson equation (Eq. 2), considering the parameters of air humidity and temperature collected during drying. The equilibrium moisture (X_e) is calculated by the relative humidity of the drying air (RH), the temperature of the drying air (T), and the parameters a = -0.00003074, b = 273.15, and c = 1.8156 previously stipulated for corn grains according to ASAE D245.5 (ASAE, 1995).

$$X_e = \frac{(0.01*(ln(1-RH))}{(a*(T+b)^{(1/c)}} \tag{2}$$

The dimensionless moisture ratio was calculated through Eq. (3), where X is the moisture content at each instant, Xe is the calculated equilibrium moisture, and X_0 is the initial grain moisture, before drying.

$$MR = \frac{(X-X_e)}{(X_0-X_e)} \tag{3}$$

To investigate the kinetic behavior of the corn drying the mathematical model represented by the Brooker equation (Eq. 4) was used. This equation is suitable for cereals, especially for drying corn grains (Brooker, 1974), where k drying constant (m m-1), t is the drying time (min), and C is the model coefficient.

$$MR = C \exp(-kt) \tag{4}$$

The drying rate was calculated by Eq. 5, where t is the drying time (min), X is the moisture content in t, X_i is the initial grain moisture in time ti, and X_{i+1} is the moisture content at time t_{i+1}.

$$\frac{dX}{dt} = \frac{(X_{i+1}-X_i)}{(t_{i+1}-t_i)} \tag{5}$$

Corn moisture diffusivities were estimated by the diffusion equation (Fick's law) and the slope method. Corn grains were considered spherical particles and the moisture diffusion mechanism was represented by Eq.6, suitable for corn (Brooker, 1974).

$$\frac{\partial X}{\partial t} = D_{eff}\left(\frac{\partial^2 X}{\partial r^2} + \frac{2}{r}\frac{\partial X}{\partial r}\right) \tag{6}$$

According to Crank (1975), an analytical solution of Eq. 6 can be obtained assuming some conditions: (a) moisture content should be uniformly distributed throughout the mass of the grain; (b) the mass transfer is symmetric from the center of the sphere; (c) at the beginning of drying, the surface of the grains reaches the equilibrium moisture content; (d) negligible surface resistance for mass transfer; (e) mass transfer occurs by diffusive mechanism; (f) shrinkage of the grains is negligible and the diffusion coefficient is constant during drying. With these assumptions, the initial and boundary conditions are used and the moisture diffusion model of spherical bodies can be solved by Eq. 7 (Crank, 1975), where Deff is the moisture diffusivity ($m^2 s^{-1}$), MR is the moisture ratio (dimensionless), and R is the corn equivalent radius (m).

$$MR = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}exp\left(-n^2\pi^2\frac{D_{eff}}{R^2}t\right) \quad (7)$$

2.3 Starch extraction

Corn starch extraction was performed according to Sandhu et al. (2005). Corn grains (200 g) were added to 500 mL of sodium bisulfite, with a concentration of 0.1%, and were submitted to 50 ± 2 ºC for 20 h. After this time the solution was drained and the grains were submitted to wet milling, with 2 L of distilled water. Ground grains were filtered in sieves of 100 and 270 mesh, respectively. Filtered material (starch-protein) was kept at rest for 4 h at 25 ºC and the supernatant was removed. Then, sediment was resuspended with distilled water and centrifuged at 5,000 x g for 20 min to separate starch and protein fractions. The upper layer (protein) was removed and the lower layer (starch) was resuspended and centrifuged another 3 times. The isolated starch was dried in a greenhouse at 40 ºC for 12 h and ground in a laboratory mill (Perten 3100, Perten Instruments, Huddinge, Sweden) with a 70-mesh sieve to uniform particle size distribution. The extraction yield (%) was calculated by the ratio between the dry starch mass (g) by initial grain mass (g).

2.4 Residual protein and fat content

The nitrogen content was determined using the AACC method 46-13 (AACC, 1995), and the protein content (%) was obtained using a conversion factor of nitrogen to the protein of 6.25. The lipid content (%) was determined according to the AACC method 30-20 (AACC, 1995).

2.5 Colorimetric profile

The color parameters of corn starches were determined using a colorimeter (Minolta, CR-310, Osaka, Japan). The parameters obtained were a* (positive = red and negative = green), b* (positive = yellow and negative = blue), and luminosity (L) (100 = white and 0 = black).

2.6 Morphology of corn endosperm and starch granules

Corn grain cut in the longitudinal section of the endosperm and corn starch (small quantity) were placed directly on the surface of the stub and coated with gold (20 nm) using a sputter coater (Denton Vacuum, Inc., Moorestown, NJ, USA). Starch morphology was examined using a scanning electron microscope (Jeol JSM6610LV, New Jersey, USA) at an accelerating voltage of 15 kV. The images were captured at magnifications of 1,000x (corn grain) and 3,000x (corn starch).

2.7 Swelling Power and Solubility

The swelling power and solubility of corn starches were determined according to Leach et al. (1959), with some modifications. The corn starches (1 g) were mixed with 50 mL of distilled water and heated at 90 ºC for 30 min. Gelatinized starches were then cooled at 25 ºC and centrifuged at 1,000 x g for 20 min. The supernatants were removed and dried at 105 ºC for 24 h. Swelling power (g g-1) was calculated by the ratio between wet sediment weight and initial dry sample weight. Solubility (%) was calculated by the ratio between dried solid weight (from supernatants) and initial dry sample weight.

2.8 Pasting properties and gel hardness

The pasting properties of corn starches (3 g, 14% moisture basis) were determined with a Rapid Visco Analyser (RVA-4; Newport Scientific, Warriewood, Australia) using the RVA profile Standard Analysis 1. The sample was held at 50 ºC for 1 min, heated to 95 ºC for 3.5 min, and held at 95 ºC for 2.5 min. The sample was then cooled to 50 ºC for 4 min and held at 50 ºC for 2 min. The rotating speed was held at 960 rpm for 10 s and then maintained at 160 rpm during the process. The parameters determined were pasting temperature (ºC), peak viscosity (RVU), breakdown (RVU), final viscosity (RVU), and setback (RVU).

The hardness (g) of corn starches was obtained using a texture analyzer (TA.XTplus, Stable Micro Systems), according to Yoenyongbuddhagal and Noohorm

(2002), with some modifications. The gelatinized mixture in a canister, after the RVA analysis, was sealed with parafilm and remained at 25 °C for 24 h allowing the formation of a solid gel. The gels were punctured at 1 mm s-1 to a distance of 10 mm using a stainless-steel cylindrical probe (P/20; diameter of 20 mm).

2.9 Thermal properties

The thermal properties of corn starches were obtained by Differential Scanning Calorimetry (DSC) (TA-60WS, Shimadzu, Kyoto, Japan). Starch samples (2.5 mg on a dry basis) were weighed directly into aluminum pans (Mettler-Toledo, ME-27331, Greifensee, Switzerland), and distilled water was added to obtain an aqueous suspension containing 75% water. The pan was hermetically sealed and allowed to equilibrate for 1 h before analysis. An empty pan was used as a reference. Sample pans were then heated from 30 to 120 °C at a rate of 10 °C min-1. The onset temperature of gelatinization (To), peak temperature (Tp), conclusion temperature (Tc), and gelatinization enthalpy (ΔH) were measured. The range of gelatinization temperature (ΔT) was calculated by subtraction between Tc and To.

2.10 X-ray diffraction patterns and relative crystallinity

The x-ray diffraction patterns of corn starch were determined with an X-ray diffractometer (XRD-6000, Shimadzu, Brazil). Scanning regions of diffraction ranged from 5 to 30° with a target voltage of 40 kV, a current of 40 mA, and a scan speed of 1° min-1.

The relative crystallinity (RC) of corn starch was calculated according to Rabek (1980) using Eq. 8.

$$RC\ (\%) = \frac{Ac}{Ac+Aa} \times 100 \tag{8}$$

Where Ac is the crystalline area and Aa is the amorphous area on X-ray diffractograms.

2.11 Statistical analysis

The experiment was performed in triplicate, except for thermal properties and relative crystallinity, which were performed only once. The results of the three determinations were submitted to analysis of variance (ANOVA) with 95% reliability. When the independent variables (drying temperature, time of separation, and part of corncob) showed significant effects, the splitting into simple effects were performed. Simple effects were observed by Tukey's test with 95% reliability.

3 Results and discussion

3.1 Moisture ratio, drying rate, and moisture diffusivity

In Figure 2 the moisture ratio and the drying rate are presented and in Figure 3 the effective moisture diffusivity is presented. A reduction in drying time (Figure 2A) and an increase in drying rate (Figure 2B) and effective moisture diffusivity (Figure 3) were observed by the increase in drying temperature. These results are in agreement with observed by Coradi et al. (2019) and Coradi et al. (2021) when the authors evaluated the drying of conventional corn AG 1051 and Herculex 30S31 transgenic at 80, 100, and 120 °C. Doymaz and Pala (2003) studied the drying characteristics of corn in a thin-layer at temperatures of 55, 65, and 75 °C. These authors reported a reduction in drying time from 135 to 70 min with an increase in drying temperature from 55 to 75 ºC. In addition, Doymaz and Pala (2003) reported that increasing the drying temperature from 55 to 75 ºC resulted in an increase in the moisture diffusivity from 9.488×10^{-11} to 17.68×10^{-11} $m^2 s^{-1}$.

At 60 ºC, drying time, drying rate, and effective moisture diffusivity showed no difference between the grains from the center and extremities of corncob (Figures 1 and 2). However, when the grains were dried at 80 and 100 ºC, a higher drying rate and effective moisture diffusivity were observed in the grains from the center of the corncob. These results were due to the lower thickness, equivalent radius, and sphericity of the corn from the center (Table 1). Inside the grains, water tends to diffuse through the shortest distance between the center and the periphery of the grain, thus, in the direction of thickness. In this way, the smaller the grain thickness, the easier it will be for water to move from the interior to the periphery and the higher the effective moisture diffusivity, resulting in the acceleration of the drying process of the grains from the center of corncob concerning the grains from extremities of the corncob.

Another characteristic that justifies the higher diffusivity of the grains from the center of corncob can be related to the consistency of the endosperm of these grains, where the floury endosperm predominates. The grains from extremities have a higher presence of vitreous endosperm. According to Muthukumarappan and Gunasekaran (1994), the diffusivity of the farinaceous endosperm can be 75 to 79% higher than the diffusivity of the vitreous endosperm.

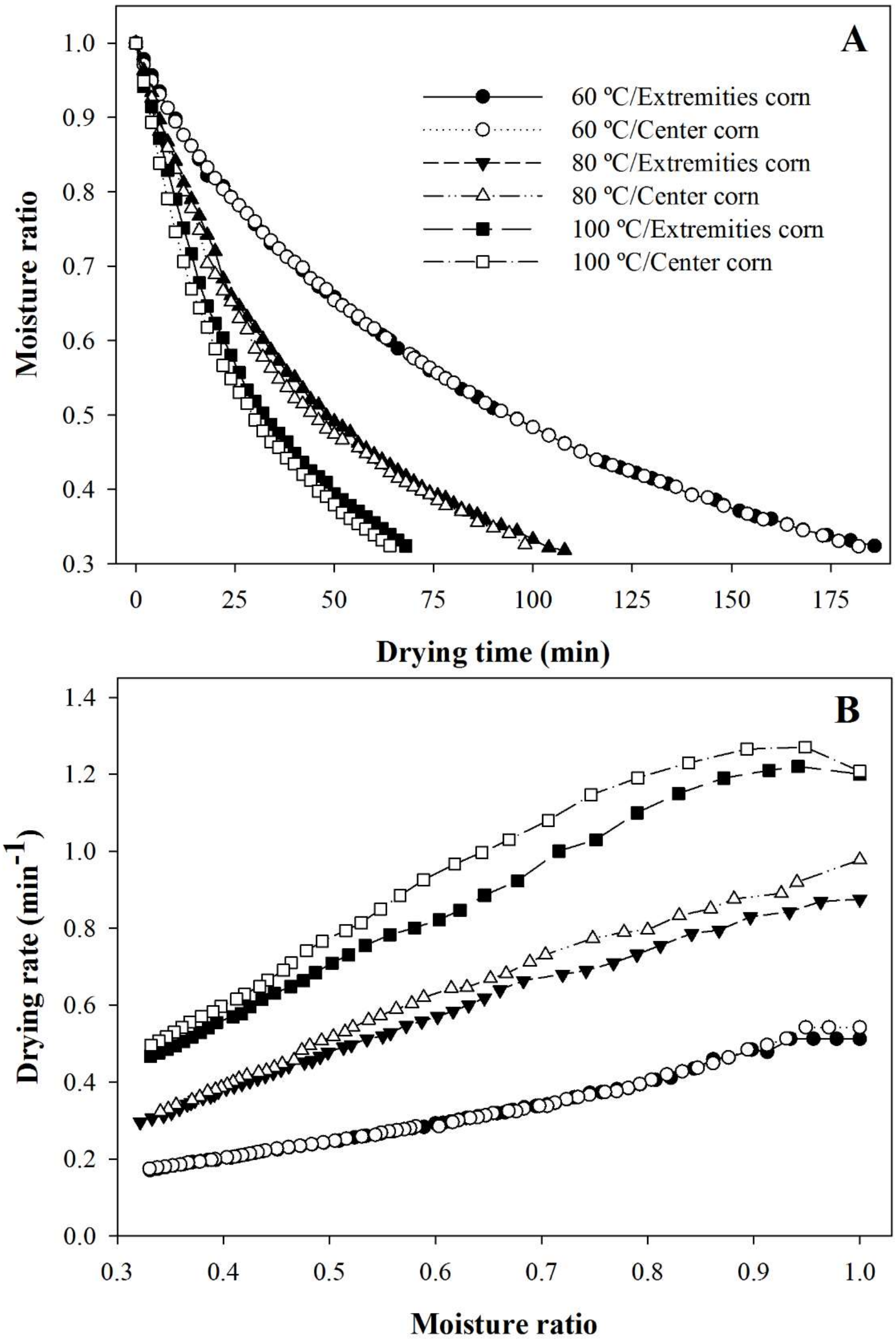


Figure 2. Dimensionless moisture ratio (A) and drying rate (B) of corn grains from center and extremities of corncob subjected to different drying temperatures.

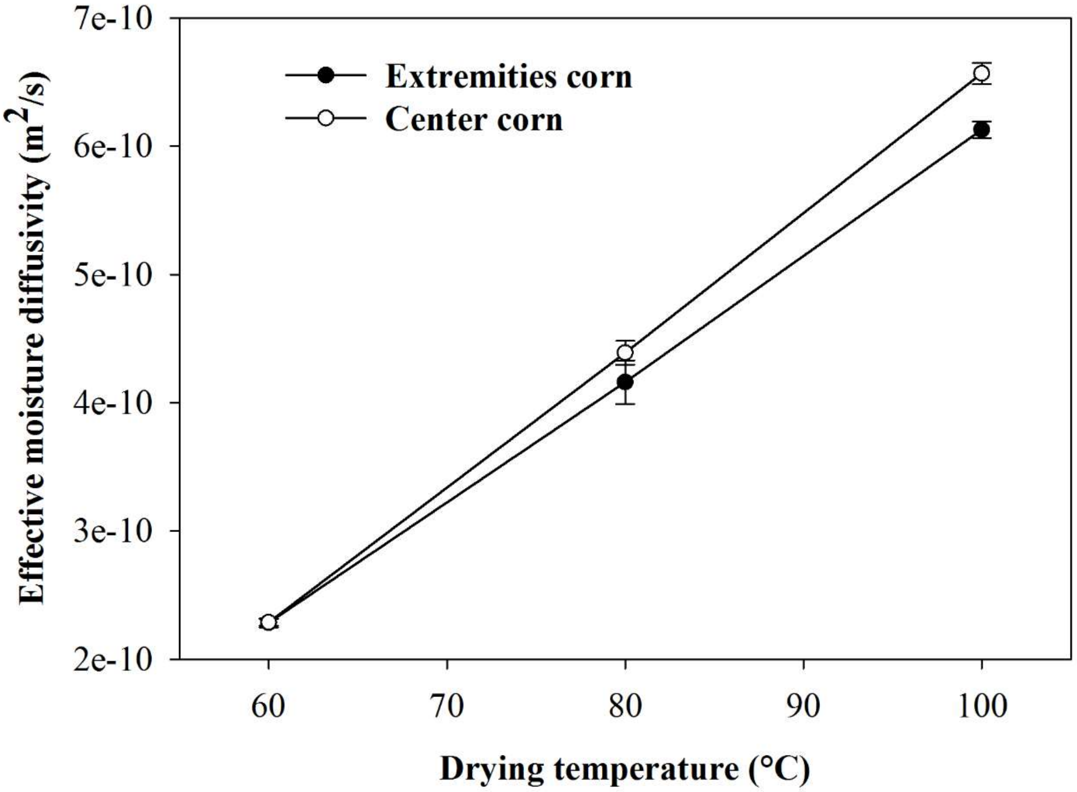


Figure 3. Effective moisture diffusivity of corn grains from center and extremities of corncob subjected to different drying temperatures.

3.2 Extraction yield of corn starch and residual protein and fat content

Analysis of variance showed significant effects ($P < 0.05$) of all the variables studied on starch extraction yield. The residual protein content was significantly affected by the variables corncob part, separation, drying temperature, and the interactions between these variables. There were no effects ($P \geq 0.05$) of the variables studied on the residual lipid content in the isolated starch (Supplementary Material 2). The lipid contents in the isolated starch ranged from 0.53 to 0.56% (Table 2).

