University of São Paulo
"Luiz de Queiroz" College of Agriculture"

Ethanol as a pre-treatment of starchy foods drying: effect on potato drying kinetics and starch properties

Jaqueline Souza Guedes

Dissertation presented to obtain the degree of Master in Science. Area: Food Science and Technology

Piracicaba
2020

Jaqueline Souza Guedes
Food Engineer

Ethanol as a pre-treatment of starchy foods drying: effect on potato drying kinetics and starch properties
versão revisada de acordo com a resolução CoPGr 6018 de 2011

Adivisor:
Prof. Dr. **PEDRO ESTEVES DUARTE AUGUSTO**

Dissertation presented to obtain the degree of Master in Science. Area: Food Science and Technology

Piracicaba
2020

Dedicated to my dear ones.

ACKNOWLEDGEMENTS

To my Familly.

To my advisor, Prof. Dr. Pedro Esteves Duarte Augusto. For the great care and persistence, for having believed and dedicated countless hours of his time guiding me. I lack words to thank you for all advice, friendly words and inspirations that he gave me.

To Dr. Nanci Castanha, Dr. Meliza Rojas, Eng. Karoline Costa, Dr. Manoel Divino and M.Sc Dâmaris Lima, for support exchange of knowledge and all support during this study.

To my dear friends of the "Grupo de Estudos em Engenharia de Processos – Ge^{2}P" for companionship and friendship.

My friends and sisters Bruna Bitencourt, Karoline Costa and Bruna Gomes for their support at all times.

To my dear undergraduate and graduate professors for their teaching and support.

To the "Escola Superior de Agricultura "Luiz de Queiroz" – ESALQ" from the "Universidade of São Paulo – USP" for providing this study and links established here, it is impossible to know this College and not fall in love with it.

"Alice: This is impossible.
The mad Hatter: Only if you believe it is."

(Alice in Wonderland – Lewis Carroll)

CONTENTS

RESUMO

Etanol como pré-tratamento da secagem de alimentos ricos em amido: efeito na cinética de secagem de batata e nas propriedades do amido

O amido é um ingrediente importante para diversas indústrias, sendo obtido comercialmente a partir de cereais, tubérculos e raízes. As raízes e os tubérculos apresentam um alto teor de umidade, e a secagem pode ser utilizada para reduzi-la e estender a vida útil desses produtos. Porém, esse método consome muito tempo, o que pode impactar negativamente nas propriedades nutricionais e físicas do produto final. Dessa forma, alternativas são necessárias para melhorar o processo de secagem, mas sem impactar a qualidade do produto final – no caso, o amido. Dentre as diversas possibilidades, o uso de etanol como pré-tratamento para a secagem tem se mostrado um método simples e eficaz para reduzir o tempo de secagem. O presente estudo propôs a secagem convectiva da batata como forma de reduzir as perdas pós-colheita com foco na obtenção do seu amido, bem como a aplicação do etanol como pré-tratamento para a secagem. As fatias de batatas foram pré-tratadas por imersão em etanol por 15 e 30 min. A secagem por convecção foi realzada com ar a 40 °C e 1 m/s. A microestrutura da batata foi avaliada por microscópia eletrônica de varredura antes e após o pré-tratamento com etanol, bem como no produto seco. Após a secagem, as fatias foram reidratadas e o amido extraído e caracterizado. Os amidos obtidos antes e após cada tratamento (etanol e secagem) foram avaliados em relação à sua estrutura granular e molecular, propriedades de pasta e gel. A cinética de secagem da batata foi descrita pelo Modelo de Page, apresentando um comportamento superdifusivo. O pré-tratamento com etanol reduziu o tempo de secagem em até 55%, e seu efeito foi discutido em relação às mudanças estruturais e mecanimos físicos observados (como o Efeito Marangoni e mudanças na pressão de vapor). A reidratação não evidenciou formação de crostas durante a secagem. O pré-tratamento com etanol não afetou a morfologia dos grânulos de amido e nem a distribuição do tamanho das moléculas. No entanto, a secagem resultou em pequenas imperfeições nas superfícies dos grânulos de amido. Além disso, a secagem afetou alguns parâmetros das propriedades de pasta e os resultados indicam que os géis obtidos tendem a ser mais fortes. Os resultados obtidos são interessantes não apenas por descrever as vantagens do pré-tratamento do etanol na secagem de produtos alimentícios, mas também por propor uma tecnologia simples para conservação de batatas, permitindo a posterior extração de seu amido.

Palavras-chave: Secagem, Etanol, Amido, Engenharia de alimentos

ABSTRACT

Ethanol as a pre-treatment of starchy foods drying: effect on potato drying kinetics and starch properties

Starch is an important ingredient for different industries, being commercially obtained from cereals, tubers, and roots. Roots and tubers have a high moisture content. Drying can be used to reduce it and extend the shelf life of these products. However, this method takes a long time, which can negatively impact the nutritional and physical properties of the final product. Consequently, alternatives are necessary to improve the drying process, but without impacting the quality of the final product – in this case, starch. Among different possibilities, the use of ethanol as a pre-treatment for drying has emerged as a simple and effective method to reduce drying time. The present study proposed the convective drying of potatoes as a way of reducing post-harvest losses focusing on obtaining its starch, as well as applying ethanol as a pre-treatment for drying. Potato slices were pre-treated by immersion in ethanol for 15 and 30 min. Convective drying was carried out using air at 40 °C and 1 m/s. The potato microstructure was evaluated by scanning electron microscopy before and after pre-treatment with ethanol, as well as in the dry product. After drying, the slices were rehydrated, and their starch was extracted and characterized. The starches obtained before and after each treatment (ethanol and drying) were evaluated in relation to their granular and molecular structure, pasting and gel properties. The potato drying kinetics was described by the Page Model, showing a super-diffusive behavior. The pre-treatment with ethanol reduced the drying time up to 55%, and its effect was discussed in relation to the observed structural changes and physical mechanisms (such as the Marangoni Effect and changes in vapor pressure). Rehydration evidenced no crusting formation during drying. The pre-treatment with ethanol increased the initial water absorption rate by 25%, although it did not affect the equilibrium moisture. The pre-treatment with ethanol did not affect neither the morphology of the starch granules nor the size distribution of the molecules. However, drying resulted in slight imperfections on the surfaces of starch granules. In addition, drying affected some parameters of pasting properties and the results indicate the obtained gels tend to be stronger. The results obtained are interesting not only for describing the advantages of the ethanol pre-treatment in drying food products, but also for proposing a simple technology for potatoes preservation, allowing the extraction of its starch.

Keywords: Drying, Ethanol, Starch, Food engineering

RESUMEN

Etanol como pretratamiento de secado de productos amiláceos: efecto en la cinética de secado de papa y propiedades del almidón

El almidón es un importante ingrediente para diferentes industrias, siendo comercialmente obtenido de cereales, tubérculos y raíces. Las raíces y tubérculos presentan un alto contenido de humedad, donde el secado puede usarse para reducirla y aumentar la vida útil de los productos. Sin embargo, este método demanda alto tiempo, lo que puede impactar negativamente las propiedades nutricionales y físicas del producto final. Consecuentemente, alternativas son necesarias para mejorar el proceso de secado sin impactar la calidad final del producto – en este caso, el almidón. Entre las diferentes posibilidades, el uso de etanol como pretratamiento para el secado ha surgido como un método simple y efectivo para reducir el tiempo de sedado. El presente estudio propuso el secado convectivo de papa como una alternativa para reducir las pérdidas postcosecha con el objetivo de obtener almidón, así como aplicar etanol como pretratamiento de secado. Rodajas de papa fueron tratadas por inmersión en etanol por 15 y 30 min. El secado convectivo fue llevado a cabo usando aire a 40°C y 1 m/s. La microestructura fue evaluada por microscopia electrónica de barrido antes y después del pretratamiento con etanol, así como en el producto seco. Después del secado, las rodajas fueron rehidratadas y su almidón extraído y caracterizado. Las muestras de almidón obtenidas antes y después del tratamiento (etanol y secado) fueron evaluadas en relación con su estructura granular y molecular, propiedades de pasta y gel. La cinética de secado fue descrita por el modelo de Page, mostrando un comportamiento superdifusivo. El pretratamiento con etanol disminuyó el tiempo de secado hasta un 55%, y su efecto fue discutido con relación a los cambios observados en su estructura y mecanismos físicos (como el Efecto Marangoni y cambios en la presión de vapor). La rehidratación evidencio que no se formó costra durante el secado. El pretratamiento con etanol aumentó en un 25% la velocidad inicial de absorción de agua, aunque esto no afectó la humedad en equilibrio. El pretratamiento con etanol no afectó la morfología de los gránulos de almidón, tampoco la distribución de tamaño de las moléculas. Sin embargo, el secado resultó en pequeñas imperfecciones en las superficies de los gránulos de almidón. Además, el secado afectó algunos parámetros de las propiedades de pasta y los resultados indicaron que los geles obtenidos tienden a ser más fuertes. Los resultados obtenidos son interesantes no solo por describir las ventajas del pretratamiento con etanol en los productos, sino también por proponer una tecnología simple para conservar la materia prima permitiendo la extracción de su almidón.