Table 2. Extraction yield, residual protein content, residual lipid content, swelling power, and solubility of starch extracted from corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Grains separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
			*Extraction yield (%)**			
Extremities grains	42.85 ± 2.87 aAα	43.38 ± 2.79 aAα	38.60 ± 3.57 aAα	40.59 ± 3.42 aAα	21.49 ± 3.49 bAα	25.97 ± 1.05 bAα
Center grains	45.58 ± 1.74 aAα	42.14 ± 1.08 aAα	39.84 ± 2.79 aAα	29.57 ± 3.68 bBβ	23.09 ± 1.76 bAα	16.42 ± 0.67 cBβ
			*Residual protein content (%)**			
Extremities grains	0.65 ± 0.01 bAα	0.56 ± 0.03 aAβ	0.46 ± 0.01 cBα	0.39 ± 0.02 bBβ	1.01 ± 0.02 aAα	0.43 ± 0.05 abBβ
Center grains	0.43 ± 0.01 cBβ	0.58 ± 0.01 cAα	0.57 ± 0.02 bAβ	1.91 ± 0.07 bAα	1.33 ± 0.03 aBβ	2.56 ± 0.01 aAα
			*Residual fat content (%)**			
Extremities grains	0.53 ± 0.04 aAα	0.54 ± 0.01 aAα	0.56 ± 0.01 aAα	0.55 ± 0.00 aAα	0.56 ± 0.01 aAα	0.56 ± 0.01 aAα
Center grains	0.55 ± 0.01 aAα	0.55 ± 0.01 aAα	0.56 ± 0.01 aAα	0.55 ± 0.01 aAα	0.56 ± 0.01 aAα	0.56 ± 0.00 aAα
			*Swelling power (g/g)**			
Extremities grains	10.25 ± 0.12 aAα	9.79 ± 0.28 aAα	9.43 ± 0.09 bAα	9.57 ± 0.16 aAα	9.28 ± 0.16 bAα	8.71 ± 0.10 bAα
Center grains	10.15 ± 0.59 aAα	9.71 ± 0.12 aAα	9.12 ± 0.13 aAα	8.34 ± 0.58 abAβ	9.04 ± 0.14 aAα	8.05 ± 0.26 bBβ
			*Solubility (%)**			
Extremities grains	3.21 ± 0.29 aAα	3.60 ± 0.15 aAα	3.05 ± 0.04 aAα	3.07 ± 0.13 bAα	2.59 ± 0.02 aAβ	3.16 ± 0.07 abAα
Center grains	3.59 ± 0.12 aAα	2.31 ± 0.36 aBβ	3.20 ± 0.03 aAα	1.95 ± 0.31 aBβ	2.99 ± 0.31 aAα	1.71 ± 0.26 aBβ

**Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

A tendency to reduce the extraction yield and an increase in the residual protein content was observed as the drying temperature increased. At 60 ºC no differences were observed between treatments. In the starch extracted from corn dried at 80 and 100 ºC, the lower extraction yield (25.57 and 16.42%) and the higher residual protein content (1.91 and 2.56%) were observed in the grains from the center of corncob and separated after drying (Table 2).

The starch extraction yield from the separated grains before drying did not differ when dried at 80 and 100°C. However, at these same temperatures, in the grains separated after drying, the grains from extremities showed a higher extraction yield. In addition, when comparing the time of separation, the grains separated before drying showed a higher starch extraction yield than the grains separated after drying (Table 2).

These results are in agreement with Malumba et al. (2009b) who studied the influence of drying temperature (54 – 130 ºC) of corn (Baltimore variety) on the functional properties of isolated starch. These authors reported that increasing the drying temperature from 54 to 130 ºC reduced the corn starch extraction yield by 28.47%. Timm et al. (2020) evaluated the effects of drying temperature (30 – 90 ºC) of different corn genotypes on the properties of isolated starch. Timm et al. (2020) reported a tendency to reduce the starch extraction yield with increasing drying temperature.

Drying, even at high temperatures, did not affect the extraction yield of corn from the center and extremities of corncob separated before drying due to uniformity in grain dimensions. For the grains separated after drying, that is, dried together and forming an uneven grain mass, lower extraction yield and higher protein residual were observed in the grains from the center of the corncob. As the grains from the center are thinner (Table 1), water tends to diffuse more quickly in these grains, when compared to the grains from extremities that are more spherical (Figure 3). Thus, when the drying of grains from the center and extremities occurs together, the corn from the center suffers higher thermal damage. This thermal damage promotes higher starch-protein and protein-protein interactions, through disulfide bonds that surround the starch granules, making their separation and purification difficult (Kaczmarek et al., 2014; Malumba et al., 2009b; Timm et al., 2020).

3.3 Morphology of corn endosperm and starch granules

The endosperm morphology of corn kernels and the morphology of isolated starch granules are shown in Supplementary Material 3 and Figure 4, respectively. When dried at 60 ºC, the endosperm (Supplementary Material 3A and 3C) and starch granules (Figure 4A and 4C) extracted from the grains at the center and extremities separated before drying showed structure without deformation. It was possible to observe the starch granules and the protein matrix in the endosperm of the grains (Supplementary Material 3A and 3C) and the well-defined polyhedral structure of the isolated starch granules (Figures 4A and 4C). These results are in agreement with Timm et al. (2020), where the authors observed a polyhedral structure of starch granules extracted from a semi-hard corn genotype.

When the grains were dried at 100 ºC, changes in the natural morphology of the corn endosperm and starch granules were observed under all conditions studied (Supplementary Material 3E, 3F, 3G, and 3H, and Figures 4E, 4F, 4G, and 4H). In these cases, the starch granules showed deformations, probably due to partial gelatinization that occurred during the initial stages of drying, where the water content (31.9%) and the temperature are sufficient for this phenomenon to occur (Ziegler et al., 2020).

When separated before drying, grains from the center and extremities of corncob dried at 100 ºC showed similar deformations, common to the effects of drying temperature only. When separated after drying, the grains from extremities remained with endosperm characteristics and isolated granules without alterations. However, the grains from the center of the corncob showed deformation of the entire endosperm (Supplementary Material 3H), loss of polyhedral shape, and roundness at the ends of the isolated starch granules (Figure 4H). These results justify the higher thermal effect suffered by the grains from the center of the corncob (lower thickness and higher drying speed) concerning the grains from extremities (higher thickness and lower drying speed) when separated after drying.

The morphological characteristics are in agreement with the results of extraction yield and residual protein content. The higher deformations of the endosperm (Supplementary Material 3H) and the isolated granules (Figure 4H) resulted in a reduction in the extraction yield and an increase in the residual protein content (Table 2). Ziegler et al. (2020) evaluated the effects of drying temperature (30 – 100 ºC) of red popcorn on the morphological properties and the technological and digestive properties of the isolated starch. Ziegler et al. (2020) reported that popcorn dried at 100 ºC resulted in a more compacted endosperm structure, probably a result of partial starch gelatinization, associated with greater starch-protein interaction. These phenomena probably occurred in the grains from the center of corncob, dried at 100 ºC, and separated after drying, which justifies the reduction in extraction yield, increase in residual protein, and changes in morphological structure.

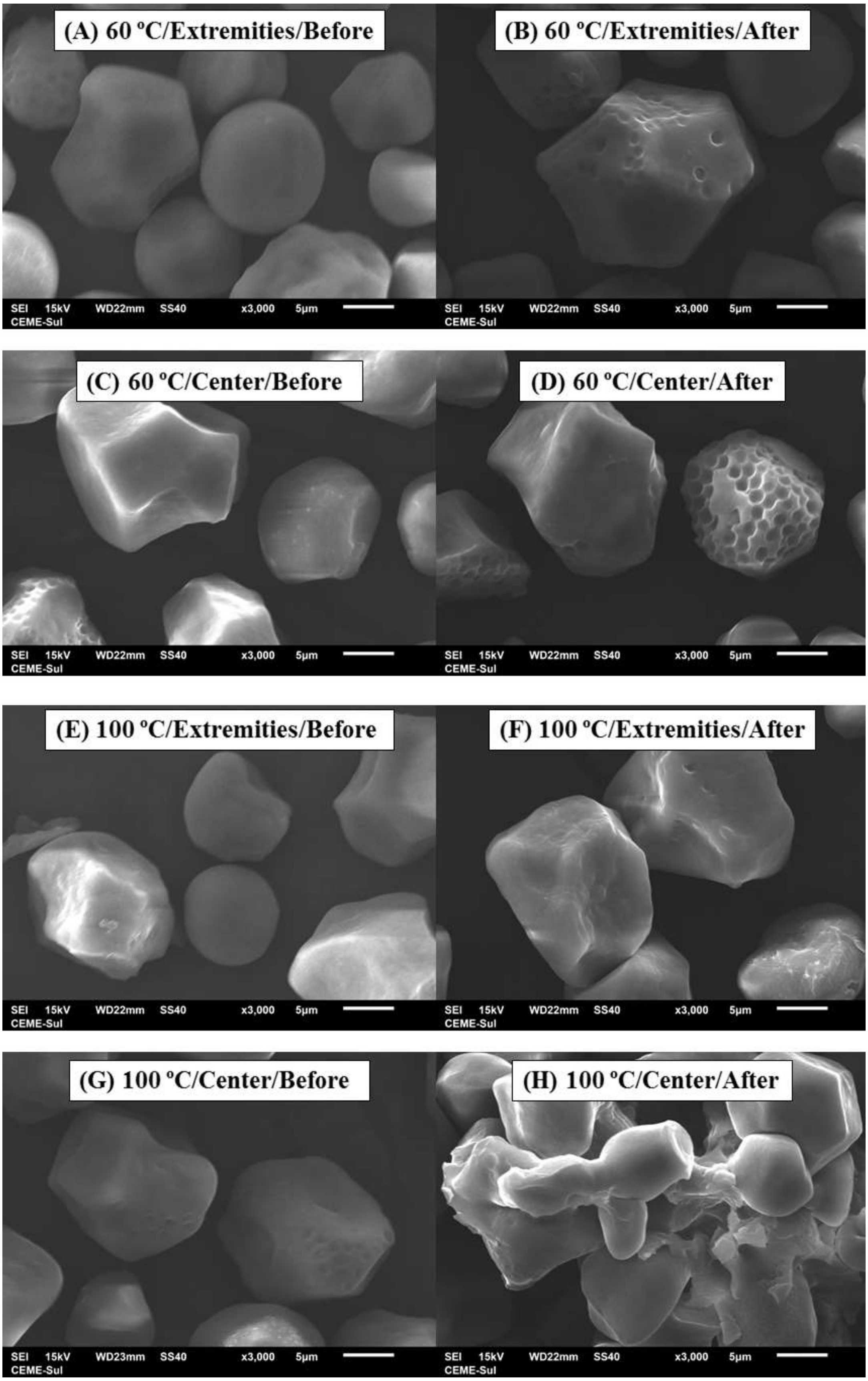


Figure 4. Scanning electron microscopy (SEM) of starch isolated from dried corn grains under different conditions

3.4 Swelling power and solubility

The analysis of variance showed significant effects ($P < 0.05$) of all the variables studied on the swelling power and the solubility of starch granules (Supplementary Material 2). A tendency to reduce swelling power and starch solubility was observed as the corn drying temperature increased (Table 2).

Regardless of the drying temperature, no differences in starch solubility were observed between the grains from the center and extremities when separated before drying. When comparing the grains separated after drying, the solubility of the starch extracted from the grains from the center of corncob was 35.8, 36.5, and 45.9% lower concerning the starch from the grains from extremities, respectively, drying at 60, 80, and 100°C (Table 2).

At 100 ºC, lower swelling power (8.05 g g-1) and lower solubility (1.71%) were observed in the grains from the center of the corncob and separated after drying. These results were due to the higher residual protein content observed under these conditions (Table 2), restricting the swelling capacity of the starch granules during gelatinization (Debet & Gidley, 2006; Timm et al., 2020).

These results are in agreement with Cruz et al. (2015), who evaluated the effects of drying temperature (45, 65, and 85 ºC) of sorghum grains on the properties of isolated starch, and according to Malumba et al (2009b), who also evaluated the effects of drying temperature (54 – 130 ºC) of corn on the properties of isolated starch. Drying corn kernels with different dimensions together, as is the case between the grains from the center and extremities of corncob, results in higher heat stress to the grains from the center. This statement can be evidenced by the higher protein residual and the lower extraction yield, solubility, and swelling power of the starch observed in the starch of the grains from the center and separated after drying (Table 2). The reduction in solubility and swelling power helps to highlight the molecular interactions of starch at high temperatures, leaving the starch with a lower capacity to bind with water (Malumba et al., 2009b; Zavareze & Dias, 2011), which affects the leaching capacity of amylose, reducing the solubility (Colussi et al., 2014).

3.5 Colorimetric profile

The analysis of variance showed significant effects (*P < 0.05*) of all the variables studied on parameters of the colorimetric profile of starch (Supplementary Material 4). It was observed a tendency to reduction of the parameter of a* and the parameter of L*, and a tendency to increase the parameter of b* according to the increase of the drying temperature (Table 3). These results are in agreement with Timm et al. (2020), who reported that according to the increase in drying temperature from 30 to 90 ºC, there was a tendency to reduce the a* parameter and a tendency to increase the b* parameter of the starch isolated from three corn genotypes.

In the drying performed at 80 and 100 ºC, the lower values of a* (-2.74 and -3.21, respectively) and L* (97.94 and 96.96, respectively), and the higher values of b * (12.62 and 15.55, respectively) in the starch extracted from the grains from the center and separated after drying (Table 3). This drying condition showed the higher thermal damage suffered during drying. Ramos et al. (2019) reported that increasing the drying temperature of red rice from 40 to 100 ºC promoted a 25% increase in the b* value of the starch extracted from these grains, probably due to the association of starch with pigments, as in the case of red rice with proanthocyanidins (Ramos et al., 2019). Timm et al. (2020) reported that corn grains with yellow pericarp result in starch with higher b* values, mainly due to the higher carotenoid content present in yellow genotypes concerning white corn (Hu & Xu, 2011; Timm et al., 2020; Timm et al., 2021).

In the starch extracted from the grains from the center of corncob, dried at 100 ºC and separated after drying, the reduction of a* and L* values, and the increase of b* values (Table 2) may indicate that during corn drying, in addition to the aforementioned interactions between starch-protein and protein-protein, interactions between starch and other constituents, such as carotenoids, which intensified in this treatment because it was the condition in which there was higher thermal damage.

Table 3. Parameters a*, b*, and L* of the colorimetric profile of starch extracted from corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
			a-value***			
Extremities grains	-1.35 ± 0.03 aBβ	-1.24 ± 0.06 aAα	-1.37 ± 0.02 aAβ	-1.21 ± 0.03 aAα	-2.28 ± 0.11bAβ	-1.51 ± 0.03 bAα
Center grains	-1.04 ± 0.03 aAα	-1.21 ± 0.04 aAβ	-1.70 ± 0.04 bBα	-2.74 ± 0.13 bBβ	-2.62 ± 0.17 cBα	-3.21 ± 0.10 cBβ
			b-value***			
Extremities grains	5.77 ± 0.14 bAα	4.91 ± 0.21 bAβ	5.61 ± 0.05 bBα	4.90 ± 0.04 bBβ	9.44 ± 0.57aBα	5.83 ± 0.02 aBβ
Center grains	3.93 ± 0.07 cBβ	4.77 ± 0.10 cAα	6.66 ± 1.70 bAβ	12.62 ± 0.65 aAα	11.39 ± 0.72 aAα	15.55 ± 0.77 aAβ
			L-value***			
Extremities grains	99.28 ± 0.11 aAα	99.37 ± 0.09 aAα	99.42 ± 0.04 aAα	99.20 ± 0.07 aAα	98.61 ± 0.21bBβ	99.51 ± 0.11 aBα
Center grains	99.25 ± 0.05 aAα	98.72 ± 0.11 aBβ	99.30 ± 0.18 aAα	97.94 ± 0.13 bBβ	98.28 ± 0.42 bAα	96.96 ± 0.30 cAα

***Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.6 Pasting properties and gel hardness

Analysis of variance showed significant effects ($P < 0.05$) of drying temperature on pasting temperature, peak viscosity, breakdown, final viscosity, and setback. The corncob part had a significant effect ($P < 0.05$) only on breakdown and gel hardness. The separation had a significant effect on the pasting temperature and the breakdown (Supplementary Material 5). According to the increase in the drying temperature, an increase in the pasting temperature and a reduction in peak viscosity, breakdown, final viscosity, and setback were observed (Table 4). These results are in agreement with Cruz et al. (2015), who dried sorghum at temperatures between 45 and 85ºC, and in agreement with Malumba et al. (2009b) and Timm et al. (2020), who dried corn at temperatures between 54 and 130 ºC and between 30 and 90 ºC, respectively.

The starch extracted from the grains from the extremities of the corncob and separated before drying at 80 and 100 ºC showed a higher breakdown and gel hardness concerning the starch extracted from the grains from the center. In addition, the grains from the center separated after drying at 80 and 100 ºC resulting in starch with higher pasting temperature and gel hardness concerning grains separation before drying (Table 4).

The grains from the center, dried at 80 and 100 ºC, separated after drying suffered the higher thermal damage resulting from drying. In these treatments, there was an increase in the thermal stability of the starch, due to changes in the amorphous and crystalline phases of the granules (Jacobs & Delcour, 1998). The increase in pasting temperature is related to the lower swelling power of the starch granules (Table 2) (Malumba et al., 2009b) and the higher residual protein content in the starch (Table 2) (Malumba et al., 2009b; Timm et al., 2020). The sum of these factors resulted in the strengthening of the molecular interactions and the crosslinking of the starch, increasing the energy needed to break these interactions, which increased the pasting temperature (Zavareze & Dias, 2011).

The increase in starch gel hardness is normally associated with retrogradation of amylose and amylopectin, respectively, associated with water syneresis and crystallization of amylopectin (Sandhu & Singh, 2007). In this study, it was observed an increase in the hardness of the starch gel extracted from the grains from the center, dried at 80 and 100 ºC, separated after drying. However, no differences were observed in starch setback under these conditions (Table 4).

Table 4. Pasting properties and gel hardness of starch extracted from corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
			*Pasting temperature (ºC)**			
Extremities grains	75.13 ± 0.04 cAα	75.60 ± 0.57 cAα	77.85 ± 0.64 bAα	77.58 ± 0.04 bAα	79.60 ± 0.64 aAα	79.93 ± 0.04 aAα
Center grains	75.53 ± 0.60 cAα	76.00 ± 0.07 cAα	77.53 ± 0.04 bAβ	78.38 ± 0.04 bAα	79.88 ± 0.04 aAβ	80.83 ± 0.04 aAα
			Peak viscosity (RVU)			
Extremities grains	250.63 ± 3.12 aAα	255.21 ± 1.36 aAα	224.67 ± 2.12 bAα	213.71 ± 1.12 bAα	181.34 ± 2.00 cAα	176.58 ± 0.71 cAα
Center grains	251.75 ± 0.95 aAα	257.04 ± 0.65 aAα	215.17 ± 6.13 bAα	216.04 ± 0.30 bAα	176.38 ± 2.06 cAα	176.50 ± 1.30 cAα
			Breakdown (RVU)			
Extremities grains	77.71 ± 0.53 aBβ	86.04 ± 6.07 aAα	58.17 ± 0.12 bAα	42.63 ± 1.94 bAβ	26.92 ± 0.71 cAα	19.54 ± 1.36 cAβ
Center grains	85.04 ± 1.82 aAα	82.96 ± 0.88 aAα	46.67 ± 3.06 bBα	41.25 ± 1.30 bAβ	21.05 ± 0.88 cBα	19.63 ± 0.53 cAα
			Final viscosity (RVU)			
Extremities grains	289.38 ± 2.18 bAα	297.67 ± 1.29 aAα	301.25 ± 1.06 aAα	295.17 ± 1.89 aAα	256.38 ± 0.77 cAα	258.55 ± 1.59 bAα
Center grains	285.59 ± 0.47 abAα	298.80 ± 1.24 aAα	302.00 ± 7.78 aAα	296.54 ± 1.47 aAα	263.96 ± 7.72 bAα	266.50 ± 2.12 bAα
			Setback (RVU)			
Extremities grains	116.46 ± 1.47 bAα	128.50 ± 6.01 aAα	134.75 ± 3.30 aAα	124.08 ± 4.95 aAα	101.96 ± 1.94 cAα	101.50 ± 0.95 bAα
Center grains	118.88 ± 0.42 abAα	124.71 ± 0.30 aAα	133.50 ± 4.71 aAα	121.75 ± 2.47 aAα	108.63 ± 6.54 bAα	109.63 ± 1.35 bAα
			Gel hardness (g)			
Extremities grains	1294.95 ± 14.64 aAα	991.19 ± 116.77 aAβ	1271.00 ± 42.90 aAα	1145.11 ± 114.75 aAα	1139.33 ± 62.67 aAα	1190.63 ± 93.50 aAα
Center grains	1016.91 ± 88.97 aBα	1108.94 ± 88.20 aAα	956.13 ± 227.71 aBβ	1216.17 ± 8.17 aAα	832.10 ± 154.14 aBβ	1101.40 ± 29.27 aAα

**Lowercase letters compare between temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.7 Thermal properties and x-ray diffraction patterns

According to the increase in the drying temperature, an increase in the onset temperature, peak temperature, and conclusion temperature of gelatinization, and a reduction in starch gelatinization enthalpy was observed. When the grains were dried at 100 ºC, a higher gelatinization enthalpy (ΔH) was observed in the starch extracted from the grains from the center of the corncob and separated after drying (Table 5 and Figure 5).

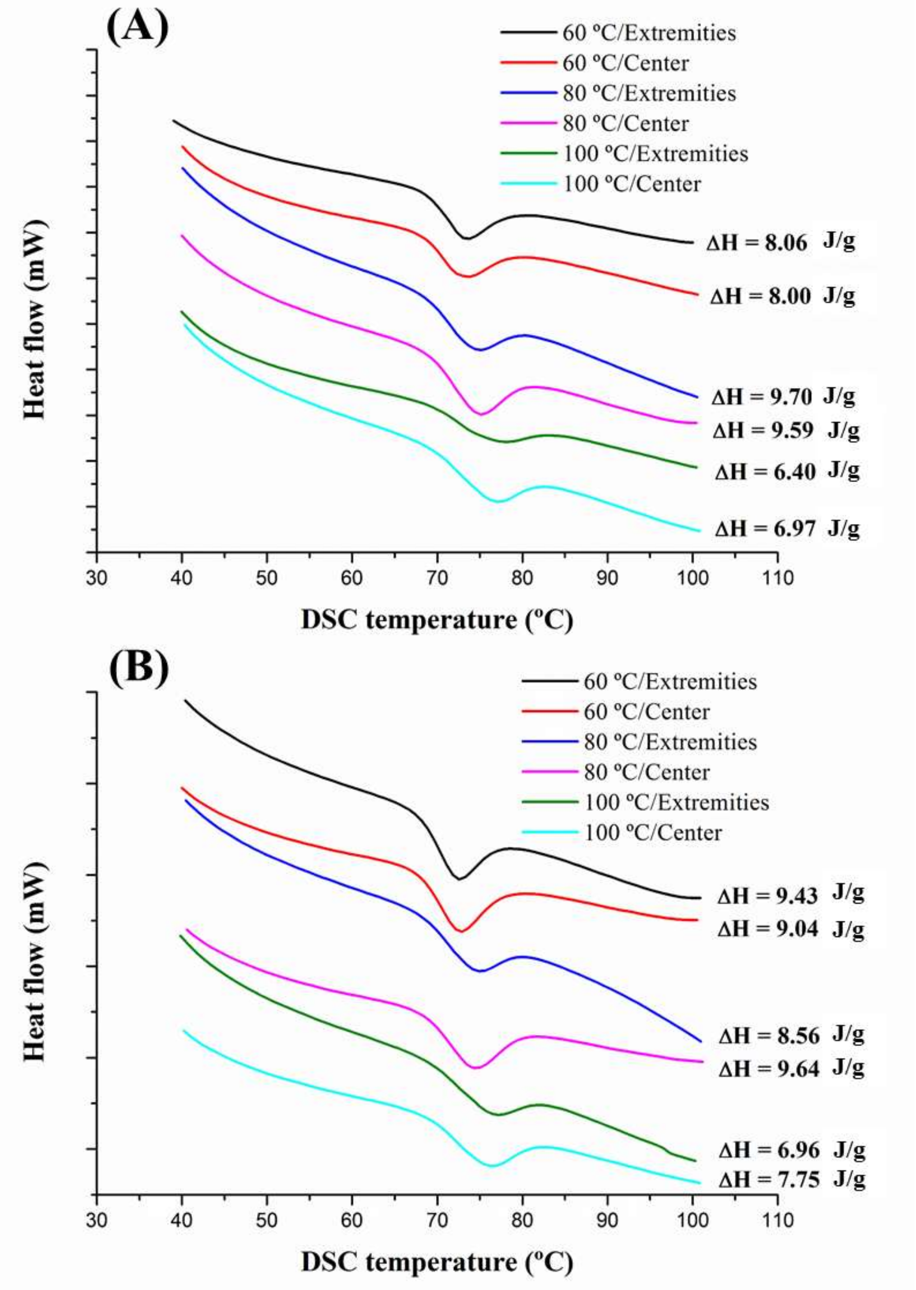


Figure 5. Gelatinization profile and gelatinization enthalpy of starch isolated from corn grains from center and extremities of corncob dried at different temperatures and separated before drying (A) and after drying (B).

Table 5. Thermal properties and relative crystallinity of starch extracted from corn grains from the center and extremities of the corncob, separated before and after drying at 60, 80, and 100 ºC.

Drying temperature	60 ºC		80 ºC		100 ºC	
Separation	Before drying	After drying	Before drying	After drying	Before drying	After drying
Onset temperature (To) (ºC)						
Extremities grains	66.99	67.27	67.73	69.07	69.01	69.52
Center grains	66.96	66.83	68.10	67.57	69.76	69.39
Peak temperature (Tp) (ºC)						
Extremities grains	73.77	72.55	75.20	75.08	78.09	77.20
Center grains	73.76	72.90	75.08	74.25	76.97	76.16
Conclusion temperature (Tc) (ºC)						
Extremities grains	81.36	79.11	81.19	81.04	84.62	82.09
Center grains	80.69	79.47	81.94	81.38	82.92	82.31
Gelatinization temperature range (ΔT=Tc-To)						
Extremities grains	14.37	11.84	13.46	11.97	15.61	12.57
Center grains	13.73	12.64	13.84	13.81	13.16	12.92
Gelatinization enthalpy (ΔH) (J/g)						
Extremities grains	8.06	9.43	9.70	8.56	6.40	6.96
Center grains	8.00	9.04	9.59	9.64	6.97	7.75
Relative Crystallinity (%)						
Extremities grains	43.52	46.70	43.62	46.38	41.56	40.59
Center grains	46.77	56.16	44.56	44.43	44.17	44.86

The grains from the center and separated after drying at 100 ºC resulted in starch with higher thermal resistance, observed by the reduction of swelling power and increase in residual protein content (Table 2), and pasting temperature (Table 4). These results are in agreement with Ziegler et al. (Ziegler et al., 2020), who reported that the increase in the gelatinization enthalpy is associated with the interaction of starch with other constituents of the grain (proteins and lipids), with the reduction of active sites for binding with water and with the increase of thermal resistance, making it difficult to transform to pasting state.

The higher the difficulty for water absorption by the starch, the higher the energy required for total swelling and, consequently, its total gelatinization, which provides an increase in enthalpy (Zavareze & Dias, 2011; Ziegler et al., 2020).

Starch isolated from grains from the center and extremities of corncob showed a Type A diffraction pattern, with marked peaks at 15°, 17°, 18°, 20°, and 23° (Figure 6), regardless of drying temperature and time separation (before or after drying). This is the diffraction pattern for starch isolated from corn grains (Malumba et al., 2009b; Timm et al., 2020).

A reduction in the relative crystallinity of the starch was observed according to the increase in the drying temperature, for grains from the center and extremities separated before and after drying (Table 5 and Figure 6). These results are in agreement with Setiawan et al. (2010), who reported a reduction in the relative crystallinity of corn starch dried at a temperature of 80 °C (27.4%) when compared to drying in the sun (28.6%). These authors attributed this reduction in crystallinity to a partial gelatinization of the starch.

Regardless of the drying temperature and the moment of separation, the grains from the center of the corncob showed higher relative crystallinity than the grains from the extremities (Table 5). These results may be associated with the characteristics of the endosperm of the grains, with the grains in the center having a higher area of floury endosperm and the grains from extremities having a higher area of the vitreous endosperm. These results are in agreement with Xu et al. (2019), who naturally dried corn grains and evaluated the starch properties of the vitreous and floury endosperm. Xu et al. (2019) reported that the starch extracted from the floury endosperm showed higher crystallinity. Timm et al. (2020) extracted starch from corn grains with floury and vitreous endosperm and reported higher relative crystallinity in floury grains, mainly at lower drying temperatures (30, 50, and 70 ºC).

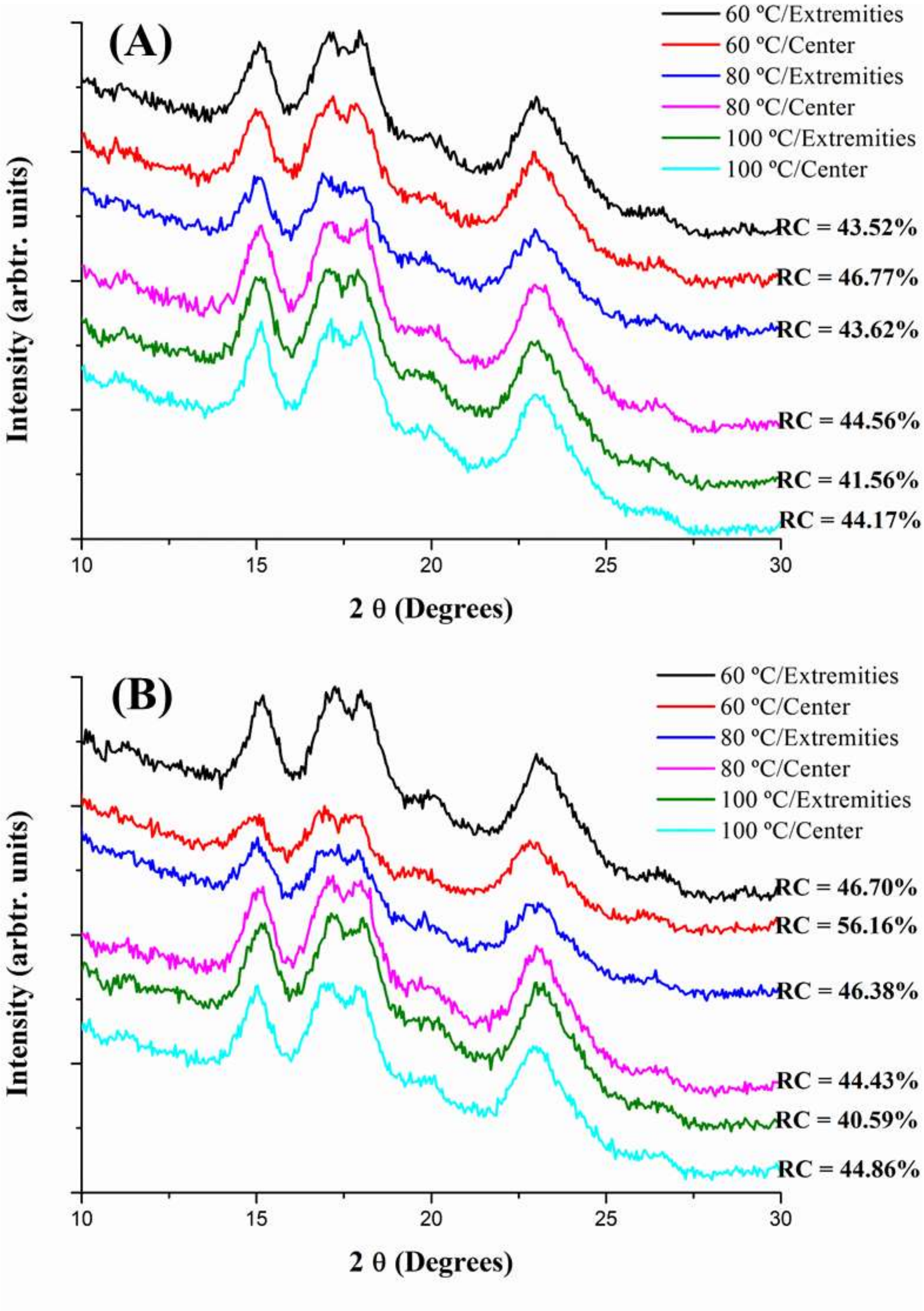


Figure 6. Diffraction profile and relative crystallinity of starch isolated from corn grains from center and extremities of corncob dried at different temperatures and separated before drying (A) and after drying (B).

4 Conclusion

Increasing the drying temperature resulted in reduced extraction yield and purity and increased the thermal resistance of the starch. When the grains from the center and extremities of corncob were separated after drying at 80 and 100 ºC, there was an intensification of these modifications in the starch isolated from the grains from the center, such as a higher reduction in extraction yield, purity, binding capacity with water, and heat resistance of starch granules. The results showed that the industrial separation of grains with different dimensions can increase the extraction yield by 35 to 40%. After this study, some research gaps were found: a) monitoring of the long-term storage of unevenly dried grains, b) breeding studies to search for new genotypes with higher grain uniformity along the corncob, and c) adding a step of separating corn grains with different dimensions before drying.

References

AACC, (1995). Approved Methods of the American Association of Cereal Chemists, American Association of Cereal Chemists, Inc., St. Paul, MN, 1995.

ASAE, American Society of Agricultural Engineers (1995). Moisture relationship of plant-based agricultural products. ASAE Standard D245.5. St. Joseph, MI: ASAE, 1995.

ASAE, American Society of Agricultural Engineers (2000). Moisture measurement-unground grain and seeds, in: Standards ASAE, Saint Joseph, 2000, pp. 563.

Brooker, D.B., Bakker-Arkem, A. F. W., Hall, C.W (1974). Drying cereal grains. Westport, AVI Publishing, 265p. 1974.

Choi, J. M., Park, C. S., Baik, M. Y., Kim, H. S., Choi, Y. S., Choi, H. W., & Seo, D. H (2018). Enzymatic extraction of starch from broken rice using freeze-thaw infusion with food-grade protease. Starch/Stärke, 70, 1700007. https://doi.org/10.1002/star.201700007

Colussi, R., Pinto, V.Z., Halal, S.L.M., Vanier, N.L., Villanova, F.A., Silva, R.M., Zavareze, E.R., & Dias, A.R.G (2014). Structural, morphological, and physicochemical properties of acetylated high-, medium-, and low-amylose rice starches. Carbohydrate Polymers, 103, 405–413.

Coradi, P.C., Souza, A.H.S., Camilo, L.J., Lemes, A.F.C., & Milane, L.V (2019). Analysis of the physical quality of genetically modified and conventional maize grains in the drying and wetting processes. Revista Ciência Agronômica, 50, 370-377. https://doi.org/10.5935/1806-6690.20190044

Coradi, P.C., Maldaner, V., Lutz, E., Daí, P.V.S., & Teodoro, P.R (2020). Influences of drying temperature and storage conditions for preserving the quality of maize postharvest on laboratory and field scales. Scientific Reports, 10, e22006. https://doi.org/10.1038/s41598-020-78914-x

Coradi, P.C., Nunes, M.T., Bellochio, S.D.C., Camilo, L.J., & Teodoro, P.E (2021). Effects of drying temperatures and storage conditions on the levels of lipids and starches in corn grains for yield ethanol industry. Biofuels, 1-10. https://doi.org/10.1080/17597269.2021.1904674

Crank, J (1975). The mathematics of diffusion (2nd ed.). Oxford, UK: Oxford University Press, 1975.

Cruz, D.B., Silva, W.S.V., Santos, I.P., Zavareze, E.R., & Elias, M.C (2015). Structural and technological characteristics of starch isolated from sorghum as a function of drying temperature and storage time. Carbohydrate Polymers, 133, 46–51. https://doi.org/10.1016/j.carbpol.2015.07.003

Debet, M. R., & Gidley, M. J (2006). Three classes of starch granule swelling: Influence of surface proteins and lipids. Carbohydrate Polymers, 64, 452-465. https://doi.org/10.1016/j.carbpol.2005.12.011

Doymaz, I., & Pala, M (2003). The thin-layer drying characteristics of corn. Journal of Food Engineering, 60, 125-130. https://doi.org/10.1016/S0260-8774(03)00025-6

Hu, Q. P., & Xu, J. G (2011). Profiles of carotenoids, anthocyanins, phenolics, and antioxidant activity of selected color waxy corn grains during maturation. Journal of Agricultural and Food Chemistry, 59, 2026-2033. https://doi.org/10.1021/jf104149q

Jacobs, H., & Delcour, J. A (1998). Hydrothermal Modifications of Granular Starch, with Retention of the Granular Structure: A Review. Journal of Agricultural and Food Chemistry, 46 (8), 2895-2905. https://doi.org/10.1021/jf980169k

Kaczmarek, S.A., Cowieson, A.J., Józefiak, D., & Rutkowski, A (2014). Effect of maize endosperm hardness, drying temperature and microbial enzyme supplementation on the performance of broiler chickens. Animal Production Science, 54, 956–965, https://doi.org/10.1071/AN13113

Leach, H.W., Mccowen, L.D., & Schoch, T.J (1959). Structure of the starch granule: I. Swelling and solubility patterns of various starches. Cereal Chemistry, 36, 534–544.