Palabras clave: Secado, Etanol, Almidón, Ingeniería de alimentos

FIGURE LIST

TABLE LIST

ABBREVIATION LIST

Treatments

F	Starch from fresh potatoes
E15	Starch from potatoes after pre-treatment with ethanol for 15 min
E30	Starch from potatoes after pre-treatment with ethanol for 30 min
D	Starch from dried potato without pre-treatment (control)
E15-D	Starch from dried potato pre-treated with ethanol for 15 min
E30-D	Starch from dried potato pre-treated with ethanol for 30 min

Rapid Viscometer Analyzer parameters

BD	Breakdown
FAV	Final Apparent Viscosity
PAV	Peak Apparent Viscosity
PT	Pasting Temperature
RBD	Relative Breakdown
RSB	Relative Setback
RVA	Rapid Viscometer Analyzer
SB	Setback
TAV	Trough Apparent Viscosity

Other analyses

BV	Blue Value
GPC	Gel Permeation Chromatography
SEM	Scanning Electronic Microscopy
TCH	Total Carbohydrate Content

1.   INTRODUCTION

Starches are natural biopolymers with great importance as ingredients for different industries, such as food, feed, chemical, petrochemical, textile, paper and cellulose, adhesives, biodegradable plastics, among others.

Commercial native starches are commonly derived from sources such as seeds (mainly maize, wheat, barley, and rice), roots and tubers (mainly cassava and potato). Roots and tubers have a high moisture content, making them highly perishable after harvesting, which can result in economic losses if they are not quickly processed. In fact, although the starches from potato and cassava present interesting industrial applications, they also present high variability and heterogenicity because of vegetable senescence and partial degradation (for example due to fermentation). Consequently, their production and use, in special in Brazil, are limited.

One way to extend the shelf life of these raw materials and expand their starch application is by applying food preservation techniques. Among different possibilities, a moisture-reducing processing of these products, without changing the starch structure and properties, is widely desired. Convective drying can be inexpensive, and efficient way to achieve it.

Drying is a widely used technique to increase food shelf life by reducing the activity of water through moisture vaporizing (CHEN, 2014). Particularly, the convective drying is a simple and widely applied technique, where hot air is employed to remove the water from the product.

However, this process can takes many hours, and the exposure of food to long drying time at high temperature can result in physical (low rehydration capacity, changes in texture), nutritional (loss of volatile compounds an vitamins) and chemical changes (Maillard reaction, oxidation and others) (CHOU; CHUA, 2001). In starchy raw materials, the presence of water (from the food itself) and the long drying time, combined with the use of high temperatures, can lead to changes in the starch, such as its gelatinization.

In order to accelerate the drying process, some pre-treatments have been proposed; particularly, studies proposing the use of ethanol are growing recently (LLAVATA et al., 2020). The pre-treatment with ethanol accelerates drying rate, and can achieve better product quality, such as color and nutrients preservation, among others (CORRÊA et al., 2012; FENG et al., 2019; ROJAS; AUGUSTO, 2018b; ROJAS; AUGUSTO; CÁRCEL, 2020; ROJAS; SILVEIRA; AUGUSTO, 2019, 2020; SANTOS;

SILVA, 2009; SILVA; BRAGA; SANTOS, 2012; SILVA; CELEGHINI; SILVA, 2018; WANG et al., 2019).

Different mechanisms are associated with the effect of pre-treatments with ethanol in drying of food products, although the relative importance of each one is associated with each specific system (vegetable and drying technique). The most cited explanation is associated with the physical interaction of ethanol with the water present in the food, which both increase the vapor pressure and promote the Marangoni Effect (SILVA; BRAGA; SANTOS, 2012). However, the effect of ethanol in promoting structural changes associated with improving further drying and rehydration, only started to be described (ROJAS; AUGUSTO, 2018a, 2018b; WANG et al., 2019).

Therefore, the pre-treatment with ethanol is an uncomplicated way to enhance food drying. Moreover, the convective drying is a simple approach to stabilize starchy vegetables, such as potatoes. Consequently, the objective of this study was to propose convective drying as a method to prolong the shelf life of potatoes, using the pre-treatment with ethanol to accelerate it, without affecting the quality of the obtained.

2. HYPOTHESIS AND OBJECTIVES

2.1 Hypothesis

Convective drying can promote stabilization of starchy raw materials without structure and property changes of starch. Ethanol pre-treatment can improve convective drying without affecting starch.

2.2 General objective

The objective of this work was to evaluate the effect of ethanol as pre-treatment of starchy raw materials drying, to provide an alternative to reduce post-harvest losses and improving industrial applications.

2.3 Specific Objectives

The specific objectives of this work were:

- evaluate the effect of pre-treatment with ethanol in potato slices convective drying;

- evaluate the effect of this pre-treatment in potato structure and rehydration properties;

- extract and isolate potato starches from different treatments, evaluating the effect of each one on starch structure (granule and molecules) and properties (pasting and gel properties).

3. LITERATURE REVIEW

3.1 Potato Starch

Starches are natural biopolymers with great importance as ingredients for different industries, such as food, feed, chemical, petrochemical, textile, paper and cellulose, adhesives, biodegradable plastics, among others. Moreover, starch is very important as the largest source of energy in human diets as a digestible food polysaccharide. It can be found in many different vegetable organs, such as roots, seeds, leaves, stems, and tubers.

Starch, regardless of botanical source, are composed of two types of polysaccharides complexly organized in granules: amylose and amylopectin. Amylose consists of long, straight, or slightly branched chains, in general composing ranges from 20-30%. Amylopectin is the major component of most starches, being composed of several short chains attached to the reducing terminal by a $\alpha(1 \rightarrow 6)$ -linkage, making this a highly branched polysaccharide (BERTOFT, 2004). Amylose and amylopectin content and architecture may influence the thermal properties and gel formation, consequently the functional properties of starch (COPELAND et al., 2009).

The composition of starches varies notably among different sources, differing the properties and functions. Starch granules are also composed of some macromolecules such as proteins and lipids, in relatively small contents (THOMAS; ATWELL, 1999).

Potato starch is unique among commercial starches, with some relevant properties, such as high consistent paste producer, low gelatinization temperature, excellent flexible films, strong gels and high paste clarity (GROMMERS; KROGT, 2009; VASANTHAN et al., 1999). Potato starch granules are composed of approximately 25% amylose (ALVANI et al., 2011). Moreover, it has large granules and a large amount of phosphate groups, which give this starch a high expansion power (JOBLING, 2004).

Potato starch characteristics make it desirable for different applications. For instance, food industry value its high clarity/transparency and neutral flavor. Besides the high molecular weight of amylose and good solubility, potato starch is widely used in the paper industry (GROMMERS; KROGT, 2009). In the textile industry, it is used due to its film properties and adhesive power. In addition, due to its large grains, potato starch is preferred pre-coating on filters. Finally, it is applied in water treatment due to

its high phosphate content, which cause special effects of flocculation (GROMMERS; KROGT, 2009).

Potato tuber plants were firstly cultivated in the Andean mountains of Peru; since then, they spread across the globe and became a culture of several countries (MARTÍNEZ et al., 2019). Starch is the largest component present in potatoes, about 85-87% of its dry matter (VASANTHAN et al., 1999). However, potato moisture corresponds to 80-85% of the tuber content, making them highly perishable.

In fact, the low stability of *in natura* potatoes limits its starch production in Brazil. Consequently, preservation methods must be studied to stabilize potato tubers without affecting its starch properties.

3.2 Drying

Drying is one of the most common and ancient food preservation processes. There are countless ways to dry food products, and the selection of method is based on the type of food, final product quality, processing time, energy efficiency, among others (CHEN, 2014).

From an Engineering perspective, drying is a unit operation based on heat and mass transfer, that promotes physical transformations, chemical alterations, and phase changes, affecting the final quality of the food (MUJUMDAR; DEVAHASTIN, 2004).

Among the drying methods, convective drying is the most used technique. In this process, the food product is exposed to a continuously blowing hot air stream, which causes moisture loss from food to the environment (RATTI, 2001). The convective drying of vegetables in general uses temperature from 40 to 70 ºC, being necessary many hours to be carried out. Therefore, the contact of the food with the hot air during the long time causes different undesirable changes, such as darkening, decreased rehydration capacity, loss of flavor, degradation of nutrients and other factors (GIRI; PRASAD, 2007).

Therefore, the challenge for drying food process is to obtain short processing times and higher quality food products, with reduced energy consumption.

Different traditional techniques such as bleaching (PANDEY; MISHRA; MISRA, 2019; TAO et al., 2019) and osmotic dehydration (DERMESONLOUOGLOU; CHALKIA; TAOUKIS, 2018) has been applied over the years to enhance drying,

showing good results. However, the application of emerging technologies as pre-treatments has gained attention.

The use of emerging technologies such as high pressures, pulsed electric fields, ultrasound, ethanol, or perforations, as well as combinations of these techniques, has recently increased (LLAVATA et al., 2020). However, some of these strategies can be complex and expensive, which limits their application for small producers.

In this sense, we opted to work with ethanol as a pre-treatment to dry potatoes, as it is among the least expensive and easy to apply technologies, whose studies are recently increasing (LLAVATA et al., 2020).

Funebo et al. (2002) observed that dry apples treated with ethanol had stiff and brittle structures. Apples showed thin cell walls, and cell order was disrupted. These structural changes led to a better ability to rehydrate apples.

Tatemoto et al. (2015) injected ethanol in balls of mixed rice and soybean protein powders to study drying. They showed the water vapor moved from the centre to the sample surface by forming channels, which allowed water to flow out easily and prevented the formation of the hard layer (crust) during drying.

Rojas & Augusto (2018a) demonstrated pumpkin pre-treated with ethanol showed faster convective drying, faster water absorption and higher water retention when compared with control treatment. Although, the formation of channels explained in the study of Tatemoto et al. (2015) was not observed by Rojas & Augusto (2018a), the authors described pumpkin microstructure changes due to ethanol as an important mechanism of mass transfer enhancement: part of the air between the cells of the parenchymatic tissue was removed, the cell walls became thinned, while no significant change was observed in the xylem vessels. Moreover, the authors also interpreted the mass transfer improvement based the discussion of Marangoni Effect in the work of Silva, Braga & Santos (2012). The Marangoni Effect occurs due to the difference in surface tension between two fluids (in the present case, water, and ethanol), from the low to the high surface tension regions. Therefore, during the pre-treatment, in which the samples are placed in contact with ethanol, this compound enters the matrix. During drying, the ethanol that remained on the surface vaporizes firstly, generating a gradient of surface tension. Therefore, more water remains on the surface of the sample, causing this region to have a higher surface tension, pulling the solution from

inside the sample and so on until a surface tension balance is reached (ROJAS; AUGUSTO, 2018a).

Many other studies show the positive effect of using ethanol as a pre-treatment in different food matrices, ways of application and drying techniques. For instance, ethanol was added to modify the drying atmosphere of pineapple (SANTOS; SILVA, 2009). Liquid ethanol was also used by being brushed in the surface of bananas (CORRÊA et al., 2012). Moreover, this pre-treatment was also used by immersing the samples into the ethanol, for further convective drying of pumpkin (ROJAS; AUGUSTO, 2018a; ROJAS; SILVEIRA; AUGUSTO, 2020), apple (ROJAS; AUGUSTO; CÁRCEL, 2020) and guaco leaves (SILVA; CELEGHINI; SILVA, 2018), and also the infrared drying of potatoes (ROJAS; AUGUSTO, 2018b; ROJAS; SILVEIRA; AUGUSTO, 2019), scallion (WANG et al., 2019) and garlic (FENG et al., 2019).

Some positive aspects reported are increasing drying kinetics, reducing drying time and improving the quality of the final product. However, other studies describe negative aspects of the ethanol pre-treatment. For instance, Rojas & Augusto (2018b) and Rojas, Silveira & Augusto (2019) studied the ethanol pre-treatment to the infrared drying of potatoes. Although infrared drying was enhanced, ethanol negatively affected rehydration, which was attributed to the large starch content present in the samples and characteristics of the drying process. Moreover, starch was not evaluated by the authors.

Consequently, it is important to evaluate the convective drying of potatoes with focus on the starch extraction, isolation, and application, also considering the pre-treatment with ethanol.

4.   MATERIAL AND METHODS

The purpose of this work was not only to study potato drying, but also to understand more deeply the effect of ethanol on drying, rehydration, and microstructure, as well as proposes drying of starchy products as an approach prior to starch extraction. To achieve it, this work was divided in different steps, as represented on Figure 1. Firstly, potato slices were obtained and convectively dried, directly or after pre-treatments using ethanol. In this step, the drying kinetics was evaluated, and the dried slices were evaluated through their structure and rehydration kinetics. Next, the potato starch was extracted and purified from the rehydrated slices. Finally, both structure (granular and molecular) and properties of the obtained starches were evaluated.
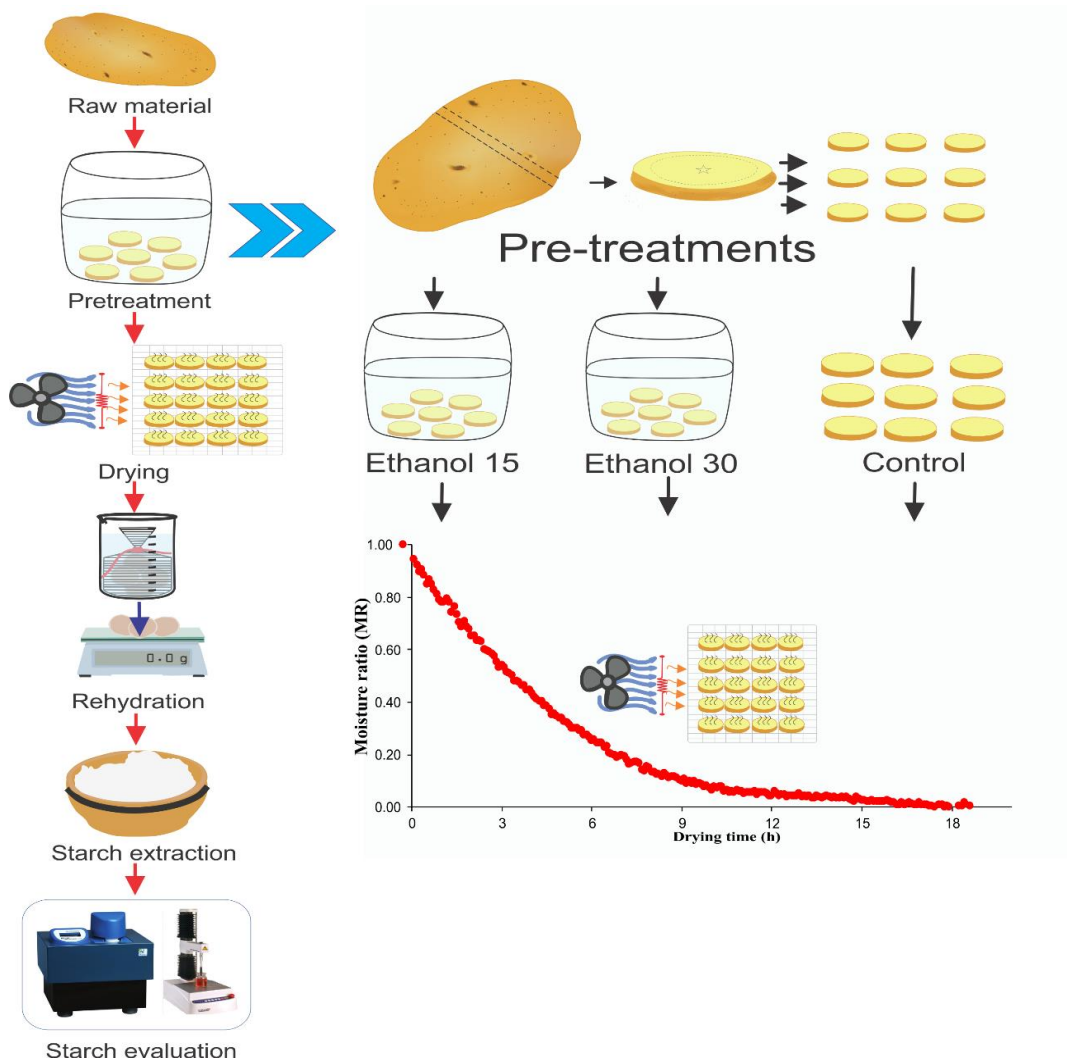
Figure 1. Schematic representation of the steps in this study.

4.1 Sample preparation and ethanol pre-treatments to drying

Potatoes (*Solanum tuberosum*) were purchased in the local market (Piracicaba, São Paulo State, Brazil), and used in this study as a representative model of high moisture starchy raw material (~ 85% w.b.). The potatoes were washed using a sponge and detergent; the excess of water on their surfaces was removed with a towel. Subsequently, the whole potatoes were sliced to a thickness of 5 mm. The fresh potato slices were then submitted to different treatments before drying: control (D, without any other treatment, being directly dried just after slicing), ethanol pre-treatment for 15 min (E15-D) and ethanol pre-treatment for 30 min (E30-D) – Table 1 shows the treatment codification. The samples were (~300 g) treated immersed in a beaker containing 1400 mL of ethanol (Scientific Exodus, Brazil) (99.8 v/v) during 15 or 30 min. Then, the slices were removed from ethanol, and their surfaces were superficially dried with absorbent paper. The samples were then weighed and dried. Pre-treatment times were determined by previous works by the research group (ROJAS; SILVEIRA; AUGUSTO, 2020).

4.2 Convective drying

The drying process was performed immediately after the pre-treatments, using air at 40 °C and 1.0 ± 0.1 m·s^{-1} in a Computer Controlled Tray Dryer (Armfield UOP8 MkII United Kingdom). The drying temperature was milder to prevent starch gelatinization.

Potato slices were placed in perforated metal trays, to allow free circulation of hot air over their whole surface. The potato mass was registered continuously by a computer connected to the drying tunnel, until constant weight. Drying process was carried out in triplicate.

Drying curves were plotted according to dimensionless moisture ratio (MR), as described in Equation 1, where "M" is the moisture content on dry basis (% d.b., i.e., kg of water·kg^{-1} dry matter) over the drying time (t), "M_e" is the equilibrium moisture (the average of the last 10 values obtained after stabilization, % d.b.), and "M_0" is the initial moisture (% d.b.). The initial moisture contents (from fresh tubers) and after the pre-treatment with ethanol were measured by complete drying crushed potatoes at 115 °C on a moisture analyzer (MX-50, A&D Company, Japan). All moisture data over time were calculated by mass balance, considering that the sample "moisture" is a lumped

parameter that includes both volatile liquids: the remaining water and the absorbed ethanol (ROJAS; AUGUSTO, 2018a). For potatoes without ethanol, the initial moisture content was the same as for fresh potatoes. Therefore, all the curves started with MR equal to 1.

$$\text{Equation 1:} \qquad (MR_t) = \frac{M_t - M_e}{M_0 - M_e}$$

Page Model Equation 2 (PAGE, 1949), where "MR" is the dimensionless moisture, "t" is the drying time (h), "k" is the drying rate parameter (h^{-n}); and "n" is a shape parameter (dimensionless). This empirical model has been widely applied to described food drying. Moreover, recently Simpson et al. (2017) demonstrated that the anomalous diffusion approach, based on fractional calculus, can attribute phenomenological interpretation to Page's parameters: the parameter "n" is related to the type of diffusion (n = 1 describes normal diffusion, n ≠ 1 describes anomalous diffusion with interference from other phenomena, such as capillarity), while the parameter k can be associated with the diffusion coefficient and sample geometry.

$$\text{Equation 2:} \qquad MR = e^{-kt^n}$$

4.3 Rehydration kinetics

Rehydration was performed by immersing the dried potato slices in distilled water at 25 °C ± 1 °C. To avoid water limitation, a ratio of 0.072:1 dry sample: water (m/m) was used. During rehydration, the samples were removed from the water, and their surfaces were superficially dried with absorbent paper. They were then weighed and returned to water until reaching constant weight.