Maldaner, V., Coradi, P.C., Nunes, M.T., Muller, A., Carneiro, L.O., Teodoro, P.E., Teodoro, L.P.R., Bresseani, J., Anschau, K.F., & Muller, E.I (2021). Effects of intermittent drying on physicochemical and morphological quality of rice and endosperm of milled brown rice. LWT-Food Science and Technology, 8, 112334. https://doi.org/10.1016/j.lwt.2021.112334

Malumba, P., Janas, J., Masimango, T., Sindic, M., Deroanne, C., & Béra F (2009a). Influence of drying temperature on the wet-milling performance and the proteins solubility indexes of corn kernels. Journal of Food Engineering, 95, 393-399. https://doi.org/10.1016/j.jfoodeng.2009.05.022

Malumba, P., Massaux, C., Deroanne, C., Masimango, T., & Béra, F (2009b). Influence of drying temperature on functional properties of wet-milled starch granules. Carbohydrate Polymers, 75, 299-306. https://doi.org/10.1016/j.carbpol.2008.07.027

Mohsenin, N. N. (1986). Physical properties of plant and animal materials. New York: Gordon and Breach Publishers, 1986. 841p.

Muthukumarappan, K., & Gunasekaran, S. (1994). Moisture Diffusivity of Corn Kernel Components During Adsorption Part III: Soft and Hard Endosperms. Transactions of the ASAE, 37, 1275–1280. doi:10.13031/2013.28207

Nunes, M.T., Coradi, P.C., Müller, A., Carneiro, L.O., Steinhaus, J.I., Anschau, K.F.. Souza, G.A.C., Muller, E.I., Teodoro, P.E., & Dutra, A.P (2022). Stationary rice drying: influence of initial moisture and impurities contents in the mass grains on the physicochemical and morphological rice quality. Journal of Food Processing and Preservation, 1, 1-10. https://doi.org/10.1111/jfpp.16558

Rabek, J.F (1980). Experimental methods in polymer chemistry: Applications of wide-angle X-ray diffraction (WAXD) to the study of the structure of polymers. Chichester: Wiley Interscience. (1980).

Ramos, A. H., Rochenbach, B. A., Ferreira, C. F., Gutkoski, L. C., & Oliveira, M (2019). Characteristics of flour and starch isolated from red rice subjected to different drying conditions. Starch/Stärke, 71, 1800257. https://doi.org/10.1002/star.201800257

Sandhu, K.S., Singh, N (2007). Some properties of corn starches. II. Physicochemical, gelatinization, retrogradation, pasting and gel textural properties. Food Chemistry, 101, 1499-1507. https://doi.org/10.1016/j.foodchem.2006.01.060

Sandhu, K.S., Singh, N., & Malhi, N.S (2005). Physicochemical and thermal properties of starches separated from corn produced from crosses of two germ pools. Food Chemistry, 89, 541–548. https://doi.org/10.1016/j.foodchem.2004.03.00

Setiawan, S., Widjaja, H., Rakphongphairoj, V., Jane, J. L (2010). Effects of drying conditions of corn kernels and storage at an elevated humidity on starch structures and properties. Journal of Agricultural and Food Chemistry, 58, 12260-12267. https://doi.org/10.1021/jf102838j

Timm, N.S., Ramos, A.H., Ferreira, C.D., Biduski, B., Eicholz, E.D., & Oliveira, M. Effects of drying temperature and genotype on morphology and technological, thermal, and pasting properties of corn starch. International Journal of Biological Macromolecules, 165, 354-364. https://doi.org/10.1016/j.ijbiomac.2020.09.197

Timm, N.S., Ramos, A.H., Ferreira, C.D., Rios, A.O., Zambiazi, R.C., & Oliveira, M (2021). Influence of germ storage from different corn genotypes on technological properties and fatty acid, tocopherol, and carotenoid profiles of oil. European Food Research and Technology, 247, 1449–1460. https://doi.org/10.1007/s00217-021-03723-z

Xu, A., Lin, L., Guo, K., Liu, T., Yin, Z., Wei, C (2019). Physicochemical properties of starches from vitreous and floury endosperms from the same maize kernels. Food Chemistry, 291, 149-156. https://doi.org/10.1016/j.foodchem.2019.04.024

Yoenyongbuddhagal, S., & Noohorm, A (2002). Effect of physicochemical properties of high-amylose Thai rice flours on vermicelli quality. Cereal Chemistry, 79, 481-485. https://doi.org/10.1094/CCHEM.2002.79.4.481

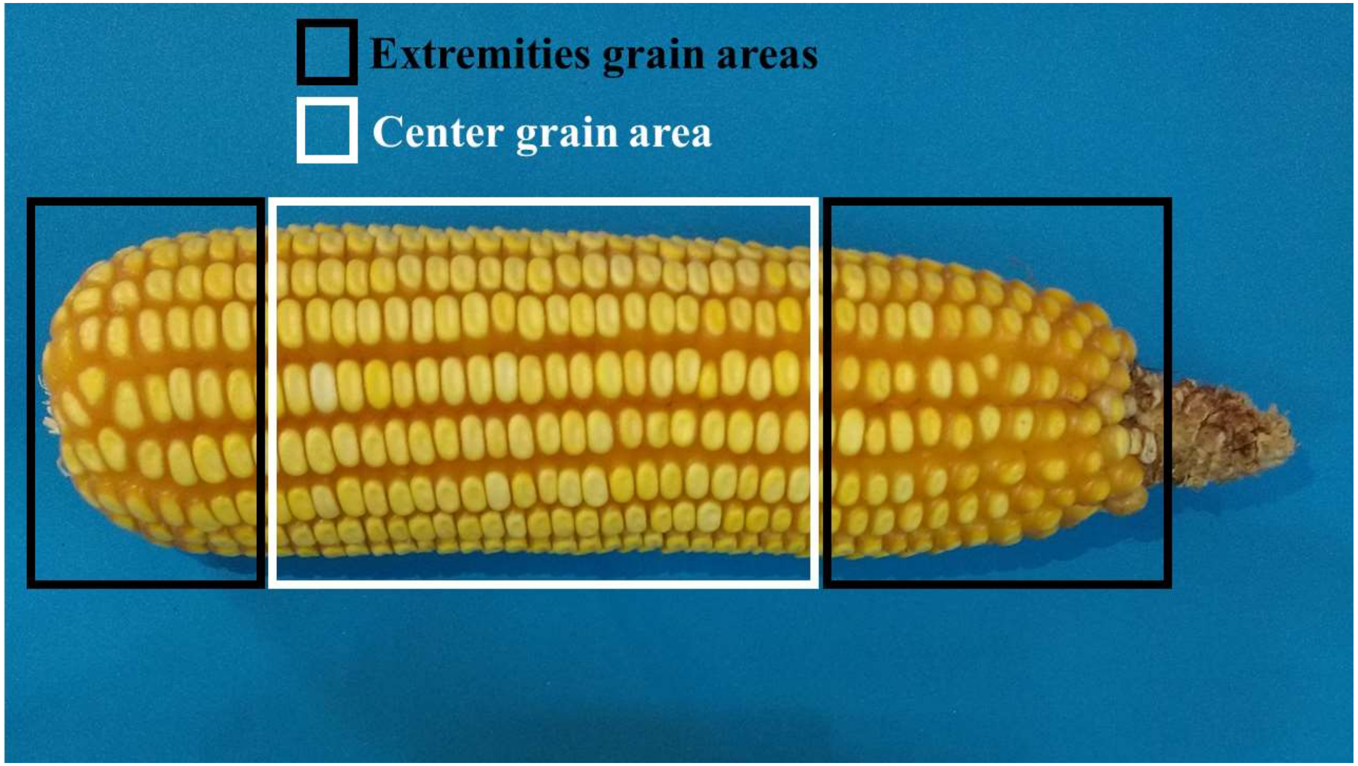
Zavareze, E. R., & Dias, A. R. G (2011). Impact of heat-moisture treatment and annealing in starches: A review. Carbohydrate Polymers, 83, 317-328. https://doi.org/10.1016/j.carbpol.2010.08.064

Zhang, R., Ma, S., Li, L., Zhang, M., Tian, S., Wang, D., Liu, K., Liu, H., & Zhu, W., Wang, X (2021). Comprehensive utilization of corn starch processing by-products: A review. Grain & Oil Science and Technology, 4, 89–107. http://dx.doi.org/10.1016/j.gaost.2021.08.003

Ziegler, V., Timm, N.S, Ferreira, C.D, Goebel, J.T., Pohndorf, R.S., & Oliveira, M. (2020). Effects of drying temperature of red popcorn grains on the morphology, technological, and digestibility properties of starch. International Journal of Biological Macromolecules, 145, 568-574. https://doi.org/10.1016/j.ijbiomac.2019.12.198

Supplementary materials

Supplementary material 1. The standard definition of the grains from the center area of the corncob and the grains from the extremities areas of the corncob.

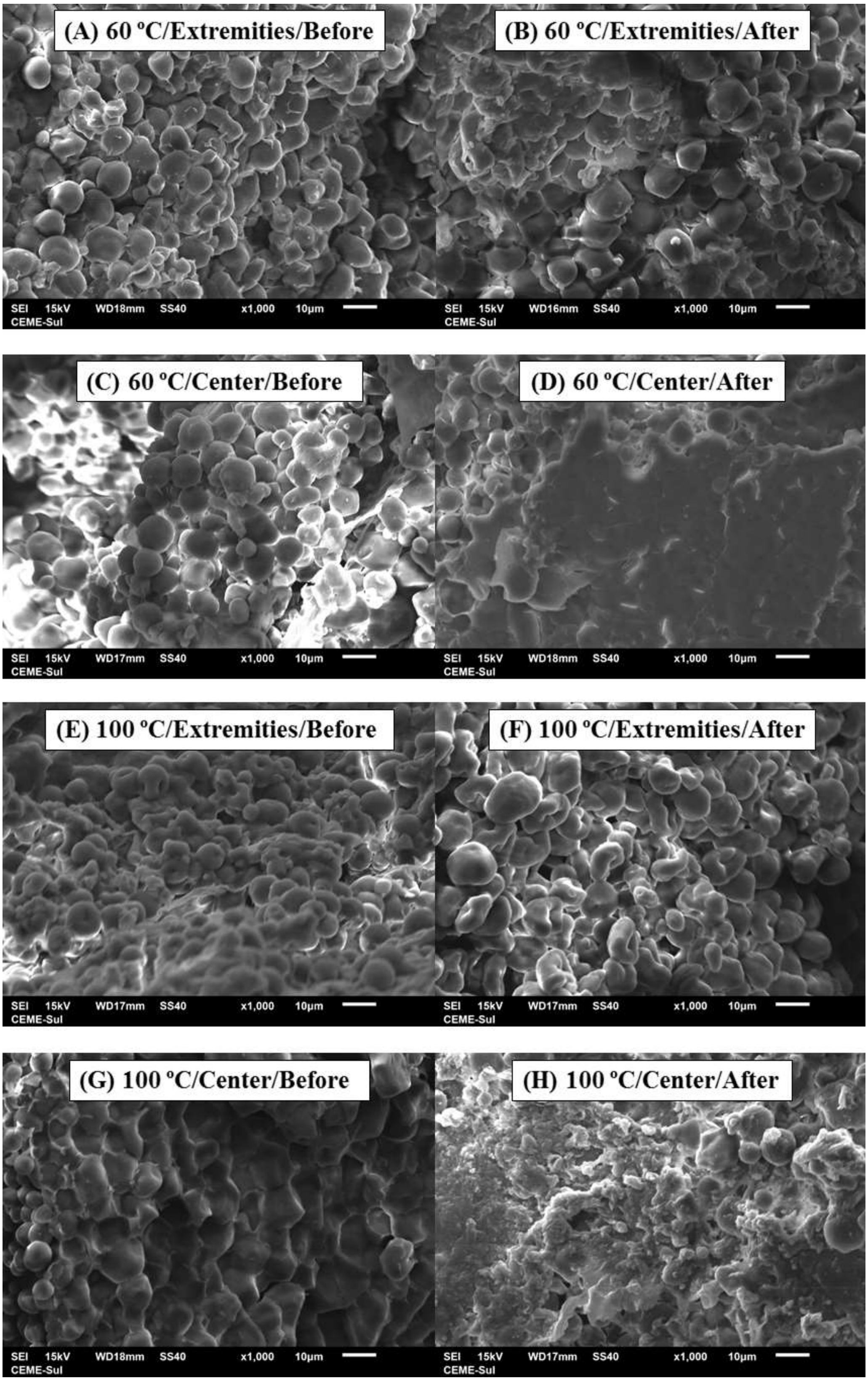


Supplementary material 2. Analysis of variance for extraction yield, residual protein, residual fat, swelling power, and solubility.

Main effects	DF	Mean Square				
		Extraction yield	Residual protein	Residual fat	Swelling power	Solubility
Corncob part	1	43.934752*	0.10086770*	0.00020417^{NS}	1.14397934*	1.42725405*
Separation	1	29.686064*	0.21238372*	0.00000417^{NS}	1.61129108*	1.33656240*
Corncob part × separation	1	125.090365*	2.02554030*	0.00003750^{NS}	0.29309020^{NS}	3.80575668*
Temperature	2	1000.614150*	1.23294913*	0.00083750^{NS}	3.07696806*	0.65790528*
Corncob part × temperature	2	18.279295^{NS}	0.72946633*	0.00015417^{NS}	0.22769841^{NS}	0.00238722^{NS}
Separation × temperature	2	5.559055^{NS}	1.80467072*	0.00007917^{NS}	0.11069995^{NS}	0.03298056^{NS}
Corncob part × separation × temperature	2	10.108175^{NS}	0.33322621*	0.00001250^{NS}	0.10951318^{NS}	0.04271369^{NS}
Repetition	2	5.912307^{NS}	0.00005133^{NS}	0.00003750^{NS}	0.00228931^{NS}	0.00954009^{NS}
CV (%)		7.738011	3.583652	2.339204	3.179875	7.682099
Error		76.712970	0.01160423	0.00181250	0.95905331	0.53458172

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation.

Supplementary material 3. Scanning electron microscopy (SEM) of corn grain endosperm after drying under different conditions.



Supplementary material 4. Analysis of variance for colorimetric profile.

Main effects	DF	Mean Square		
		Colorimetric profile		
		a	*b*	*L*
Corncob part	1	1.22122667*	16.2240000*	1.13437500*
Separation	1	0.49322667*	17.3451267*	0.30388167*
Corncob part × separation	1	3.37962667*	108.5415000*	6.62008167*
Temperature	2	7.15920667*	163.4044617*	3.64421167*
Corncob part × temperature	2	1.64754667*	42.6480650*	1.01169500*
Separation × temperature	2	2.83928667*	93.6490817*	6.73063167*
Corncob part × separation × temperature	2	0.42800667*	13.1141850*	0.82598167*
Repetition	2	0.00809417^{NS}	0.2189692^{NS}	0.02663583^{NS}
CV (%)		4.481676	5.204818	0.187852
Error		0.28274333	6.9126033	1.51629667

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 5. Analysis of variance for pasting properties and gel hardness.

Main effects	DF	Mean Square					
		Pasting temperature	Peak viscosity	Breakdown	Final viscosity	Setback	Gel hardness
Corncob part	1	0.12041667^{NS}	14.29127^{NS}	34.63204*	37.525004^{NS}	16.137600^{NS}	106813.8507*
Separation	1	1.30666667*	3.90427^{NS}	92.08084*	35.843704^{NS}	2.666667^{NS}	9843.6588^{NS}
Corncob part × separation	1	0.51041667^{NS}	50.57607*	5.34870^{NS}	5.831204^{NS}	5.664817^{NS}	166571.6969*
Temperature	2	40.38885417*	11547.34674*	7550.87866*	3234.388204*	1137.730204*	10212.7516^{NS}
Corncob part × temperature	2	0.50135417^{NS}	14.25793^{NS}	37.02204*	44.508204^{NS}	50.330962^{NS}	10189.4345^{NS}
Separation × temperature	2	0.06135417^{NS}	53.21280*	92.86321*	136.508429*	204.283929*	21538.3871^{NS}
Corncob part × separation × temperature	2	0.15885417^{NS}	15.80663^{NS}	58.97905*	3.267879^{NS}	7.613954^{NS}	19934.5986^{NS}
Repetition	2	0.00666667^{NS}	11.56482^{NS}	0.22620^{NS}	1.339537^{NS}	3.124817^{NS}	8238.3233^{NS}
CV (%)		0.474280	1.035669	4.583502	1.261342	3.094199	9.664290
Error		1.49833333	55.17558	59.24135	141.465813	148.370583	125519.0747

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation.

CHAPTER 4 – EFFECTS OF THE STORAGE TEMPERATURE AND TIME OF CORN FROM THE CENTER AND EXTREMITIES OF CORNCOB ON QUALITY PARAMETERS

Abstract

The grains in the center have a higher drying rate and effective moisture diffusivity. Thus, when the grains from different parts of the corncob are dried together in a process with high air temperature (> 60°C), the grains from the center suffer higher thermal damage. This damage that occurs during drying can worsen during storage, due to the latent effect of drying. Therefore, the objective was to evaluate the effects of storage temperature (15 and 25 ºC) and storage time (0, 3, and 6 months) of corn from the center and extremities of corncob on quality parameters. Even though 60 ºC is considered an indicated temperature for corn drying air when the mass presents uneven dimensions, the grains from the center are still more affected. In this case, the latent damage caused to the grains from the center of the corncob was pronounced during storage, worsening with increasing temperature and storage time. In the grains from the center, separated after storage for 6 months at 25 ºC, the higher acidity (1.29 mg NaOH 100g-1), lipase activity (10.51%), fermented grains (3.32%), rotten grains (0.58%), moldy grains (1.06%), and pasting temperature (91.08 ºC), and by the lower soluble protein (14.56%) and not defects grains (94.35%). These results suggest that: a) the separation of grains from the center and extremities of the corncob during the post-harvest stages can increase the amount of not defects grains by more than 2% after 6 months of storage at 25 ºC, and b) genetic improvement studies should be carried out to search for new genotypes with higher grain uniformity along the corncob.

Keywords: *Cereal storage, Soluble protein, Fermented grains, Moldy grains, Pasting proprieties.*

1 Introduction

Corn (*Zea mays* L.) is the most produced and processed cereal in the world, having an application for human food, animal feed, pharmaceutical, and chemical industry. In the post-harvest, the corn grains are submitted to a series of industrial steps, being cleaning, drying, storage, and industrialization. The corn when harvested with high moisture content (25-30%) is then subjected to a drying step. During drying, the drying air and grain mass temperature, initial and final grain moisture, air and grain flow in the dryer, and ambient air conditions must be monitored and controlled (Coradi et al., 2021; Nunes et al., 2021). Drying occurs until the grains reach safe moisture content (12-14%) to preserve the initial physical-chemical characteristics throughout storage (Coradi et al., 2020; Paraginski et al., 2014a).

The losses in the post-harvest stages of grains are in the range of 25 to 30% of the value produced (Coradi et al., 2020; Reed et al., 2007). In storage, the main factors that must be monitored and controlled are temperature and moisture content. The storage of corn grains at high temperatures and moisture contents causes negative changes in the physical-chemical and technological properties (Paraginski et al., 2014a; Paraginski et al., 2014b; Reed et al., 2007; Rehman et al., 2002). In addition to the effects caused by the storage conditions, some changes in the corn may also come from the drying conditions used, worsening storage (Coradi et al., 2020; Setiawan et al., 2010).

Paraginski et al. (2014a) evaluated the effects of corn storage temperature (5, 15, 25, and 35 ºC) on the physical-chemical and pasting properties of corn. These authors reported that that the proximate composition of corn was not affected by storage conditions. However, they reported a reduction in pH, protein solubility, and yellow color, and an increase in acidity, percentage of grains infected with visible molds, pasting temperature, setback, and final viscosity during storage (Paraginski et al. 2014a).

All these studies considered the corn grains to be homogeneous in the total grain mass. However, the insertion of grains along a corncob originates grains with different dimensions, with the grains from the extremities of the corncob having a spherical shape and the grains from the center having a higher length and less thickness. These differences in grain dimensions affect the properties of the corn, as the drying kinetics are different between the corn from center and extremities. The grains in the center have a higher drying rate and effective moisture diffusivity. Thus, when the grains from different parts of the corncob are dried together in a process with high air temperature (> 60°C), the grains from the center suffer higher thermal damage. This damage that occurs during drying can worsen during storage, due to the latent effect of drying.

Therefore, the objective was to evaluate the effects of storage temperature (15 and 25 ºC) and storage time (0, 3, and 6 months) of corn from the center and extremities of corncob on quality parameters.

2 Material and methods

2.1 Material

Yellow flint corn (Pioneer P3016 VYHR) was used, harvested in Canguçu, the Rio Grande do Sul, Brazil, in the crop year 2020/2021. Immediately after harvesting, grains were packed in plastic bags and transported to the Laboratory of Postharvest (LAPOS) at Federal University of Santa Maria (UFSM), Campus Cachoeira do Sul, where drying experiments were carried out.

Table 1 presents the physical properties and chemical composition of corn from the center and extremities of the corncob. The physical properties were determined according to Mohsenin (1986) and the chemical properties were determined using the NIRS equipment (Near Infrared Reflectance Spectroscopy, DS2500, FOSS, Brazil). The grains from the center and extremities of the corncob were manually separated. This separation was standardized by defining corncob areas. Therefore, the grain area at the center of the corncob and the areas of the grain at the extremities of the corncob were defined, as illustrated in Supplementary Material 1.

Table 1. Physical properties and chemical composition of corn from the center and extremities of the corncob.

Corncob part	Extremities corn	Center corn
	Physical properties	
Length (mm)	11.94	13.06
Width (mm)	9.15	9.06
Thickness (mm)	5.81	5.23
Bulk density (kg/m^3)	702.33	712.33
Unit mass (g)	0.35	0.38
Volume (mm^3)	276.67	296.67
Equivalent radium (mm)	4.30	4.26
Sphericity	0.72	0.65
	Chemical composition	
Protein (%)	8.63	9.24
Fat (%)	3.92	4.03
Fiber (%)	2.58	2.45
Ash (%)	1.43	1.36
Starch (%)	83.44	82.92

Figure 1 shows a graphic summary of the sample preparation for the experiment. Initially, the grains were threshed into three groups: (1) grains from the center of the corncob (10 kg), (2) grains from the extremities of the corncob (10 kg), and (3) grains from the center and extremities together (20 kg). The threshed corn was then cleaned and the initial moisture content of the grains was measured in an oven at 140 ºC for 3 h (ASAE, 2000).

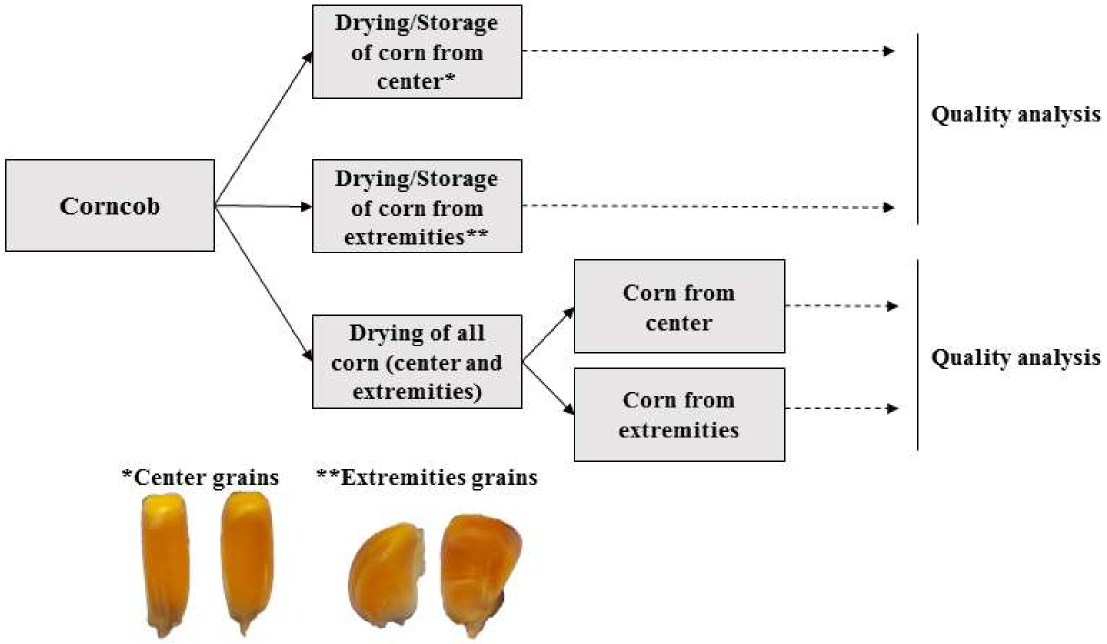


Figure 1. Graphical summary of the preparation of corn samples for experimenting.

The drying and storage were carried out in these three groups of samples, being the group 1 and the group 2 denominated as separate corn before drying/storage, where the grains from the center and extremities were dried/stored and evaluated separately. Group 3, which consists of grains from the center and extremities together, was subjected to drying/storage in this way. After drying/storage, the grains from the center and extremities of the corncob were separated and analyses were performed. This group was called separation after drying/storage. The separation of the corn from the center and extremities of group 3 was performed using a digital caliper, according to the grain dimensions shown in Table 1.

2.2 Drying and storage conditions

The grains with an initial moisture content of 30.10±0.20% were dried at 60 ºC in an experimental fixed bed dryer, with an airflow rate of 0.5 m s-1, until reaching a water content of 13.00±0.20%. In all treatments the water content was monitored by the difference in mass, following Eq. 1, where wf is the final weight of the sample (g), wi is the initial weight of the sample (g), mi is the initial moisture (g g^{-1}), and mf the final moisture (g g^{-1}).

$$\mathrm{wf} = \mathrm{wi} \times \left(\frac{100-\mathrm{mi}}{100-\mathrm{mf}}\right) \qquad (1)$$

Subsequently, the corn grains were stored in an environment with a controlled temperature of 15 and 25 ºC. Grain mass evaluations were performed initially (0 months) and at 3 and 6 months of storage.

2.3 Acidity

Acidity (mg NaOH 100g^{-1}) was determined according to as described in the AACC method 02-01A (AACC, 2000). The acidity was expressed as the mg of sodium hydroxide required to neutralize the acids in 100 g of sample, using phenolphthalein solution as an indicator.

2.4 Lipase activity

The lipase activity (%) was measured according to Kaur, Ramamurthy, and Kothari (1993) and expressed in the lipolysis percentage (%), based on the saponification index of the substrate.

2.5 Soluble protein

The soluble protein in water was determined according to Liu, McWatters, and Phillips (1992). The nitrogen content was determined by the Kjeldahl method and the resulted nitrogen value was converted to protein using factor 6.25. The soluble protein (%) was expressed in the percentage of total protein content on corn.

2.6 Electric conductivity

The electrical conductivity (µS cm^{-1}) was determined from four replicates of 25 grains, weighed and immersed in 75 mL of water (in 250-mL beakers), placed in an incubator at 20 °C constant temperature, and then incubated for 24 h (ISTA, 2008). The solutions were shaken gently, and the electrical conductivity was determined from an unfiltered solution.

2.7 Not defective, fermented, rotten, and moldy grains

The not defective, fermented, rotten, and moldy grains were determined according to BRASIL (2011).

2.8 Pasting properties

The corn grains were grounded in a laboratory mill (Perten 3100, Perten Instruments, Huddinge, Sweden) equipped with 35-mesh sieves to obtain flour samples with uniform particle sizes. The pasting properties of the corn flour (4 g, 14% moisture basis) were determined with a Rapid Visco Analyser (RVA-4; Newport Scientific, Warriewood, Australia) using the RVA profile Standard Analysis 1. The sample was held at 50 ºC for 1 min, heated to 95 ºC for 3.5 min, and held at 95 ºC for 2.5 min. The sample was then cooled to 50 ºC for 4 min and held at 50 ºC for 2 min. The rotating speed was held at 960 rpm for 10 s and then maintained at 160 rpm during the process. The parameters determined were pasting temperature (ºC), peak viscosity (RVU), breakdown (RVU), final viscosity (RVU), and setback (RVU).

2.9 Statistical analysis

The results were submitted to analysis of variance (ANOVA) with 95% reliability. When the independent variables (corn separation, corncob part, and storage temperature) showed significant effects, the splitting into simple effects was performed, compared by the t-test with 95% reliability. When a significant effect of storage time (quantitative variable) was observed, the results were submitted to linear regression, with adjustment of the polynomial of higher significant degree (n-1).

A multivariate statistical analysis was then applied to verify the association between the treatments and variables, as well as cluster analysis, according to Supplementary material 2. A biplot was built using the first two principal components due to the ease of interpreting the results. A correlation network was built to plot the results graphically. In this procedure, the green lines link variables to the positive correlation, and the red lines join negatively correlated variables. The line thickness is proportional to the magnitude of the correlation.

3 Results

3.1 Acidity, lipase activity, soluble protein, and electric conductivity

Analysis of variance showed significant effects ($P < 0.05$) of corncob part, separation, and storage temperature, and no significant effect ($P \geq 0.05$) of storage time on corn acidity. Analysis of variance showed a significant effect of all variables studied on lipase activity and electrical conductivity. As for soluble protein, a significant effect was observed for all variables, except for grain separation (Supplementary material 3). Mathematical equations representing the effects of storage time are presented in Supplementary material 4.

A tendency to increase lipase activity was observed with increasing storage time for grains from the center and extremities, separated after storage at 25 °C, and a tendency to reduce lipase activity was observed in the grains from the extremities, separated after storage at 15°C (Supplementary material 5A). A tendency to reduce soluble protein was observed with increasing storage time for grains from the center, separated after storage at 15 and 25°C (Supplementary material 5B). As for the electrical conductivity, a tendency to increase was observed according to the increase in storage time for the grains from the center, separated before storage at 15 and 25 ºC (Supplementary material 5C).

In 3 months of storage, higher acidity and lipase activity were observed in the grains from the center, separated after storage at 25 ºC. In addition, in 6 months of storage, the lower soluble protein and higher acidity, lipase activity, and electrical conductivity were observed in the grains from the center, separated after storage at 25 ºC (Table 2).

Table 2. Acidity, lipase activity, soluble protein, and electric conductivity of the corn grains from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC during 6 months.

Temperature	15 ºC		25 ºC	
Grains separation	Before drying/storage	After drying/storage	Before drying/storage	After drying/storage
0 months (Initial)				
	*Acidity (mg NaOH $100g^{-1}$)**			
Extremities grains	0.72 ± 0.08 aBα	1.06 ± 0.04 aAβ	0.72 ± 0.08 aBα	1.06 ± 0.04 aAβ
Center grains	0.96 ± 0.05 aAα	0.94 ± 0.22 aAα	0.96 ± 0.05 aAα	0.94 ± 0.22 aAα
	*Lipase activity (% of lipolysis)**			
Extremities grains	7.07 ± 0.24 aAα	6.65 ± 1.07 aAα	7.07 ± 0.24 aAα	6.65 ± 1.07 aAα
Center grains	7.40 ± 0.24 aAα	5.97 ± 0.59 aAβ	7.40 ± 0.24 aAα	5.97 ± 0.59 aAβ
	*Soluble protein (%)**			
Extremities grains	18.39 ± 0.11 aAα	17.98 ± 1.21 aBα	18.39 ± 0.11 aAα	17.98 ± 1.21 aBα
Center grains	18.43 ± 0.14 aAα	19.22 ± 0.49 aAα	18.43 ± 0.14 aAα	19.22 ± 0.49 aAα
	*Electric conductivity ($\mu S\ cm^{-1}$)**			
Extremities grains	134.00 ± 5.66 aAα	140.00 ± 2.83 aAα	134.00 ± 5.66 aAα	140.00 ± 2.83 aAα
Center grains	147.00 ± 11.31 aAα	138.00 ± 21.21 aAα	147.00 ± 11.31 aAα	138.00 ± 21.21 aAα
3 months				
	*Acidity (mg NaOH $100g^{-1}$)**			
Extremities grains	0.78 ± 0.00 aAβ	0.88 ± 0.04 aAα	0.72 ± 0.05 aAβ	0.92 ± 0.09 aBα
Center grains	0.82 ± 0.10 aAα	0.85 ± 0.13 bAα	0.82 ± 0.19 aAβ	1.25 ± 0.08 aAα
	*Lipase activity (% of lipolysis)**			
Extremities grains	6.31 ± 0.12 bAβ	6.98 ± 0.12 aAα	7.65 ± 0.59 aAα	6.48 ± 0.36 aBβ
Center grains	6.31 ± 0.12 bAβ	6.98 ± 0.12 bAα	7.49 ± 0.12 aAβ	7.91 ± 0.24 aAα
	*Soluble protein (%)**			
Extremities grains	18.66 ± 0.14 aAα	18.20 ± 0.09 aAα	17.58 ± 1.27 aAα	18.17 ± 0.44 aAα
Center grains	18.73 ± 0.26 aAα	18.63 ± 0.50 aAα	18.40 ± 0.12 aAα	17.93 ± 0.32 aAα
	*Electric conductivity ($\mu S\ cm^{-1}$)**			
Extremities grains	128.50 ± 13.44 bAα	122.00 ± 8.49 bBα	151.00 ± 5.66 aAα	150.00 ± 5.66 aAα
Center grains	130.50 ± 10.61 aAα	163.50 ± 7.78 aAα	147.00 ± 9.90 aAα	135.50 ± 41.72 aBα
6 months				
	*Acidity (mg NaOH $100g^{-1}$)**			
Extremities grains	0.61 ± 0.05 bAβ	0.85 ± 0.02 bBα	0.94 ± 0.04 aAα	0.97 ± 0.00 aBα
Center grains	0.67 ± 0.09 bAβ	1.14 ± 0.01 bAα	0.90 ± 0.01 aAβ	1.29 ± 0.00 aAα
	*Lipase activity (% of lipolysis)**			
Extremities grains	6.31 ± 1.31 aAα	6.48 ± 0.36 aAα	7.57 ± 0.24 aBα	6.06 ± 0.48 aBα
Center grains	6.48 ± 0.12 bAα	6.56 ± 0.24 bAα	8.66 ± 0.12 aAβ	10.51 ± 0.36 aAα
	*Soluble protein (%)**			
Extremities grains	18.59 ± 0.28 aAα	18.18 ± 0.45 aAα	17.78 ± 0.92 aAα	16.71 ± 0.85 bAα
Center grains	18.20 ± 0.53 aAα	17.63 ± 0.01 aBα	17.75 ± 0.59 aAα	14.56 ± 0.34 bBβ
	*Electric conductivity ($\mu S\ cm^{-1}$)**			
Extremities grains	144.50 ± 7.78 aAα	142.00 ± 5.66 bAα	151.00 ± 9.90 aAα	161.00 ± 8.49 aAα
Center grains	147.50 ± 10.61 aAα	152.00 ± 8.49 bAα	162.00 ± 5.66 aAβ	200.00 ± 7.07 aAα

**Lowercase letters compare between storage temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

As the grains from the center of the corncob are thinner, during drying, water tends to diffuse more quickly into these grains, when compared to the grains from the extremities that are more spherical (Table 1). Thus, when the drying of grains from the center and extremities of the corncob occurred together, even if 60 ºC is an indicated temperature for the drying air, it can still result in a latent effect during storage. In this way, the grains from the center, separated after storage at 25 ºC pronounced the negative effects of drying with a mass of grains with non-uniform dimensions (grains from the center and extremities together). The latent effect was pronounced after 6 months of storage due to higher lipase activity, which accelerates the process of hydrolysis of triacylglycerol into free fatty acids, increasing grain acidity (Stewart et al., 2003).

The acidity and soluble protein results are in agreement with Paraginski et al (2014a), who evaluated the effects of storage temperature (5 – 35 ºC) on corn grain quality. Paraginski et al (2014a) reported that soluble protein reduced dramatically after 6 months of storage at 25 and 35°C. The reduction of soluble protein during storage is related to the strengthening of intermolecular bonds between starch and the protein network (Paraginski et al., 2014a; Sirisoontaralak & Noomhorm, 2007).

This strengthening of intermolecular bonds (starch-protein) is probably higher in the grains from the center and separated after drying/storage, intensifying even more at higher storage temperatures. In addition, the increase in the electrical conductivity of corn grains in this storage condition indicates that these grains present a higher degradation of the cell membrane since this grain quality parameter is related to the amount of ions leached in the solution, which is directly associated with the cell membrane integrity (Lima et al., 2021; Coradi et al., 2020).

3.2 Not defective, fermented, rotten, and moldy grains

Analysis of variance showed significant effects ($P < 0.05$) of all variables evaluated on not defective, fermented, rotten, and moldy grains, except for the effect of corncob part which was not significant ($P \geq 0.05$) on not defective and moldy grains (Supplementary material 6). Mathematical equations representing the effects of storage time are presented in Supplementary material 4.