The moisture obtained in each time "M_t" was calculated by mass balance, considering the initial mass of the sample, the initial moisture content (M_0) and the mass obtained at each time. The rehydration was performed in triplicate.

Peleg Model (PELEG, 1988), was used to describe the rehydration kinetics, being presented in equation 3, where "M_t" is the moisture content over time, "M_0" is the initial moisture, "t" is the time, and "k_1" and "k_2" are the model parameters. The inverse of k_1 describes the rate of water absorption at the beginning of the process, while the inverse of k_2 is related to the equilibrium moisture content.

$$\text{Equation 3:} \qquad M_t = M_0 + \frac{t}{K_1 + K_2 \cdot t}$$

4.4 Potato structure

Scanning electron microscopy (SEM) technique was used to observe the structure of fresh, pre-treated, dried, and rehydrated potato slices. The internal surfaces of potato slices were observed, i.e., the surfaces correspondent to the slice thickness.

For this, rectangular cuts were made in the moist sample, using a blade with a smooth comb. After cutting, the obtained pieces were fixed overnight in 2.5% (v/v) glutaraldehyde and cacodylate buffer (pH 7.2), to avoid structural changes during the dehydration. Subsequently, the samples were removed from the solution and washed three times with cacodylate buffer. Then, the samples were dehydrated in a graded ethanol series ((v/v) 20%, 40%, 60%, 70% and 90%) and finally absolute ethanol three times during 1 h. After the last immersion (using absolute ethanol) samples were transferred to capsules and washed three times using the same ethanol. The capsules were placed in a critical point drier (Leica EM CPD300, Austria) to remove solvent without causing changes due to surface tension in the delicate details of the cells and tissues.

Subsequently, the samples were transferred to stubs, which contained a double-sided carbon tape to hold the samples. The metallization process deposited a thin layer of gold in the stubs, which were placed in a scanning electron microscope (LEO 435 VP, Leo Electron Microscopy Ltd., United Kingdom) operation at an acceleration voltage of 20 kV. The samples were then evaluated in the microscope using the magnification of 500x.

4.5 Starch extraction and treatments

The starch extraction was performed according to (CASTANHA; MATTA JUNIOR; AUGUSTO, 2017), with few modifications.

The dried samples (80 g) were rehydrated at 5 ℃ for 12 h in 1000 mL of distilled water with the addition of 1 g of potassium sorbate. The hydrated slices (200 g) were grounded in a blender with 1000 mL of water for 5 min at room temperature. The obtained suspension was passed through a 250 µm (60 mesh) sieve. The filtrated sample was sieved again using 149 µm, 60 µm and 50 µm (100, 250 and 300 mesh,

respectively) sieves and the obtained starch slurry could settle for 1 h. The procedure was repeated 4 to 5 times until the supernatant became clear. The obtained starch was then oven dried at 35 °C until reaching moisture of ~15%. The obtained starch was grounded in a mortar, sieved (250 µm) and stored in glass containers until further use.

In order to evaluate the effect of both ethanol pre-treatments and/or convective drying on starch structure and properties: the evaluated starch were obtained directly from fresh potatoes (F), and after pre-treatments with ethanol for 15 min (E15) and 30 min (E30). Table 1 summarizes the treatments and codifications.

Table 1. Treatments obtained for this study and their respective codifications

Pre-treatment with ethanol (min)	Before drying	With drying potato
0	F: Starch from fresh potatoes	D: Starch from dried potato without pre-treatment (control)
15	E15: Starch from potatoes after pre-treatment with ethanol	E15-D: Starch from dried potato pre-treated with ethanol
30	E30: Starch from potatoes after pre-treatment with ethanol	E30-D: Starch from dried potato pre-treated with ethanol

4.5.1 Starch structure

Both starch granular and molecular structures were evaluated.

Starch granule morphology was evaluated using light microscopy (Model L10000, Bioval, Curitiba, Brazil; with a 20 W halogen lamp) and a polarized light filter. The starch was placed on a glass slide, a drop of lugol solution (1% I_2 and 2% KI) was poured, and the system was covered by a glass slip. The magnification of 40x was used to obtain the images. Several glass slides were used for the analysis, in order to be representative.

The molecular size distribution profile was evaluated by gel permeation chromatography (GPC), as described by Song and Jane (2000), with modifications. A GE XK 26/70 column (2.6 cm diameter and 70 cm high) packed with Sepharose CL-2B gel (Sigma, Sweden) was used. Starch samples (0.1 g, on dry basis) were gelatinized in a boiling water bath for 1 h after being mixed with 10 mL of dimethylsulfoxide (DMSO; 90%, Labsynth, Brazil), being then kept at 25 °C for 16 h

under constant stirring. Using a pipette, 3 mL of the obtained sample were blended with 10 mL of absolute ethanol (Êxodo Cientifica, Brazil), and then centrifuged for 30 min at 3000 g. The supernatant was discarded, and the precipitated starch was dissolved in 9 mL of boiling distilled water, being then placed in a bath of boiling water for 30 min.

In sequence, 4 mL of the gelatinized sample were injected into the chromatographic column, using a solution of 25 mmol·L^{-1} of NaCl (Química moderna, Brazil) and 1 mmol·L^{-1} of NaOH (Synth, Brazil) as mobile phase, at a rate of 60 mL·L^{-1}. A fraction collector (Gilson, model FC203B, Middleton, England) was used to separate the sample into 4 mL portions. The samples were evaluated through two techniques: the blue value (BV) method (JULIANO, 1971), and total carbohydrate content (TCH), by the phenol sulfuric method (DUBOIS et al., 1956).

In the BV analysis, 0.12 mL of diluted iodine solution (1.0 g iodine (Vetec, Brazil) and 0.1 g potassium iodide (Dinâmica Química Contemporânea, Brazil) in 100 mL of 0.2 M acetate buffer pH 5.0) was added to 0.025 mL of sample and the absorbance was read using a spectrophotometer at a wavelength of 620 nm (Femto spectrometer, Model 600S, São Paulo, Brazil). The analysis of TCH was performed by adding 25 μL phenol (5% w/v), 125 μL sulfuric acid concentrated (Cromoline – Química Fina, Brazil) in 25 μL sample, and the absorbance was read at 490 nm.

The BV analysis is based on the ability of amylose to form a helical inclusion complex with iodine, featured with a maximum absorption wavelength 620 nm (LIU, 2005), generating blue color in the presence of amylose and purple in the presence of amylopectin. The phenol-sulfuric acid method determines all carbohydrates in sample. It is possible to analyze whether there were changes in the proportions of amylose and amylopectin that were not complexed with iodine. In this method, concentrated sulfuric acid disintegrates any large chain carbohydrate into monosaccharides. These smaller chain compounds react with phenol to produce a yellow color.

4.5.2 Starch properties

The starch pasting properties were evaluated using a Rapid Visco Analyzer equipment (RVA-4, Newport Scientific Pvt. Ltd., Australia, with the Thermocline for Windows software, version 3.0). A suspension of 3 g starch (14% moisture basis) in 25 g of distilled water was analyzed on a programmed heating, retention, and cooling

temperature cycle, under constant shear. The suspensions were initially held at 50 °C for 1 min, heated to 95 °C at 6 °C/min and kept at 95 °C for 5 min, being then cooled to 50 °C at 6 °C/min, and kept at this temperature for 2 min. The pasting parameters were then obtained.

Following, the obtained pastes were stored in plastic cups (40 mm diameter x 20 mm height) and reserved in a closed chamber (similar to a desiccator) with water at the bottom avoid drying. The chamber with the gels was kept in the refrigerator at 8 °C for 24 h. The firmness of the starch gels was set by instrumental texture using a Texture Analyzer (TA. XT Plus, Stable Micro Systems Ltd., Surrey, UK) with a load cell of 50 kgf (490.3 N). A 0.5" cylindrical probe was selected to puncture the sample until the distance of 4 mm at 1 mm·s^{-1}. The starch gel strength was determined as the maximum force achieve during the penetration assay.

4.6 Experimental design, regressions, and statistics

Each process was performed in triplicate and the analysis in duplicate.

The parameters of Page and Peleg Models were obtained by non-linear regression using the "Solver (GRG Nonlinear method)" tool from Excel 2016 software (Microsoft, USA). For this, an error minimization calculation was made through the quadratic sum of the SSE errors (Equation 4), between the experimental and the predicted values. The parameters were defined as optimal solution when convergence reached 10^{-6}.

$$\text{Equation 4:} \qquad SSE = \sum_{i=1}^{X}((predicted) - (experimental))_i^2$$

The statistical analysis was performed using an entire randomized test. The data was analyzed using ANOVA and the averages were compared using Tukey test using the Minitab software (version 18) using a significance level of $\alpha = 0.05$. Even so, for better understanding the phenomenon and description of some processes, $\alpha = 0.1$ and $\alpha = 0.2$ were also used in specific parts, as described in the next section.

5. RESULTS AND DISCUSSION

5.1 Effect of ethanol pre-treatment on potato structure and drying

The progress of dimensionless moisture content (MR) over the drying time, for the different treatments, are shown in Figure 2.
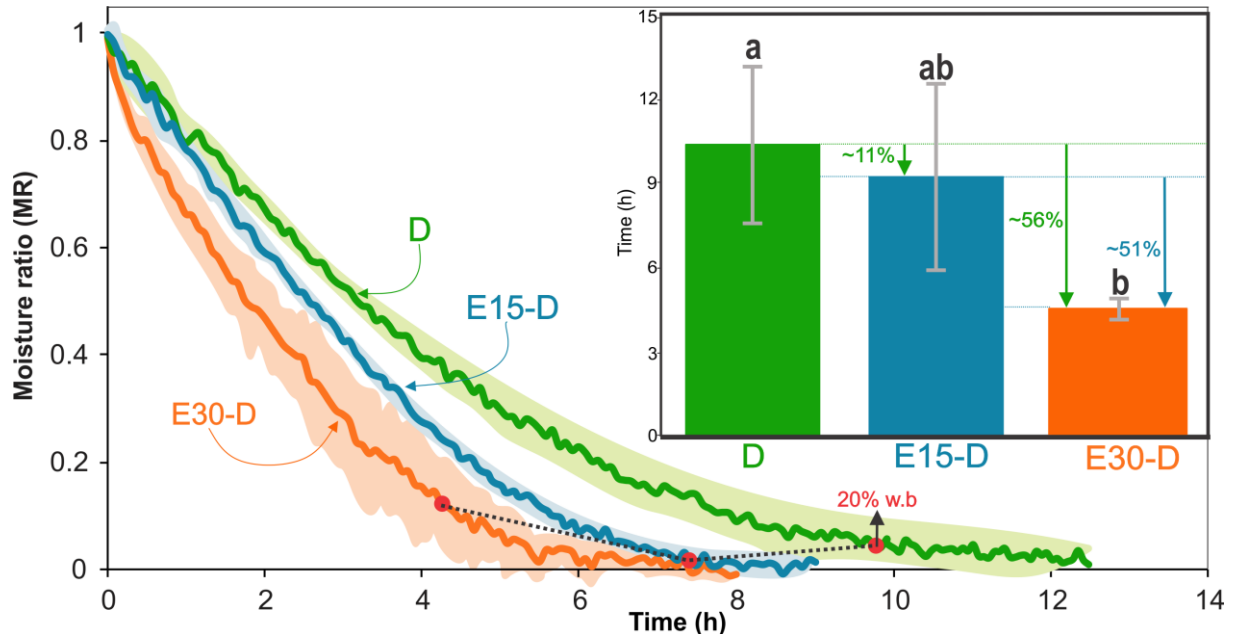
Figure 2. Convective drying (40 ºC, 1.0 m/s) of potato slices with different treatments: D and drying after pre-treatments E15-D and E30-D. The lines are the experimental averages, and the shaded areas represent the standard deviation of the experimental data. The inserted graphic shows the time required for all treatments to reach a final moisture of 20% w.b (average ± standard deviation). Different letters represent significant statistical difference (p < 0.05) among treatments. Down arrows represent the percentage time difference among treatments.

Pre-treatments with ethanol resulted in faster drying than the control (D), which can be evaluated by the time needed to achieve a moisture of 20% (on wet basis), which represents a moisture level to achieve microbial stability in dry vegetables (CHEN; PATEL, 2008): the necessary time to achieve it was reduced by ~22% using the pre-treatment E15-D, and ~56% using E30-D (p <0.05).

These results are in the same order of magnitudes of previous studies with other vegetables. Considering convective drying and the pre-treatment by immersion in ethanol, a reduction of 34-53% was reported for apples (ROJAS; AUGUSTO; CÁRCEL, 2020), and pumpkins (ROJAS; AUGUSTO, 2018a; ROJAS; SILVEIRA; AUGUSTO, 2020). Moreover, a reduction of ~ 6 to ~ 34% was observed in banana, pineapple and apple when ethanol was applied only onto the sample surface, while

this reduction was from ~ 7 to ~ 17% when ethanol was applied in the drying atmosphere (SANTOS; SILVA, 2009; SILVA; BRAGA; SANTOS, 2012). Furthermore, considering infrared drying, this treatment resulted in processing time reduction of ~25% for scallions (WANG et al., 2019), ~12% in potato cylinders (ROJAS; AUGUSTO, 2018b) and ~ 14% in garlic slices (FENG et al., 2019).

Different possibilities can explain the effect of ethanol in reducing drying time.

Firstly, ethanol can promote structural changes (ROJAS; AUGUSTO, 2018a; WANG et al., 2019). When in contact with food, ethanol causes extraction of water and other components, as well as the incorporation of ethanol, resulting in structural changes. These effects can be evidenced by Figure 3, which shows SEM images of potato slices after pre-treatment, after drying and after rehydration. In these images, it is possible to observe that after the pre-treatments with ethanol, the cells became withered in relation to the control. After rehydration, the thinner cells can be better noticed. In fact, ethanol extracts some components of cell walls and/or membrane, which became thinner. Moreover, the cells lose turgidity, changing its initial shape and becoming more distorted and compacted. These permanent structural modifications can facilitate the entry of water during hydration, even though ethanol is not in the sample anymore. Similarly, this indicates water can leave the product easily during drying. More information about this process is highlighted in section 5.2.

The cell wall and membrane of vegetables have a diversified composition. According to Canteri et al. (2019), ethanolic solutions can extract polyphenols, some classes of proteins and lipids from cell walls and/or membrane. On the other hand, the compounds related to the structure of the cell wall, such as cellulose, lignin or hemicellulose, are not extracted. Therefore, once the overall cell structure is maintained, although, with thinner walls, it avoids collapsing and ensures enhanced water flux through it during both drying and rehydration process.

Moreover, once starch granules are not soluble in ethanol, they are not extracted during pre-treatment – which is important if the objective is to obtain starch. However, ethanol can modify starch – the reason by how we added three more treatments in the evaluation, in order to identify, if there are changes, which process caused them, as described in the next section and Table 1.

Therefore, structural modifications caused by ethanol can affect both drying and rehydration. In fact, the effect of ethanol on food products structure is still

beginning to be described, but the changes caused by it in the drying process are remarkable, as discussed as follows.

Another possible mechanism that corroborates to explain the effect to ethanol promoting structural changes is the osmotic dehydration caused by it. Osmotic dehydration is based on the removal of water by direct contact of the food material with a hypertonic medium. In this case, the cell wall acts semipermeable membranes that allow the passage of small molecules, such as water (SHI; LE MAGUER, 2002). Therefore, the difference in osmotic pressure between ethanol and the vegetable (intracellular and intercellular content) can remove part of the product's water to the ethanol. In fact, according to Wang et al. (2019), the pre-treatment using vacuum showed a good osmotic dehydration effect on scallion. In the present study, the combination of structural changes, combined with the osmotic process and the Marangoni effect, which will be explained below, can explain the success of ethanolic pre-treatment in reducing drying time.
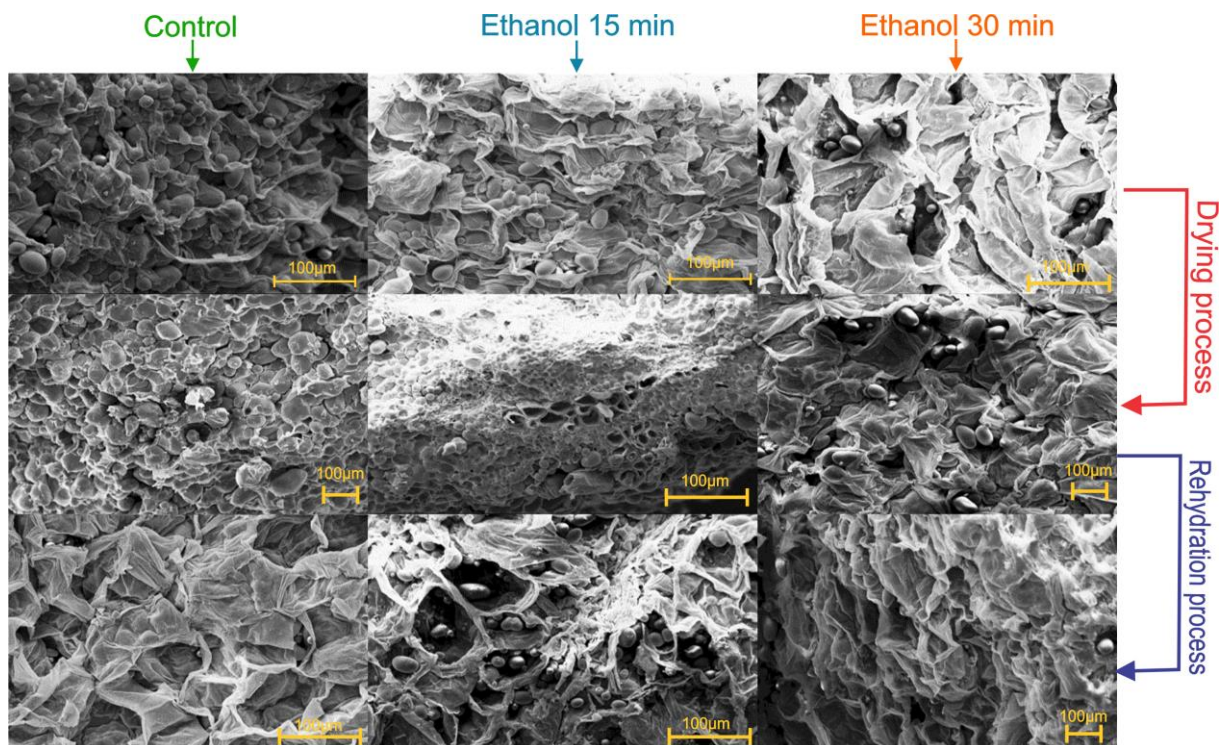

Figure 3. Structural changes inside the potato slices before drying, after drying and rehydration of each treatment: control and pre-treatments with ethanol for 15 and 30 min (E15, E30, E15-D and E30-D). Images obtained by scanning electron microscopy (SEM) with magnifications of 500x (the inserted bar represents 100 µm).

Therefore, the third explanation for the effect of ethanol in improving dying is due to the interaction of ethanol with the water present in the food, which increase the vapor pressure and promote the Marangoni effect.