A tendency to increase not defective, fermented, rotten, and moldy grains was observed with increasing storage time (Supplementary material 7). Initially (0 months), no differences were observed between treatments in not defective, fermented, and rotten grains. In 3 months, the lower content of not defective grains and the higher content of fermented and moldy grains were observed in the grains from the center, separated after storage at 25 ºC. In 6 months, the lower content of not defective grains and the higher content of fermented, rotten, and moldy grains were observed in the grains from the center, separated after storage at 25 ºC (Table 3).

The reduction of not defective grains and the increase of fermented, rotten, and moldy grains are in agreement with the higher degradation of the cell membrane presented by the increase in electrical conductivity (Table 2). Under these extreme drying and storage conditions that result in cell membrane degradation, the number of antioxidant compounds is also reduced (Lang et al., 2019; Ferreira et al., 2019). These compounds act in the defense of the grain itself during storage and without them, the grains are more conducive to fermentation and mold development (Cañizares et al., 2021; Coradi et al., 2020; Sravanthi et al., 2013).

Even though the content of fermented, rotten, and moldy grains increased in the grains from the center of the corncob, separated after storage at 25 ºC, these values were within the best standard for commercialization according to Brazilian legislation (BRAZIL, 2011).

Table 3. Not defective, fermented, rotten, and moldy grains of the corn from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC during 6 months.

Temperature	15 ºC		25 ºC	
Grains separation	Before drying/storage	After drying/storage	Before drying/storage	After drying/storage
0 months (Initial)				
	*Not defective grains (%)**			
Extremities grains	97.64 ± 0.29 aAα	98.38 ± 0.21 aAα	97.64 ± 0.29 aAα	98.38 ± 0.21 aAα
Center grains	98.01 ± 0.21 aAα	97.86 ± 0.17 aAα	98.01 ± 0.21 aAα	97.86 ± 0.17 aAα
	*Fermented grains (%)**			
Extremities grains	1.15 ± 0.22 aAα	1.19 ± 0.23 aAα	1.15 ± 0.22 aAα	1.19 ± 0.23 aAα
Center grains	1.53 ± 0.19 aAα	1.14 ± 0.10 aAα	1.53 ± 0.19 aAα	1.14 ± 0.10 aAα
	*Rotten grains (%)**			
Extremities grains	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα
Center grains	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα
	*Moldy grains (%)**			
Extremities grains	0.70 ± 0.14 aAα	0.37 ± 0.04 aAβ	0.70 ± 0.14 aAα	0.37 ± 0.04 aAβ
Center grains	0.43 ± 0.03 aAα	0.50 ± 0.14 aAα	0.43 ± 0.03 aAα	0.50 ± 0.14 aAα
3 months				
	*Not defective grains (%)**			
Extremities grains	97.51 ± 0.27 aAα	97.48 ± 0.66 aAα	96.87 ± 0.49 aAα	97.03 ± 0.42 aAα
Center grains	96.76 ± 0.28 aAα	97.56 ± 0.21 aAα	97.14 ± 0.47 aAα	95.96 ± 0.84 bAβ
	*Fermented grains (%)**			
Extremities grains	1.25 ± 0.08 aAβ	1.53 ± 0.19 aAα	1.25 ± 0.01 aBβ	1.73 ± 0.18 aBα
Center grains	1.31 ± 0.04 bAβ	1.49 ± 0.09 bAα	1.79 ± 0.02 aAβ	2.11 ± 0.08 aAα
	*Rotten grains (%)**			
Extremities grains	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα
Center grains	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα	0.00 ± 0.00 aAα
	*Moldy grains (%)**			
Extremities grains	0.55 ± 0.07 aAα	0.43 ± 0.02 aAβ	0.45 ± 0.07 aAα	0.54 ± 0.08 aAα
Center grains	0.49 ± 0.01 aAα	0.58 ± 0.11 bAα	0.58 ± 0.04 aAβ	0.78 ± 0.11 aAα
6 months				
	*Not defective grains (%)**			
Extremities grains	96.58 ± 0.20 aAα	96.65 ± 0.24 aAα	96.47 ± 0.13 aAα	96.31 ± 0.19 aAα
Center grains	96.65 ± 0.23 aAα	96.48 ± 0.13 aAα	95.82 ± 0.50 aAα	94.35 ± 0.38 bAβ
	*Fermented grains (%)**			
Extremities grains	1.38 ± 0.14 bBα	1.45 ± 0.04 bBα	1.97 ± 0.12 aAβ	2.40 ± 0.06 aBα
Center grains	2.06 ± 0.08 aAα	2.19 ± 0.09 bAα	2.36 ± 0.20 aAβ	3.32 ± 0.17 aAα
	*Rotten grains (%)**			
Extremities grains	0.00 ± 0.00 bBα	0.00 ± 0.00 bBα	0.09 ± 0.01 aAβ	0.21 ± 0.01 aBα
Center grains	0.06 ± 0.01 aAα	0.07 ± 0.01 bAα	0.11 ± 0.00 aAβ	0.58 ± 0.11 aAα
	*Moldy grains (%)**			
Extremities grains	0.53 ± 0.01 aAα	0.62 ± 0.06 bAα	0.57 ± 0.07 aAβ	0.80 ± 0.05 aAα
Center grains	0.64 ± 0.03 bAα	0.64 ± 0.08 bAα	0.78 ± 0.04 aAβ	1.06 ± 0.06 aAα

**Lowercase letters compare between storage temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.3 Pasting properties

Analysis of variance showed significant effects ($P < 0.05$) of all variables studied on pasting temperature. For peak viscosity, effects of all variables were observed, except for the corncob part. For breakdown, significant effects were observed on the corncob part and storage time, and there was no effect on separation and storage temperature. For final viscosity and setback, only the effect of storage time was observed (Supplementary material 8). Mathematical equations representing the effects of storage time are presented in Supplementary material 4.

A tendency to increase pasting temperature (Supplementary material 9A) and final viscosity (Supplementary material 9D) was observed with increasing storage time. In 6 months, the higher pasting temperature and peak viscosity were observed in the grains from the center, separated after storage at 25 ºC (Table 4).

These changes observed in the pasting properties demonstrated that the gelatinization of corn starch can be difficult during the post-harvest handling of grains with very different dimensions (corns from the center and extremities of the corncob). These results are related to reduced protein solubility (Table 2), higher degradation of the cell membrane of grains (Table 2), and strengthening of starch-protein and protein-protein bonds (Paraginski et al., 2014; Zavareze & Dias, 2011).

Table 4. Pasting proprieties of grains of the corn from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC during 6 months.

Temperature	15 ºC		25 ºC	
Grains separation	Before drying/storage	After drying/storage	Before drying/storage	After drying/storage
0 months (Initial)				
		*Pasting temperature (ºC)**		
Extremities grains	85.15 ± 0.64 aAα	82.38 ± 0.04 aBβ	85.15 ± 0.64 aAα	82.38 ± 0.04 aBβ
Center grains	83.13 ± 0.11 aBβ	86.40 ± 0.07 aAα	83.13 ± 0.11 aBβ	86.40 ± 0.07 aAα
		*Peak viscosity (RVU)**		
Extremities grains	169.88 ± 3.95 aAα	154.33 ± 3.65 aAβ	169.88 ± 3.95 aAα	154.33 ± 3.65 aAβ
Center grains	185.71 ± 6.66 aAα	174.71 ± 4.66 aAβ	185.71 ± 6.66 aAα	174.71 ± 4.66 aAβ
		*Breakdown (RVU)**		
Extremities grains	23.25 ± 3.42 aAα	18.92 ± 1.65 aAα	23.25 ± 3.42 aAα	18.92 ± 1.65 aAα
Center grains	32.58 ± 0.59 aAα	8.04 ± 1.71 aBα	32.58 ± 0.59 aAα	8.04 ± 1.71 aBα
		*Final viscosity (RVU)**		
Extremities grains	452.54 ± 13.02 aAα	393.21 ± 5.95 aAα	452.54 ± 13.02 aAα	393.21 ± 5.95 aAα
Center grains	435.92 ± 12.26 aAα	502.33 ± 6.60 aAα	435.92 ± 12.26 aAα	502.33 ± 6.60 aAα
		*Setback (RVU)**		
Extremities grains	305.92 ± 12.49 aAα	257.79 ± 3.95 aAα	305.92 ± 12.49 aAα	257.79 ± 3.95 aAα
Center grains	282.79 ± 6.19 aAα	335.67 ± 3.65 aAα	282.79 ± 6.19 aAα	335.67 ± 3.65 aAα
3 months				
		*Pasting temperature (ºC)**		
Extremities grains	83.60 ± 0.49 bAβ	87.60 ± 0.71 aAα	89.03 ± 0.04 aAα	86.75 ± 0.71 aBβ
Center grains	83.60 ± 0.49 bAβ	88.10 ± 0.00 aAα	88.10 ± 0.07 aAβ	89.75 ± 0.71 aAα
		*Peak viscosity (RVU)**		
Extremities grains	218.46 ± 5.13 aAα	151.46 ± 3.12 bAβ	155.08 ± 0.82 bAβ	201.29 ± 1.47 aAα
Center grains	219.96 ± 7.25 aAα	151.96 ± 2.42 bAβ	155.58 ± 0.12 bAβ	202.84 ± 2.25 aAα
		*Breakdown (RVU)**		
Extremities grains	33.00 ± 3.65 aAα	3.42 ± 3.65 aAα	4.63 ± 2.77 aAα	15.83 ± 4.12 aAα
Center grains	32.50 ± 4.36 aAα	4.42 ± 2.24 aAα	4.73 ± 2.63 aAα	16.88 ± 4.20 aAα
		*Final viscosity (RVU)**		
Extremities grains	558.04 ± 25.63 aAα	479.04 ± 15.97 aAα	493.92 ± 11.08 aAα	593.13 ± 0.53 aAα
Center grains	538.04 ± 2.65 aAα	574.04 ± 8.90 aAα	488.92 ± 18.15 aAα	591.63 ± 1.59 aAα
		*Setback (RVU)**		
Extremities grains	337.58 ± 32.64 aAα	331.00 ± 16.50 aAα	343.46 ± 13.02 aAα	407.67 ± 3.18 aAα
Center grains	350.58 ± 14.26 aAα	326.50 ± 8.72 aAα	338.06 ± 20.66 aAα	405.67 ± 0.35 aAα
6 months				
		*Pasting temperature (ºC)**		
Extremities grains	88.48 ± 0.60 aAα	87.18 ± 0.04 bBα	86.75 ± 0.64 bAβ	88.63 ± 0.53 aBα
Center grains	87.58 ± 0.74 aAα	88.18 ± 0.05 bAα	87.63 ± 0.46 aAβ	91.08 ± 0.18 aAα
		*Peak viscosity (RVU)**		
Extremities grains	148.71 ± 9.84 bAβ	187.71 ± 0.41 aAα	213.92 ± 2.47 aAα	179.38 ± 17.03 aAα
Center grains	153.71 ± 2.77 bAβ	197.71 ± 0.42 bAα	212.92 ± 2.47 aAβ	233.88 ± 1.92 aAα
		*Breakdown (RVU)**		
Extremities grains	3.42 ± 0.12 aBα	11.46 ± 0.29 aAα	20.00 ± 1.65 aAα	11.96 ± 0.29 aBα
Center grains	13.42 ± 0.12 aAα	11.46 ± 0.22 aAα	18.30 ± 0.66 aAα	26.96 ± 9.93 aAα
		*Final viscosity (RVU)**		

Extremities grains	511.17 ± 37.59 aAα	558.25 ± 3.89 aAα	556.67 ± 13.55 aAα	520.04 ± 56.86 aAα
Center grains	476.17 ± 11.90 aAα	558.25 ± 3.89 aAα	556.17 ± 12.85 aAα	470.04 ± 13.04 aAα
	*Setback (RVU)**			
Extremities grains	365.88 ± 27.64 aAα	382.00 ± 4.60 aAα	362.75 ± 12.73 aAα	352.63 ± 40.13 aAα
Center grains	335.88 ± 14.79 aAα	372.00 ± 4.60 aAα	361.55 ± 11.03 aAα	263.13 ± 5.83 aAα

**Lowercase letters compare between storage temperatures, uppercase letters between corncob parts, and Greek letters compare separation before and after drying.*

3.4 Multivariate statistical analysis

Figure 2 shows the principal components analysis (Figure 2A) and Pearson's correlation network (Figure 2B) between the evaluated variables. In the principal component analysis, the treatments that are distributed close present higher similarity. Therefore, it was observed that treatment 24 (Center of corncob × After storage × 25 ºC × 6 months) differed from the other treatments in the study, which corroborates the results presented previously for the analysis of acidity, lipase activity, protein soluble, electrical conductivity, and fermented and moldy grains (Figure 2A).

A strong negative correlation was observed between fermented grains (FEG) × soluble protein (SOP), not defective grains (NDG) × rotten grains (ROG), and not defective grains (NDG) × moldy grains (MOG). A moderate negative correlation was observed between not defective grains (NDG) × pasting temperature (PAT), not defective grains (NDG) × fermented grains (FEG), rotten grains (ROG) × soluble protein (SOP), electric conductivity (ELC) × soluble protein (SOP), and lipase activity (LIA) × soluble protein (SOP) (Figure 2B).

On the other hand, a strong positive correlation was observed between electric conductivity (ELC) × fermented grains (FEG), fermented grains (FEG) × rotten grains (ROG), and final viscosity (FIV) × setback (SET). A moderate positive correlation was observed between electric conductivity (ELC) × rotten grains (ROG), moldy grains (MOG) × rotten grains (ROG), moldy grains (MOG) × fermented grains (FEG), and lipase activity (LIA) × fermented grains (FEG) (Figure 2B).

With the multivariate analysis, it was possible to better elucidate the phenomena that occurred during the storage of the grains. It was clear that the reduction in not defective grains is associated with an increase in fermented grains, rotten grains, moldy grains, soluble protein, and electrical conductivity.

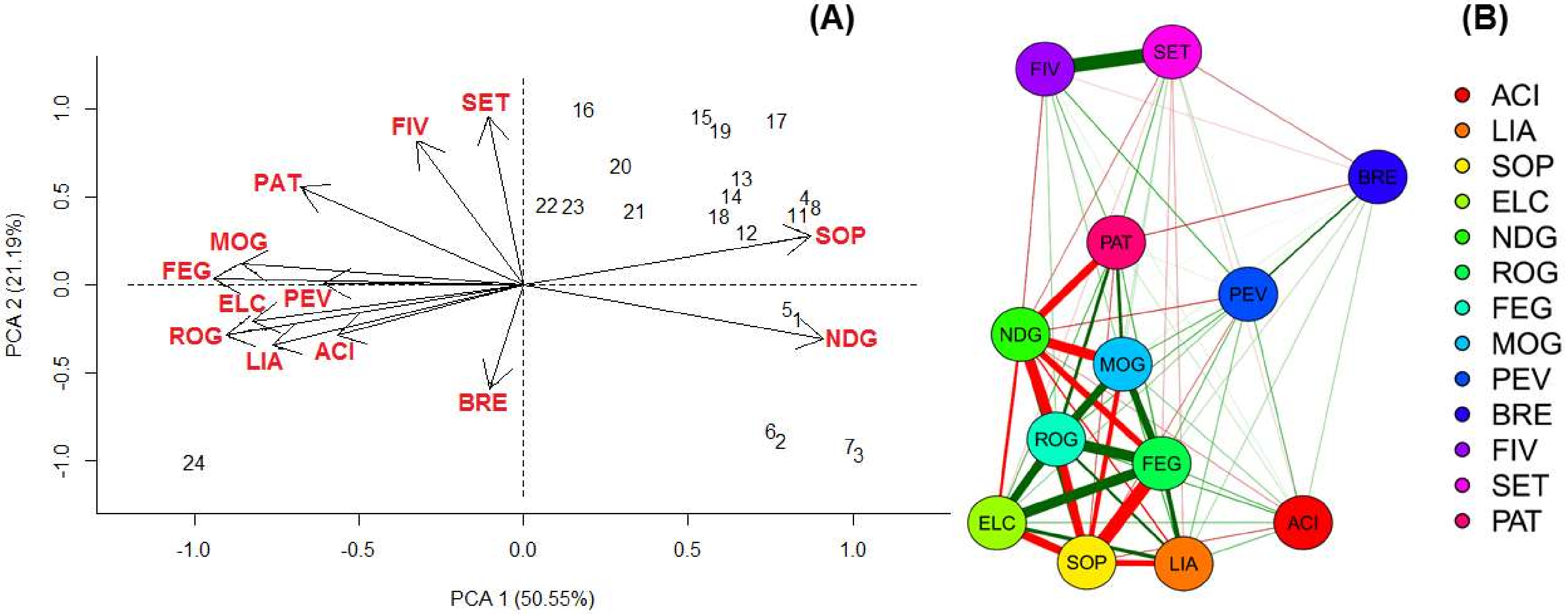


Figure 1. Figure 2. Biplot for factorial loads of PC1 and PC2 related to variables (A) and Pearson's correlation network between the following variables: acidity (ACI), lipase activity (LIA), soluble protein (SOP), electric conductivity (ELC), not defect grains (NDG), rotten grains (ROG), fermented grains (FEG), moldy grains (MOG), peak viscosity (PEV), breakdown (BRE), final viscosity (FIV), setback (SET), and pasting temperature (PAT). The green lines indicate positive correlations, while the red lines represent negative correlations (B).

4 Conclusion

Even though 60 ºC is considered an indicated temperature for corn drying air when the grain mass presented uneven dimensions, the grains from the center were more affected by the latent drying damage. In grains from the center of the corncob, separated after storage at 25 ºC, the effects of damage suffered during drying appeared during storage for 6 months, quantified by the increase in acidity, lipase activity, fermented grains, rotten grains, moldy grains, and pasting temperature, and by the reduction of the soluble protein and not defective grains. These results suggest that: a) the separation of grains from the center and extremities of the corncob during the post-harvest stages can increase the amount of not defective grains by more than 2% after 6 months of storage at 25 ºC, and b) genetic improvement studies should be carried out to search for new genotypes with higher grain uniformity along the corncob.

References

AACC, 2000. Fat acidity e general method. Method 02-01A. In: Approved Methods of the American Association of Cereal Chemists. American Association of Cereal Chemists, Inc, St. Paul, MN, USA.

ASAE, American Society of Agricultural Engineers. Moisture measurement- unground grain and seeds, in: Standards ASAE, Saint Joseph, 2000, pp. 563.

BRASIL., 2011. Ministério da Agricultura, Pecuária e Abastecimento. Comissão Técnica de Normas e Padrões, Regulamento Técnico do Milho. Instrução Normativa N° 60, de 23.12.2011.