The Marangoni effect was first described by Thomson (1855), being associated to food drying for the first time by Silva, Braga & Santos (2012). It constitutes a mass flow mechanism with the differences in surface tension. In the present work, the Marangoni effect occurs during both pre-treatment and drying. During the pre-treatment, ethanol enters the potato slices and water flows from the food to ethanol. The food surface is then composed of a mixture of water and ethanol. Due to the lower boiling point of ethanol, it evaporates faster during drying than water, leaving more water than ethanol on the surface. As ethanol concentration is reduced in the sample surface during drying, this region reaches a higher surface tension in relation to the layers below. This gradient in surface tension pulls the fluid from the next layer. It results in continuous flow within the adjacent inner layers of the food to surface, which happens until a balance of surface tension is achieved (ROJAS; AUGUSTO, 2018a).

Page Model was empirically proposed by Msc. Glen Page (1949), in order to improve the fitting of experimental drying data. However, a phenomenological explanation was proposed by Simpson et al. (2017). According to the authors, the parameter "k" is associated to the effective diffusivity and sample geometry, while the parameter "n" is related to the microstructure of the food and the mechanism of mass transfer (type of diffusion). When n > 1, the process is characterized as super-diffusive, while n < 1, the process is sub-diffusive.

Analyzing the parameters of the Page Model (Figure 4), an increase in the "k" parameter is noticeable for E30-D treatment: this treatment presented an   of 108% in this parameter, when compared to the "D" treatment. By representing an increase in the drying rate, this is consistent with the mass transfer improvement.

The parameter "n" had values always greater than 1, demonstrating a super-diffusive behavior (n > 1). This is similar to the convective drying of pumpkin (ROJAS; SILVEIRA; AUGUSTO, 2020) and apple (ROJAS; AUGUSTO; CÁRCEL, 2020), and infrared drying of potato (ROJAS; AUGUSTO, 2018b). This indicates the presence of other phenomena that accelerates mass transfer in relation to pure diffusion, such as capillarity. Moreover, n values did not show any difference among treatments by

considering p > 0.05, but so with p < 0.2. This indicates although ethanol accelerates drying, the overall super-diffusive behavior is not affected.

Therefore, ethanol reduced the drying time, which is interesting and desirable. However, ethanol can affect starch structure and properties, which can impair the product quality. the quality of the obtained product should not be impaired. Consequently, it was evaluated as follows.
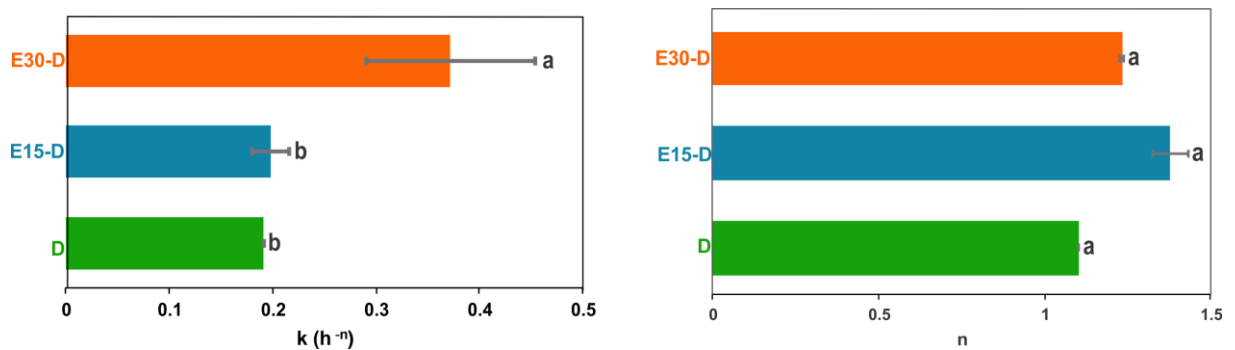
Figure 4. Page Model parameters (Equation 2) for convective drying (40ºC, 1.0 m/s) of potato slices after different pre-treatments (D, E15-D, E30-D). Results represent mean ± standard deviation of treatments. Different letters represent significant statistical difference (p < 0.05) among treatments.

5.2 Effect of ethanol on rehydration kinetics

Figure 5 shows the rehydration kinetics of potatoes slices after different pre-treatments and convective drying, as well as the Peleg Model (Equation 3) parameters, k_1 and k_2.

Ethanol treatments showed a slightly faster rehydration at the beginning of processing, whose behavior become similar to the processing time is increased. Therefore, smaller values (p < 0.05) for "k_1" were achieved using the pre-treatments with ethanol (Figure 5). This result is interesting since rehydration would be the first step in the starch extraction processing. Moreover, this effect can be associated to the structural changes caused by ethanol (section 5.1), which facilitates the water flow into the sample due to modifications in the cell wall.

This result is in line with those reported for convective drying of pumpkins (ROJAS; AUGUSTO, 2018a; ROJAS; SILVEIRA; AUGUSTO, 2020), or even other drying strategies, such as infrared and vacuum drying of scallion (WANG et al., 2019), drying apple slices microwave-assisted (FUNEBO et al., 2002) or ultrasound-assisted convectively dried (ROJAS; AUGUSTO; CÁRCEL, 2020). All these works described a positive impact of ethanol in the rehydration properties.
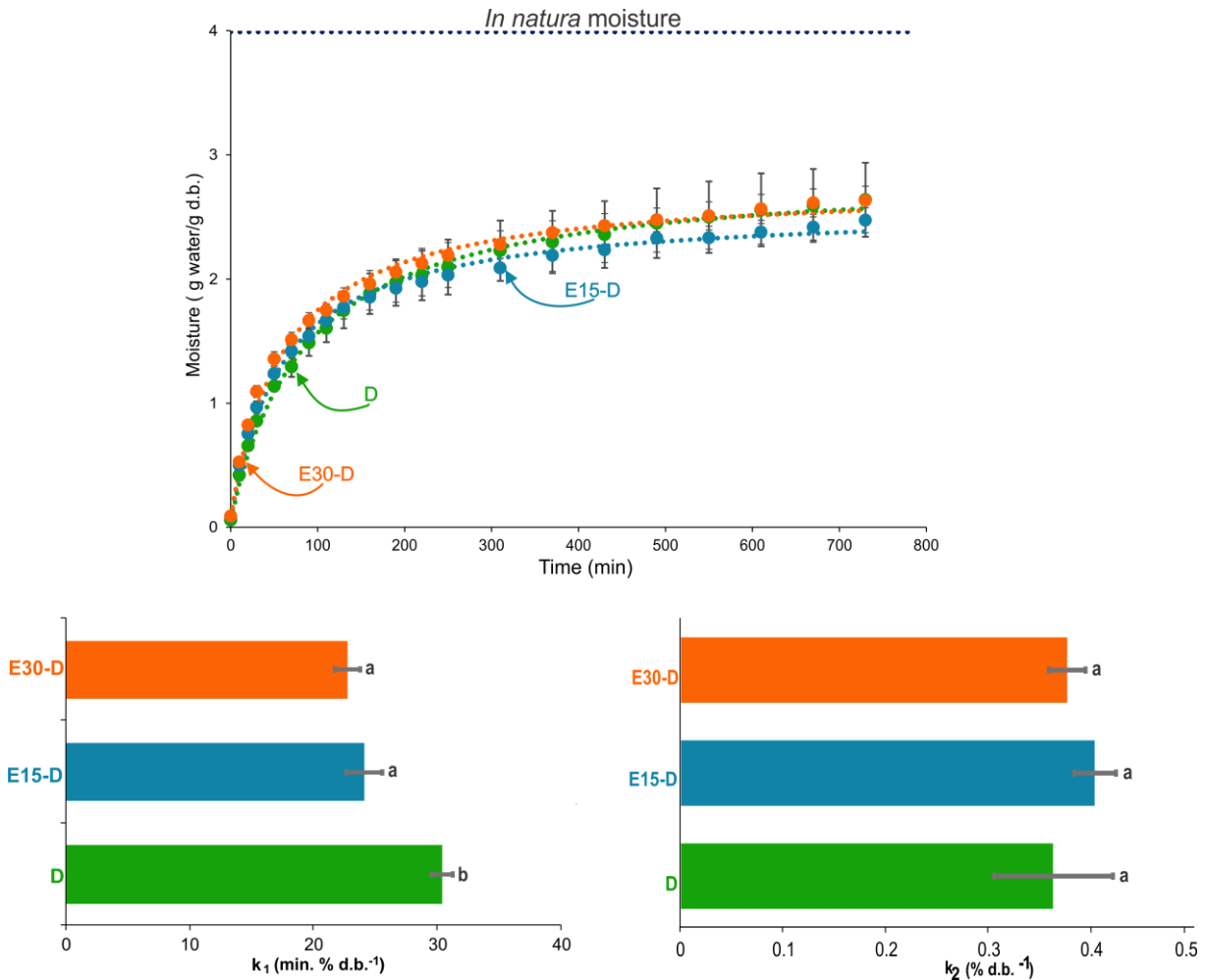
Figure 5 – Up: Rehydration kinetics (25 °C) of potato slices after pre-treatments (D, E15-D, and E30-D) and convective drying (40 ºC). Dots are experimental data and bars ± standard deviation over rehydration time. The dotted line represents the moisture of *in natura*. The Peleg Model (Equation 3) is represented by the dotted curves. Down: Parameters of Peleg Model for the rehydration kinetics. Results represent mean ± standard deviation of treatments. Different letters represent significant statistical difference ($p < 0.05$) among treatments.

However, a different behavior to this rehydration kinetics was observed when potato slices were dried using infrared radiation Rojas & Augusto (2018b) and Rojas, Silveira & Augusto (2019). The mentioned works, the ethanol pre-treatment negatively affected the potato rehydration. However, the studies mentioned above were conducted using infrared drying, whose mechanisms of heat transfer and the temperature reached by samples are different. In that works, samples reached higher temperatures, causing the formation of crust, and hindering the rehydration process.

In the present work, using convective drying, these problems were not evidenced. Moreover, convective drying is a method much simpler and cheaper than

infrared drying. In fact, convective drying can be performed even by small farmers, which can achieve potato preservation at low costs and through a simple approach – even considering the pre-treatments with ethanol. Therefore, we highlight once again this is an interesting result, in view of obtaining starch as a final product.

For the parameter k_2, no differences were evidenced among treatments ($p > 0.05$). As observed in the hydration curve (Figure 5), at the end of rehydration all treatments had the same profile and achieve the same moisture contents. Even so, the achieved equilibrium moisture was always ~ 70% of the original moisture (i.e., the *in natura* potatoes): ~ 72% (2.64 kg water/ kg dry matter) for the D treatment, ~ 71% (2.47 kg water/ kg dry matter) for the E15-D and 72% (2.63 kg water/ kg dry matter) for E30-D.

A possible explanation for this behavior is associated with changes on structure and air presence. After drying, some air can get trapped inside the pores, forming bubbles that can obstruct the water flow (SAGUY; MARABI; WALLACH, 2005). This is in fact very common in dry products, where the structural changes reduce the ability to accommodate water in relation to the fresh product (MORAES, 2018).

Once again, the results of this work are better than those obtained by the infrared drying of potatoes pre-treated with ethanol (ROJAS; AUGUSTO, 2018b; ROJAS; SILVEIRA; AUGUSTO, 2019). In these two works, rehydrated ethanol-pretreated potato slices reached equilibrium moistures than those of the control samples. Once again, the effect of convective drying on potatoes in relation to infrared drying stands out.

However, the results here obtained for potatoes are different from those obtained for other vegetables, such as pumpkins, highlighting the differences among vegetables matrixes (ROJAS; AUGUSTO, 2018a). The pre-treatment with ethanol resulted not only in higher rehydration rate in pumpkins, but also higher equilibrium moisture content – which was closer to the *in natura* vegetable, when compared with the control. Moreover, some studies showed equilibrium moisture content higher than the fresh product by using ethanol treatments. For example, Rojas, Augusto & Cárcel (2020) described rehydrated apples presented moisture ~ 5% higher than the fresh product moisture when ethanol pre-treatment was applied. For comparison, the control treatment obtained an equilibrium moisture content ~ 6% lower than the fresh product. Once more, these differences can be associated with differences in composition and

structure among the products, where their tissues and the ways in which they are arranged can influence the drying and rehydration properties.

In summary, the results presented in this section are interesting as they reveal that ethanol treatment did not negatively affect the rehydration properties. On the contrary, the longer contact time with ethanol provided a higher rate of rehydration. Furthermore, it does not indicate crusting due to starch gelatinization. However, the structure and properties of the resulted starches must be evaluated, as described in the next sections.

5.3 Structure and properties of the obtained starches

Starch were extracted and evaluated before pre-treatment, after pre-treatment and after rehydration of dry potato slices.

Therefore, this section organizes these results into two sub-sections: starch structure (molecular and granular structure), and starch properties (paste and gel properties).

5.3.1 Starch structure: molecular and granular structure

The results of gel permeation chromatography (GPC) for starches extracted from dried potatoes and after pre-treatments (before drying), are shown in Figure 6 (for both the blue value (BV) and total carbohydrates (TCH).

This chromatographic analysis is based on separation of starch molecules by their sizes. When a polymeric solution is propelled through the column, the column packaging material, separates the polymer chains according to their differences in their hydrodynamic volume (WANG; CUI, 2005): bigger molecules elute firstly and smaller molecules, latter. Considering starch molecules, the first fractions to leave the column are composed by amylopectin molecules, for being larger and more branched when compared to amylose. Consequently, the second peak comprises fractions of amylose molecules.

The blue value (BV) analysis is based on the ability of starch to form a helical inclusion complex with iodine. Consequently, this iodometric method only covers long and medium chains of α (1 $\rightarrow$ 4) – glucan contents, mainly amyloses (LIU, 2005). The phenol-sulfuric method can measure all the carbohydrate content (TCH) present in the

sample. Combining both methods is an interesting approach to evaluated modified starches.

Both the results of TCH and BV (Figure 6) present a first large peak (corresponding to amylopectin) and a second small and wide peak (amylose), for all treatments. Moreover, the curve profile and order of magnitudes are the same for all treatments. This indicates that the size of potato starch molecules was not affected by any treatment here described (ethanol pre-treatment and/or convective drying).
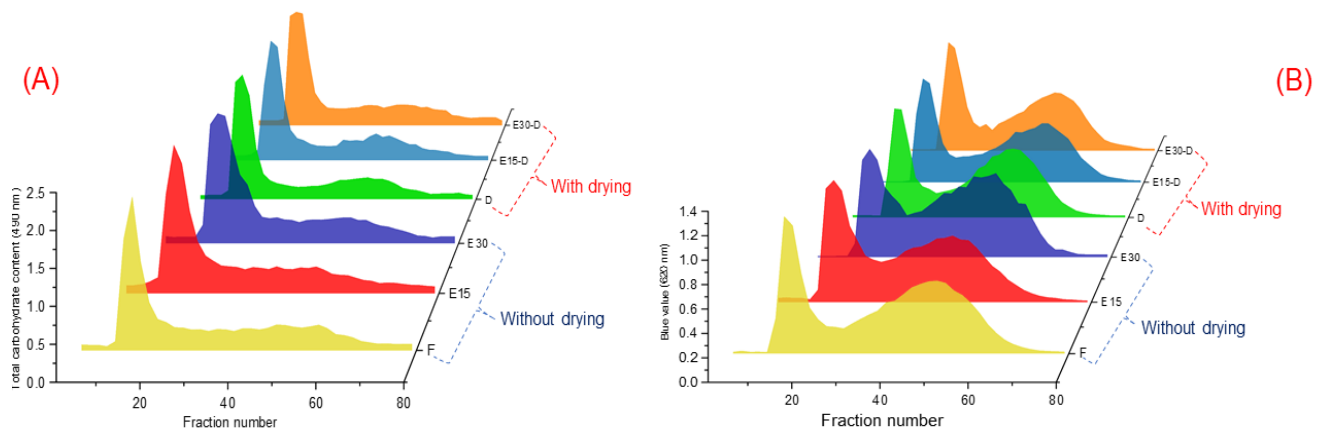
Figure 6. Molecular size distribution profiles of potato starch after different treatments: The first three samples correspond to the starches extracted from potatoes without drying (F, E15, E30) and last three correspond to starches extracted from dried potatoes (D, E15-D, E30-D). After gel permeation chromatography (GPC), the molecular profiles were based on the samples blue value (A) and total carbohydrates (B) techniques.

Starches are organized in structures called granules, which are different in size and shape. Starch granules from tubers are mostly bulky and oval shape with an eccentric hilum, and potato starch has the largest granules of all starches (LIU, 2005). Light microscopy was performed, with and without polarized light, to evaluate starch granule structures. The results are presented in Figure 7.
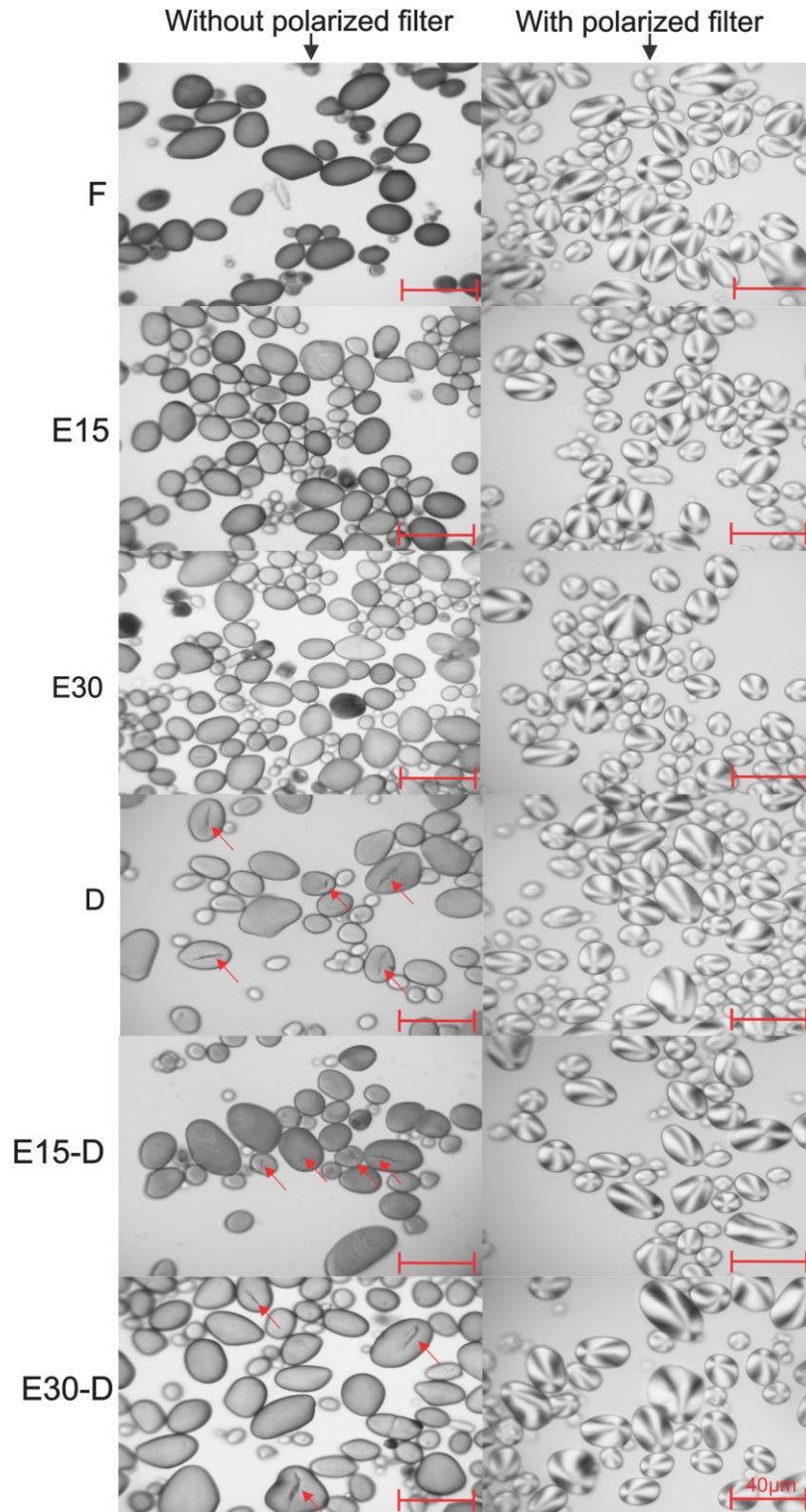
Figure 7. Microscopic images of the potato starch granules extracted before and after drying, without and with polarized filter (left and right column, respectively), and with different pre-treatments: starches extracted from potatoes before drying (F, E15, E30), and starches extracted from dried potatoes (D, E15-D, E30-D). Images from light microscopy, where the red line represents 40 μm. The red arrows indicate granule imperfections.