Cañizares, L. C. C., Timm, N. S., Lang, G. H., Gaioso, C. A., Ferreira, C. D., Oliveira, M., 2021. Effects of using wind exhausters on the quality and cost of soybean storage on a real scale. Journal of Stored Products Research, 93, 101834. https://doi.org/10.1016/j.jspr.2021.101834

Coradi, P.C., Maldaner, V., Lutz, E., Daí, P.V.S., Teodoro, P.R., 2020. Influences of drying temperature and storage conditions for preserving the quality of maize postharvest on laboratory and field scales. Scientific Reports, 10, e22006. https://doi.org/10.1038/s41598-020-78914-x

Coradi, P.C., Nunes, M.T., Bellochio, S.D.C., Camilo, L.J., Teodoro, P.E., 2021. Effects of drying temperatures and storage conditions on the levels of lipids and starches in corn grains for yield ethanol industry. Biofuels, 1-10. https://doi.org/10.1080/17597269.2021.1904674

Ferreira, C.D., Ziegler, V., Goebel, J. T. S., Hoffmann, J. F., Carvalho, I. R., Chaves, F. C., Oliveira, M., 2019. Changes in Phenolic Acid and Isoflavone Contents during Soybean Drying and Storage. Journal of Agricultural and Food Chemistry, 67, 1146-1155. https://doi.org/10.1021/acs.jafc.8b06808

ISTA. International Seed Testing Association, 2008. Determination of other seeds by number. In: International rules for seed testing. Bassersdorf: ISTA, 4, 1-43.

Kaur, J., Ramamurthy, V., Kothari, R. M., 1993. Characterization of oat lipase for lipase for lipolysis of rice bran oil. Biotechnology Letters, 15, 257-262. https://doi.org/10.1007/BF00128315

Lang, G. H., Lindemann, I.S., Ferreira, C. D., Hoffmann, J. F., Vanier, N. L., Oliveira, M., 2019. Effects of drying temperature and long-term storage conditions on black rice phenolic compounds. Food chemistry, 287, 197-204. https://doi.org/10.1016/j.foodchem.2019.02.028

Lima, R. E., Coradi, P. C., Nunes, M. T., Bellochio, S. D. C., Timm, N. S., Fontoura, C. N., Carneiro, L. O., Teodoro, P. E., Campabadal, C., 2021. Mathematical modeling and multivariate analysis applied earliest soybean harvest associated drying and storage conditions and influences on physicochemical grain quality. Scientific Reports, 11, 23287. https://doi.org/10.1038/s41598-021-02724-y

Liu, K., McWatters, K. H., Phillips, R. D., 1992. Protein insolubilization and termal destabilization during storage as related to hard-to-cook defect in cowpeas. Journal of Agricultural and Food Chemistry, 40(12), 2483-2487. https://doi.org/10.1021/jf00024a028

Mohsenin, N. N., 1986. Physical properties of plant and animal materials. New York: Gordon and Breach Publishers, 1986. 841p.

Nunes, M.T., Coradi, P.C., Müller, A., Carneiro, L.O., Steinhaus, J.I., Anschau, K. F., Souza, G.A.C., Muller, E.I., Teodoro, P.E., Dutra, A.P, 2022. Stationary rice drying: influence of initial moisture and impurities contents in the mass grains on the physicochemical and morphological rice quality. Journal of Food Processing and Preservation, 1, 1-10. https://doi.org/10.1111/jfpp.16558

Paraginski, R.T., Vanier, N.L., Berrios, J.J., Oliveira, M., Elias, M.C., 2014a. Physicochemical and pasting properties of maize as affected by storage temperature. J. Stored Prod. Res. 59:209-214. https://doi.org/10.1016/j.jspr.2014.02.010

Paraginski, R.T., Vanier, N.L., Moomand, K., Oliveira, M., Zavareze, E.R., Silva, R.M., Ferreira, C.D., Elias, M.C., 2014b. Characteristics of starch isolated from maize as a function of grain storage temperature. Carbohydr. Polym. 102:88-94. https://doi.org/10.1016/j.carbpol.2013.11.019

Reed, C., Doyungan, S., Ioerger, B., Getchell, A., 2007. Response of storage molds to different initial moisture contents of maize (corn) stored at 25 °C, and effect on respiration rate and nutrient composition. J. Stored Prod. Res. 43:443–458. https://doi.org/10.1016/j.jspr.2006.12.006

Rehman, Z.U., Habib, F., Zafar, S.I., 2002. Nutritional changes in maize (Zea mays) during storage at three temperatures. Food Chem. 77:197-201. https://doi.org/10.1016/S0308-8146(01)00337-5

Setiawan, S., Widjaja, H., Rakphongphairoj, V., Jane, J., 2010. Effects of Drying Conditions of Corn Kernels and Storage at an Elevated Humidity on Starch Structures and Properties. J. Agr. Food Chem. 58:12260–12267. http://doi.org/10.1021 / jf102838j

Sirisoontaralak, P., Noomhorm, A., 2007. Changes in physicochemical and sensory-properties of irradiated rice during storage. J. Stored Prod. Res. 43, 282e289. https://doi.org/10.1016/j.jspr.2006.06.008

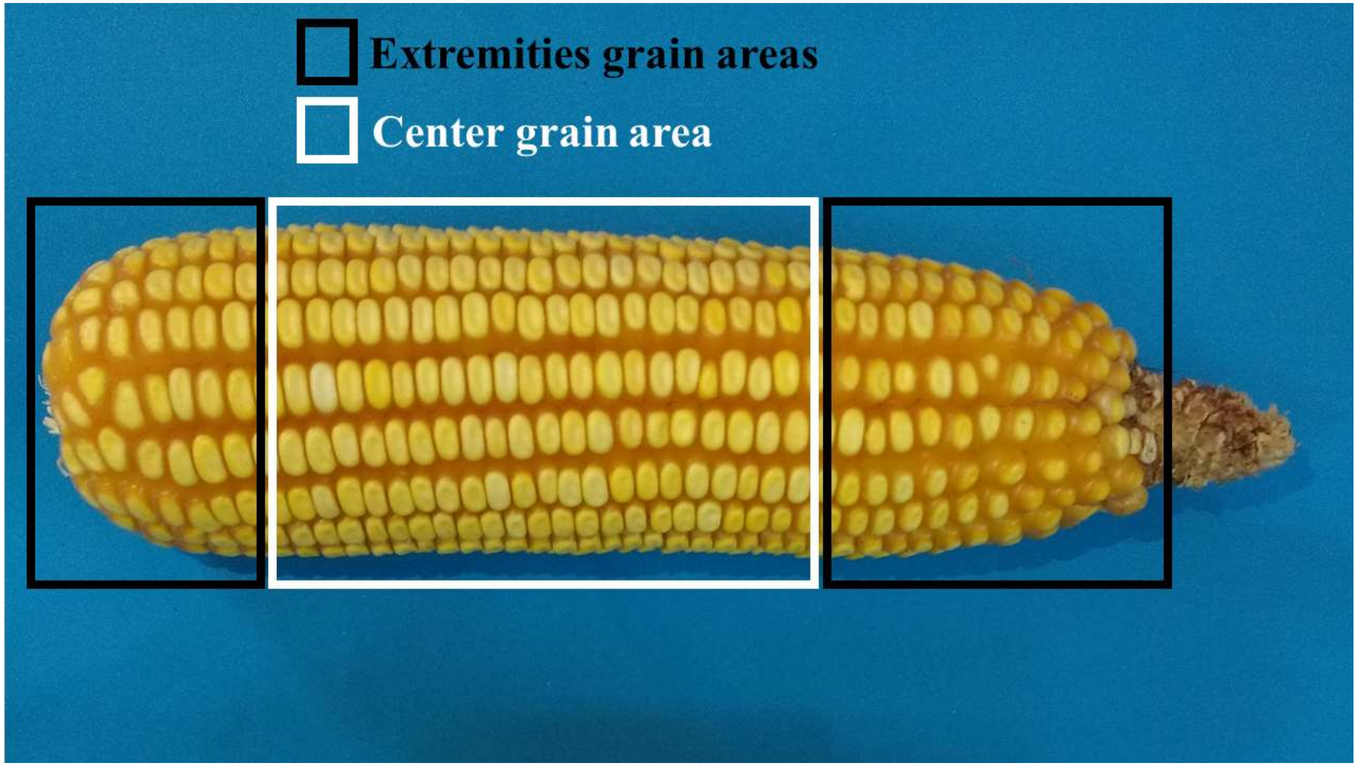
Sravanthi, B., Jayas, D.S., Alagusundaram, K., Chelladurai, V., White, N.D.G., 2013. Effect of storage conditions on red lentils. J. Stored Prod. Res. 53, 48e53. https://doi.org/10.1016/j.jspr.2013.01.004

Stewart, O. J., Ragha, G. S. V, Orsat, V., Golden, K. D., 2003. The effect of drying on unsaturated fatty acids and trypsin inhibitor activity in soybean. Process Biochemistry, 39, 483-489. https://doi.org/10.1016/S0032-9592(03)00130-4

Zavareze, E. R., Dias A. R. G., 2011. Impact of heat-moisture treatment and annealing in starches: A review. Carbohydrate Polymers. 83, 317-328. https://doi.org/10.1016/j.carbpol.2010.08.064

Supplementary materials

Supplementary material 1. The standard definition of the grains from the center area of the corncob and the grains from the extremities areas of the corncob.



Supplementary material 2. Multivariate statistical analysis of corncob part, separatin, storage temperature, and storage time.

Corncob part	Separation	Storage temperature	Storage time	Clusters
Extremities	Before	15 ºC	0 months	1
Extremities	After	15 ºC	0 months	2
Center	Before	15 ºC	0 months	3
Center	After	15 ºC	0 months	4
Extremities	Before	25 ºC	0 months	5
Extremities	After	25 ºC	0 months	6
Center	Before	25 ºC	0 months	7
Center	After	25 ºC	0 months	8
Extremities	Before	15 ºC	3 months	9
Extremities	After	15 ºC	3 months	10
Center	Before	15 ºC	3 months	11
Center	After	15 ºC	3 months	12
Extremities	Before	25 ºC	3 months	13
Extremities	After	25 ºC	3 months	14
Center	Before	25 ºC	3 months	15
Center	After	25 ºC	3 months	16
Extremities	Before	15 ºC	6 months	17
Extremities	After	15 ºC	6 months	18
Center	Before	15 ºC	6 months	19
Center	After	15 ºC	6 months	20
Extremities	Before	25 ºC	6 months	21
Extremities	After	25 ºC	6 months	22
Center	Before	25 ºC	6 months	23
Center	After	25 ºC	6 months	24

Supplementary material 3. Analysis of variance for acidity, lipase activity, soluble protein, and electric conductivity.

Main effects	DF	Mean Square			
		Acidity	Lipase activity	Soluble protein	Electric conductivity
Corncob part	1	0.37807500*	0.52291875*	2.00900833*	280.333333*
Separation	1	0.24653333*	3.40800208*	0.02340833NS	1008.333333*
Corncob part × separation	1	0.00000833NS	0.68401875*	0.02803333NS	96.333333NS
Temperature	1	0.12000000*	8.22535208*	5.24040833*	1344.083333*
Corncob part × temperature	1	0.00367500NS	0.34510208NS	0.57203333NS	4.083333NS
Separation × temperature	1	0.01080000NS	3.59160208*	0.11213333NS	52.083333NS
Corncob part × separation × temperature	1	0.01540833NS	2.12941875*	0.96900833NS	70.083333NS
Time	2	0.00992500NS	1.24999375*	5.22033958*	1570.333333*
Corncob part × time	2	0.04997500*	1.53905625*	2.50502708*	201.333333NS
Separation × time	2	0.00343333NS	2.77333958*	2.16755208*	130.583333NS
Corncob part × separation × time	2	0.10965833*	1.83484375*	1.41506458*	322.583333*
Temperature × time	2	0.04322500*	3.07896458*	2.15650208*	486.083333*
Corncob part × temperature × time	2	0.03992500*	0.38740208NS	1.11816458NS	452.583333*
Separation × temperature × time	2	0.01710000NS	1.91547708*	0.13528958NS	625.583333*
Corncob part × separation × temperature × time	2	0.00525833NS	0.74510625*	0.26047708NS	332.583333*
Repetition	2	0.02340833	0.00226875	0.64403333	70.083333
CV (%)		9.909145	7.360106	3.206366	9.053280
Error		0.18599167	6.16958125	7.72236667	4022.91667

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 4. Polynomial equations for the dependent variables evaluated as a function of storage time.

Treatment	Response variable	Equation	R²
Extremities – Before – 15 ºC	Lipase activity (%)	NS	
Extremities – After – 15 ºC		0.070277778*x^2-0.575833333*x+7.40	0.941250
Center – Before – 15 ºC		NS	
Center – After – 15 ºC		NS	
Extremities – Before – 25 ºC		NS	
Extremities – After – 25 ºC		0.210833333*x+7.21750	0.766905
Center – Before – 25 ºC		NS	
Center – After – 25 ºC		0.757500*x+5.859166667	0.967765
Extremities – Before – 15 ºC	Soluble protein (%)	NS	
Extremities – After – 15 ºC		NS	
Center – Before – 15 ºC		NS	
Center – After – 15 ºC		-0.26416667*x+19.287500	0.825534
Extremities – Before – 25 ºC		NS	
Extremities – After – 25 ºC		NS	
Center – Before – 25 ºC		NS	
Center – After – 25 ºC		-0.77666667*x+19.5650	0.920482
Extremities – Before – 15 ºC	Electric conductivity (μS cm^{-1})	NS	
Extremities – After – 15 ºC		NS	
Center – Before – 15 ºC		2.1111111*x^2+12.33333*x+140.0	0.812500
Center – After – 15 ºC		NS	
Extremities – Before – 25 ºC		NS	
Extremities – After – 25 ºC		NS	
Center – Before – 25 ºC		3.500*x+139.83333	0.796988
Center – After – 25 ºC		NS	

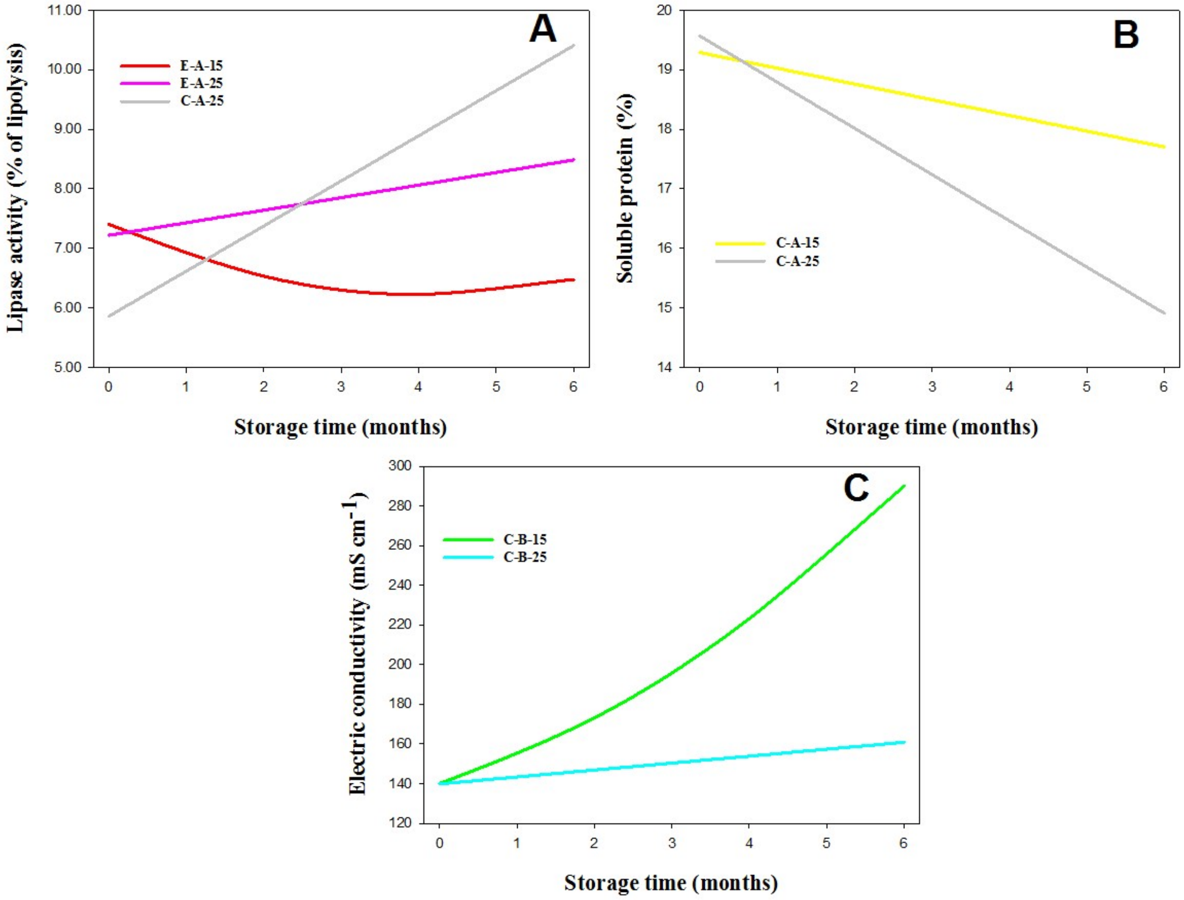
Extremities – Before – 15 ºC	Not defective grains (%)	-0.17583333*x+97.7725	0.729302
Extremities – After – 15 ºC		0.06416667*x^2-0.61083333*x+98.01	0.928548
Center – Before – 15 ºC		-0.28833333*x+98.36833333	0.845659
Center – After – 15 ºC		-0.23000*x+97.9900	0.866739
Extremities – Before – 25 ºC		-0.19500000*x+97.5800	0.780200
Extremities – After – 25 ºC		-0.36583333*x+98.08583333	0.891916
Center – Before – 25 ºC		-0.34500*x+98.27500	0.915303
Center – After – 25 ºC		-0.58416667*x+97.812500	0.931432
Extremities – Before – 15 ºC	Fermented grains (%)	NS	
Extremities – After – 15 ºC		0.054722222*x^2-0.240833333*x+1.5350	0.930272
Center – Before – 15 ºC		NS	
Center – After – 15 ºC		0.129166667*x+1.305833333	0.792869
Extremities – Before – 25 ºC		0.135833333*x+1.045833333	0.772235
Extremities – After – 25 ºC		0.13750*x+1.480833333	0.859447
Center – Before – 25 ºC		0.20000*x+1.173333333	0.936321
Center – After – 25 ºC		0.318333333*x+1.323333333	0.964370
Extremities – Before – 15 ºC	Rotten grains (%)	NS	
Extremities – After – 15 ºC		0.0030555556*x^2-0.0091666667*x	0.987755
Center – Before – 15 ºC		NS	
Center – After – 15 ºC		0.0036111111*x^2-0.0108333333*x	0.991202
Extremities – Before – 25 ºC		NS	
Extremities – After – 25 ºC		0.0061111111*x^2-0.0183333333*x	0.987755
Center – Before – 25 ºC		NS	
Center – After – 25 ºC		NS	
Extremities – Before – 15 ºC	Moldy grains (%)	NS	
Extremities – After – 15 ºC		0.0350000000*x+0.4150	0.907407
Center – Before – 15 ºC		0.0408333333*x+0.354166666	0.855870
Center – After – 15 ºC		NS	

Extremities – Before – 25 ºC		NS	
Extremities – After – 25 ºC		0.0575000*x+0.4208333333	0.965068
Center – Before – 25 ºC		0.07000*x+0.3583333333	0.930953
Center – After – 25 ºC		0.0941666667*x+0.4941666667	0.907577
Extremities – Before – 15 ºC	Pasting temperature (ºC)	0.35694444*x^2-1.58750000*x+85.15	0.960845
Extremities – After – 15 ºC		0.19444444*x^2-0.425*x+83.125	0.967299
Center – Before – 15 ºC		-0.31388889*x^2+2.68333333*x+82.3750	0.985300
Center – After – 15 ºC		-0.09027778*x^2+0.8375000*x+86.40	0.998452
Extremities – Before – 25 ºC		-0.34166667*x^2+2.31666667*x+85.15	0.949229
Extremities – After – 25 ºC		-0.30277778*x^2+2.56666667*x+83.12500	0.992511
Center – Before – 25 ºC		1.03333333*x+82.80	0.928727
Center – After – 25 ºC		0.77916667*x+86.73750	0.919898
Extremities – Before – 15 ºC	Peak viscosity (RVU)	-6.5736111*x^2+35.9141667*x+169.8750000	0.973583
Extremities – After – 15 ºC		-5.5827778*x^2+28.1633333*x+185.71	0.976732
Center – Before – 15 ºC		2.1736111*x^2-7.4791667*x+154.3350	0.985856
Center – After – 15 ºC		3.8055556*x-19.00*x+174.7100	0.986955
Extremities – Before – 25 ºC		4.0902778*x^2-17.2008333*x+169.8750	0.994048
Extremities – After – 25 ºC		4.8588889*x^2-24.6183333*x+185.7100	0.984881
Center – Before – 25 ºC		-3.8261111*x^2+27.1300*x+154.33500	0.878391
Center – After – 25 ºC		9.8608333*x+174.2258333	0.990608
Extremities – Before – 15 ºC	Breakdown (RVU)	-2.18527778*x^2+9.80583333*x+23.25	0.973197
Extremities – After – 15 ºC		-3.19500000*x+35.75166667	0.724610
Center – Before – 15 ºC		1.30805556*x^2-9.09083333+18.9150	0.936979
Center – After – 15 ºC		NS	
Extremities – Before – 25 ºC		1.88888889*x^2-11.8750*x+23.2500	0.947141
Extremities – After – 25 ºC		2.30194444*x^2-16.19250*x+32.5850	0.990219
Center – Before – 25 ºC		-1.15916667*x+19.04750	0.707402
Center – After – 25 ºC		3.153333333*x+7.83500	0.749602

Extremities – Before – 15 ºC	Final viscosity (RVU)	-8.4658333*x^2+60.5658333*x+452.54	0.833039
Extremities – After – 15 ºC		-9.1116667*x^2+61.3783333*x+435.9150	0.972548
Center – Before – 15 ºC		27.5066667*x+394.3133333	0.988384
Center – After – 15 ºC		6.2502778*x^2-28.1825000*x+502.3350	0.981589
Extremities – Before – 25 ºC		17.3541667*x+448.9775000	0.945210
Extremities – After – 25 ºC		20.0416667*x+433.5400	0.953046
Center – Before – 25 ºC		-15.1666667*x^2+112.1383333*x+393.2100	0.926028
Center – After – 25 ºC		-11.7152778+64.9091667*x+502.33500	0.985236
Extremities – Before – 15 ºC	Setback (RVU)	9.9933333*x+306.4783333	0.643728
Extremities – After – 15 ºC		-4.5833333*x^2+36.3466667*x+282.795	0.917010
Center – Before – 15 ºC		20.7016667*x+261.4916667	0.970223
Center – After – 15 ºC		3.0369444*x^2-12.1658333*x+335.6650	0.954417
Extremities – Before – 25 ºC		9.4725000*x+308.9575000	0.843605
Extremities – After – 25 ºC		13.1258333*x+288.0908333	0.870412
Center – Before – 25 ºC		-11.3847222*x^2+84.1141667*x+257.790	0.933572
Center – After – 25 ºC		-11.8083333*x^2+58.7600*x+335.6650	0.997667

x=storage time; NS=Non-significant results as a function of storage time.

Supplementary material 5. Lipase activity (A), soluble protein (B), and electric conductivity (C) of the corn grains from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC as a function storage time.

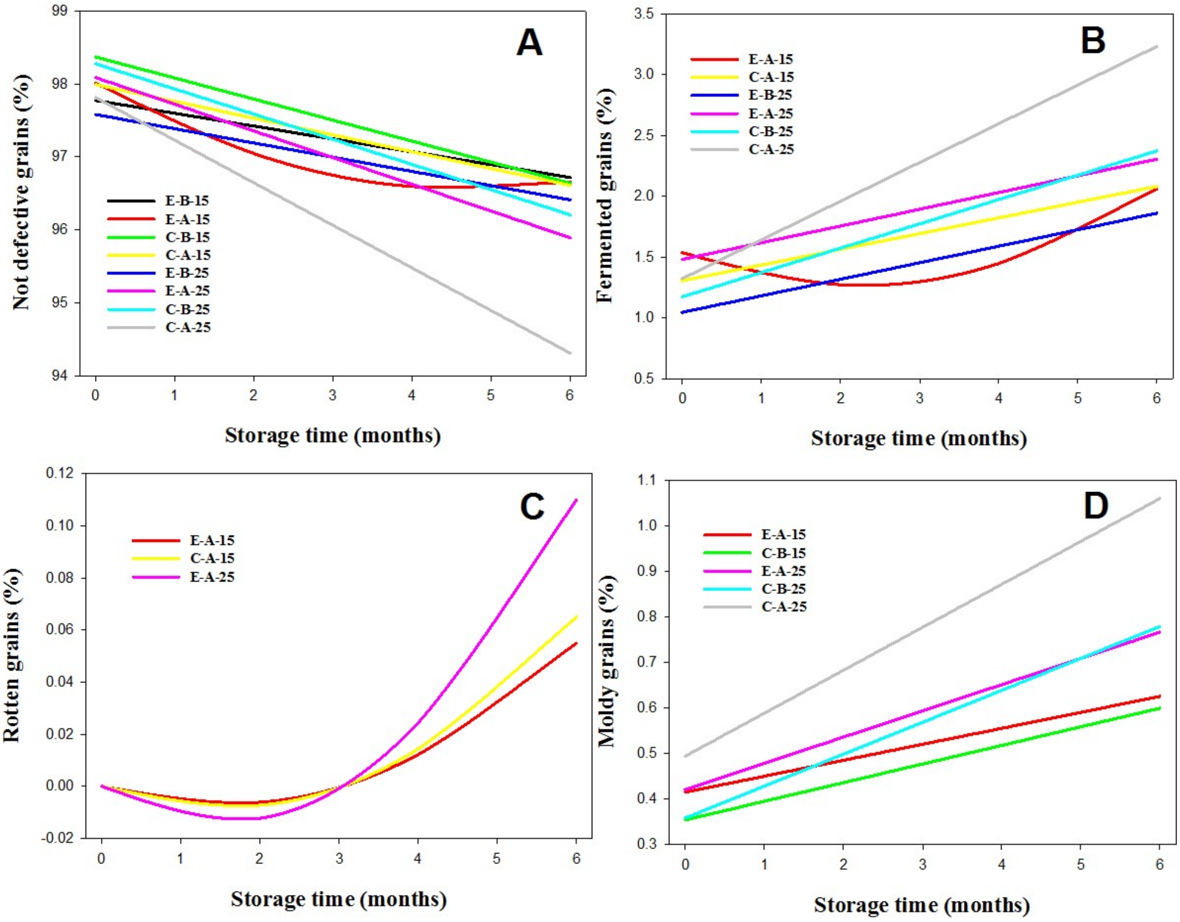


Supplementary material 6. Analysis of variance for not defective grains, fermented grains, rotten grains, and moldy grains.

Main effects	DF	Mean Square			
		Not defective grains	Fermented grains	Rotten grains	Moldy grains
Corncob part	1	0.05266875NS	0.59853333*	0.03000000*	0.01020833NS
Separation	1	1.67626875*	1.96830000*	0.02167500*	0.04813333*
Corncob part × separation	1	1.21285208*	0.00000833NS	0.01080000*	0.09187500*
Temperature	1	2.72176875*	1.51230000*	0.06307500*	0.09363333*
Corncob part × temperature	1	0.91025208*	0.20020833*	0.02803333*	0.04440833*
Separation × temperature	1	0.57860208*	0.05467500NS	0.00607500*	0.03203333*
Corncob part × separation × temperature	1	0.86671875*	0.01333333NS	0.00963333*	0.00040833NS
Time	2	13.07282708*	2.83540208*	0.10267500*	0.18195208*
Corncob part × time	2	0.52933125*	0.21483958*	0.03000000*	0.08128958*
Separation × time	2	0.36308125NS	0.23783125*	0.02167500*	0.05695208*
Corncob part × separation × time	2	0.11670208NS	0.06535208NS	0.01080000*	0.04073125*
Temperature × time	2	0.75954375*	0.55238125*	0.06307500*	0.03841458*
Corncob part × temperature × time	2	0.23263958NS	0.09415208*	0.02803333*	0.01172708NS
Separation × temperature × time	2	0.50016458*	0.07616875NS	0.00607500*	0.00816458NS
Corncob part × separation × temperature × time	2	0.29299375NS	0.02223958NS	0.00963333*	0.00370208NS
Repetition	2	0.11310208	0.00440833	0.00020833	0.01333333
CV (%)		0.365736	8.956894	51.97734	12.71683
Error		2.89824792	0.51589167	0.01329167	0.12656667

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 7. Not defective (A), fermented (B), rotten (C), and moldy grains (D) of the corn from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC as a function storage time.

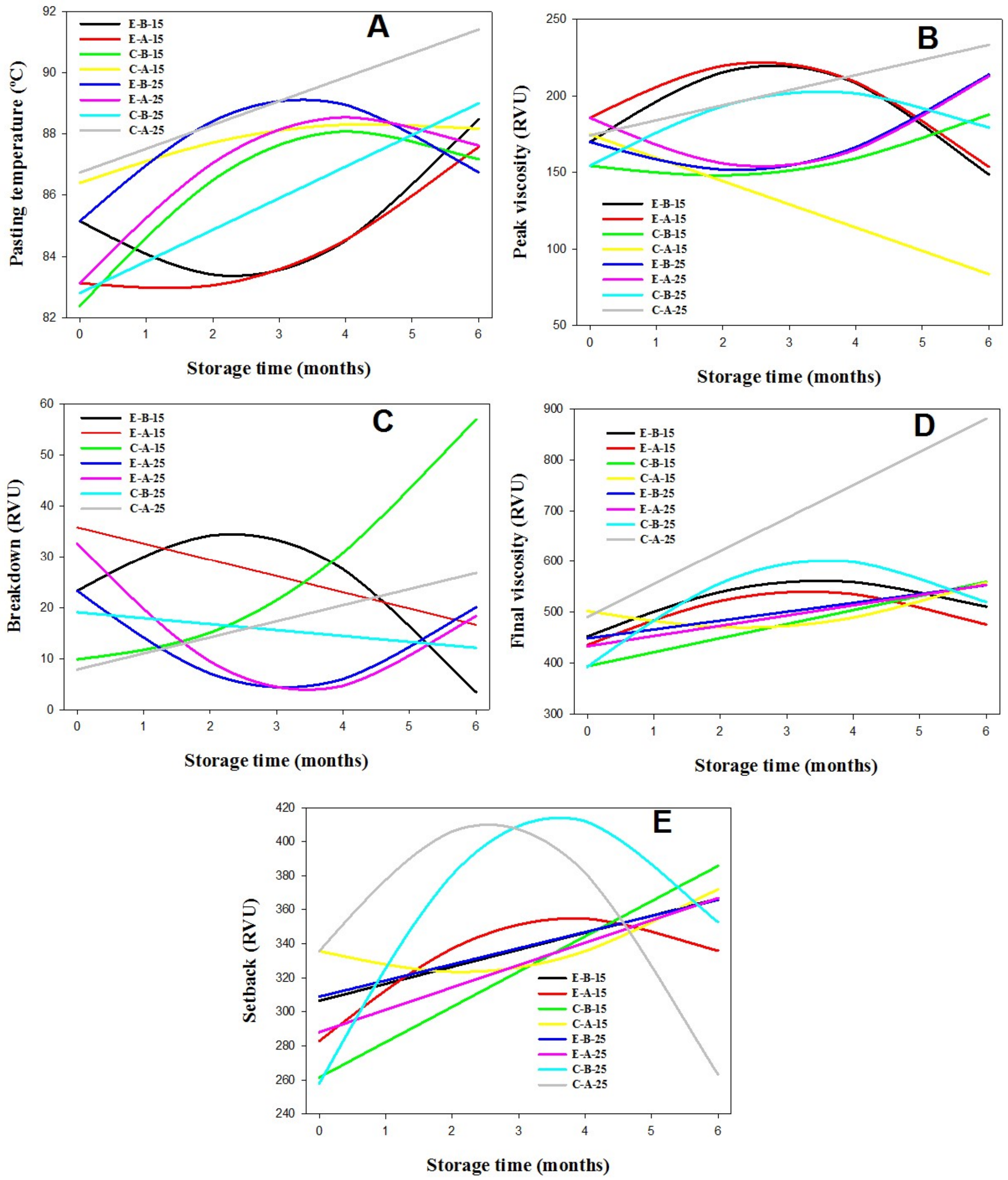


Supplementary material 8. Analysis of variance for pasting temperature, peak viscosity, breakdown, final viscosity, and setback.

Main effects	DF	Mean Square				
		Pasting temperature	Peak viscosity	Breakdown	Final viscosity	Setback
Corncob part	1	15.0752083*	52.92000NS	607.051875*	526.82001NS	246.06963NS
Separation	1	8.4168750*	1751.35841*	39.858075NS	385.33333NS	33.63401NS
Corncob part × separation	1	33.5002083*	404.02808*	81.484408*	5440.02083*	1191.81401*
Temperature	1	14.8518750*	1306.67070*	3.213675NS	1150.32501NS	93.46501NS
Corncob part × temperature	1	0.8268750NS	1448.92163*	475.902075*	720.90501NS	0.23801NS
Separation × temperature	1	1.9602083*	123.84188NS	1.300208NS	0.75000NS	369.63000NS
Corncob part × separation × temperature	1	0.8268750NS	230.12521*	56.985208*	768.00000NS	636.56333NS
Time	2	65.1394271*	1578.89066*	203.476225*	34540.23126*	17288.89891*
Corncob part × time	2	2.9556771*	1143.53693*	266.190525*	200.67461NS	1563.34926*
Separation × time	2	0.1298437NS	368.48441*	49.458325*	5123.27083*	3617.70051*
Corncob part × separation × time	2	5.5519271*	265.82332*	169.841408*	5255.58333*	5112.05051*
Temperature × time	2	7.8135938*	2335.50008*	296.041725*	1177.55931*	4408.78576*
Corncob part × temperature × time	2	14.4573438*	6965.41801*	586.724275*	22444.59641*	6532.33601*
Separation × temperature × time	2	0.6706771NS	123.36062*	0.763958NS	72.43750NS	168.09750NS
Corncob part × separation × temperature × time	2	1.0623438*	204.24396*	60.656458*	525.06250NS	1202.43083*
Repetition	2	0.0075000	2.17601	15.187500	26.49241	54.44280
CV (%)		0.521334	3.043606	18.73779	3.634286	4.668050
Error		4.6775000	701.16989	222.023700	7583.8527	5569.65140

*Significant effect; NS = Non-significant effect; DF = Degree of freedom; CV = Coefficient of variation

Supplementary material 9. Pasting temperature (A), peak viscosity (B), breakdown (C), final viscosity (D), and setback (E) of the corn grains from the center and extremities of the corncob, separated before and after storage at 15 and 25 ºC as a function storage time.



5 CONSIDERAÇÕES FINAIS

Nas temperaturas de secagem mais altas (80 e 100 ºC), a taxa de secagem e a difusividade efetiva de umidade dos grãos do centro da espiga de milho são maiores em relação aos grãos das extremidades. A separação dos grãos não afetou significativamente as propriedades de pasta do milho. No entanto, causaram alterações significativas nas propriedades das proteínas dos grãos, principalmente a redução da solubilidade e inativação da enzima lipase, e a redução dos teores de luteína e β-caroteno nos grãos do centro da espiga, separados após a secagem.

O aumento da temperatura de secagem resultou na redução do rendimento e pureza da extração e aumentou a resistência térmica do amido. Os resultados mostraram que a separação industrial de grãos com diferentes dimensões pode aumentar o rendimento da extração em 35 a 40%.

Apesar de 60 ºC ser considerada uma temperatura indicada para ar de secagem de milho, quando a massa de grãos apresentou dimensões desiguais, os grãos do centro foram mais afetados pelos danos latentes de secagem. Nos grãos do centro da espiga, separados após armazenamento a 25 ºC, os efeitos dos danos sofridos durante a secagem apareceram durante o armazenamento por 6 meses, quantificados pelo aumento da acidez, atividade de lipase, grãos fermentados, ardidos e mofados e temperatura de pasta, e pela redução da proteína solúvel e grãos sadios. A separação dos grãos do centro e das extremidades da espiga de milho durante as fases de pós-colheita pode aumentar a quantidade de grãos sem defeitos em mais de 2% após 6 meses de armazenamento a 25 ºC.

Após este estudo, algumas lacunas de pesquisa foram encontradas: a) estudos de melhoramento para buscar novos genótipos com maior uniformidade de grãos ao longo da espiga de milho, e b) adição de uma etapa de separação de grãos de milho com dimensões diferentes antes da secagem/armazenamento.