No changes were observed between starches extracted from potatoes after pre-treatment (E15 and E30) and from fresh potatoes (F). Therefore, apparently, the application of ethanol to the potato slices did not alter the starch granules. This result is different from those reported by Sarifudin et al. (2020), who observed that potato starches had their structure drastically altered when immersed in ethanol in the temperature ranges of 90 °C to 100 °C. However, their work was conducted by immersing the isolated starch into hot ethanol, which is a condition much drastic then the present work. In this work, the potato slices were immersed in ethanol at room temperature, while the starch granules were still protected inside the cells.

Within addition, the mild drying conditions (40 ºC), can also explain the fact that starches extracted from dried potatoes have not undergone major changes in structure (Figure 7 – D, E15-D and E30-D). Even so, some imperfections, as small "scratches", are observed in the granule of starches extracted from dried potatoes. These scratches could indicate that granules started to shrink and crack due to water loss during the drying process. In fact, according to Liu (2005), type B starches (characteristic of potato starch) have a significant amount of water in their crystalline regions, and these granules are expected to shrink and crack during dehydration. Probably what prevent the granules from collapsing was the fact that they were protected inside the potato tissues and the relatively low temperature used for drying.

Using polarized light under microscope, a typical birefringence cross is seen as two intersecting parts, called Maltese Crosses. This indicates there is a radial orientation of the crystallites or there is a high degree of the molecular order within the granules (LIU, 2005). As shown in Figure 7, there were no changes in the granules' Maltese Crosses: all treatments showed a characteristic behavior of potato starch. This indicates that the drying treatment and pre-treatment with ethanol did not cause loss of birefringence of starches – which can indicate the observed imperfections are only superficial. Even so, the starch properties must be assessed in order to evaluate possible applications and also possible limitations of the present approach.

Moreover, the loss of birefringence is an indicator of gelatinization (THOMAS; ATWELL, 1999), thus, no evidence of gelatinization was observed in the present study.

Few studies evaluated starch structure and properties after the vegetable drying. Recently, Duan et al. (2020) conducted different types of drying of Yam: convective drying and microwave freeze drying, also using the ultrasound pre-treatment. The authors reported that convective drying at milder temperatures (40 °C

and 50 °C) did not alter the molecular distribution of starch. However, according to the authors, drying at higher temperatures (60 °C, 70 °C and 80 °C) resulted in molecular degradation. However, the authors did not analyse the granular structure of yam's starch, which could indicate changes in the granules, due to the gelatinization process for example.

Therefore, no changes were observed in the starch granules and molecules. However, the starch properties must also be evaluated.

5.3.2 Starch properties: pasting and gel properties

The starches pasting properties are important evaluation not only to characterize starch samples, but also to illustrate possible changes in modified starches when compared to their native version. The pasting profile of the potato starch sample is shown in Figure 8, and their main parameters are presented in Table 2.
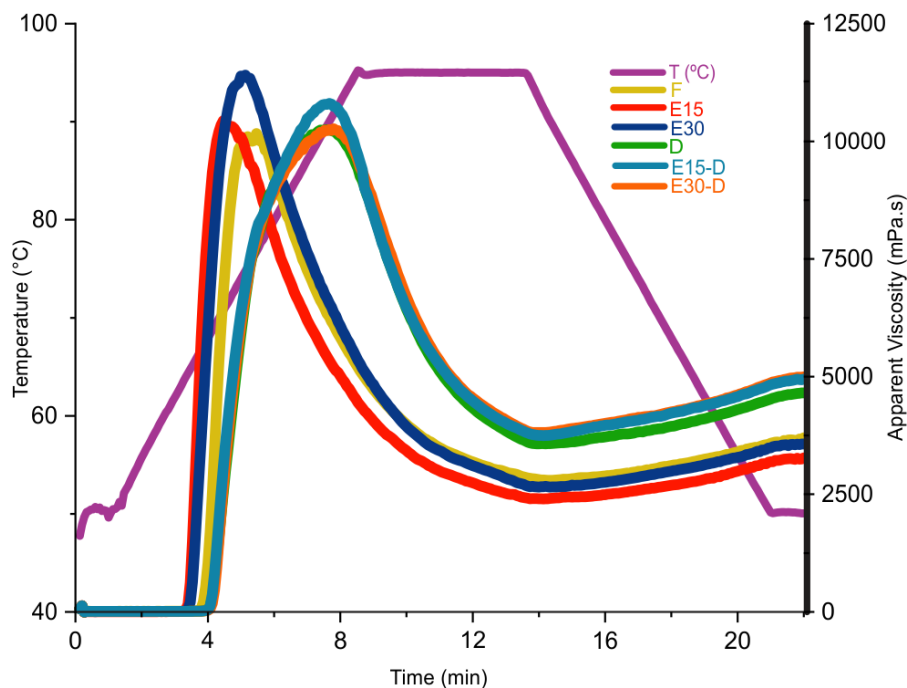

Figure 8. Potato starch pasting: RVA curves obtained from different treatments: starches extracted from potatoes before drying (F, E15, E30), and starches extracted from dried potatoes (D, E15-D, E30-D). Average values.

Table 2 – Pasting properties of potato starch obtained from different treatments (F, E15, E30, D, E15-D and E30-D).

Treatments		PAV (mPa.s)	TAV (mPa.s)	RBD (%)	FAV (mPa.s)	RSB (%)	PT (°C)
Starches obtained from fresh potatoes or after pre-treatments	F	10052 ± 160.0[a]	2793.5 ± 20.5[a]	72.0 ± 0.6[a]	3637.5 ± 70.0[a]	30.2 ± 1.6[a]	66.9 ± 0.8[ac]
	E15-S	10437 ± 157.8[a]	2378 ± 148.9[a]	77.2 ± 1.1[a]	3290 ± 48.8[a]	38.6 ± 7.1[a]	63.8 ± 0.3[b]
	E30-S	11407.5 ± 9.2[a]	2643 ± 70.7[a]	76.8 ± 0.6[a]	3560 ± 7.1[a]	34.7 ± 3.9[a]	64.4 ± 0.0[bc]
Starches obtained after drying	D	10309 ± 299.0[a]	3557 ± 306.0[b]	65.5 ± 2.6[b]	4688 ± 331.0[b]	31.9 ± 2.8[a]	68.9 ± 1.6[a]
	E15	10240 ± 425.0[a]	3812.6 ± 153.4[b]	62.7 ± 2.9[b]	5014 ± 220.4[b]	32.4 ± 4.0[a]	68.6 ± 0.3[a]
	E30	11039 ± 875.0[a]	3770 ± 247.0[b]	65.8 ± 1.6[b]	4982 ± 257.0[b]	32.3 ± 3.3[a]	68.2 ± 0.4[a]

Average ± standard deviations. Different letters represent significant statistical difference ($p < 0.05$) among treatments. Peak Apparent Viscosity (PAV), Trough Apparent Viscosity (TAV), Relative Breakdown (RBD), Final Apparent Viscosity (FAV), Relative Setback (RSB) and Pasting Temperature (PT).

When the starch granules are heated in the presence of water, they absorb water and begin to swell, increasing the consistency of the system. The temperature recorded by the RVA equipment when the apparent viscosity starts to increase is called pasting temperature (PT). When enough granules are swollen, a rapid increase in apparent viscosity occurs. The peak apparent viscosity (PAV) is recorded at the equilibrium point between swelling of granules and leaching of polymers. As the temperature rises further and remains constant, there are granules' rupture, followed by an alignment of the polymers, decreasing the paste apparent viscosity until the called Trough Apparent Viscosity (TAV). This step is known as Breakdown (BD), and this parameter represents the difference between PAV and TAV. Then, as the system is cooled, there is a re-association of the starch molecules, mainly amylose. In sufficient concentration, a gel is formed, and the consistency increases to a final apparent viscosity (FAV). This process is called Setback (SB) and involves the molecular re-association of starch molecules (LIU, 2005).

These parameters are shown in Table 2. The results concerning the fresh (F) and control (D) samples are similar to those reported for potato starch in the literature (CASTANHA; MATTA JUNIOR; AUGUSTO, 2017; LIU et al., 2007; NODA et al., 2005).

The starches extracted after the pre-treatments with ethanol (E15 and E30) showed slightly smaller PT than the other treatments. There was no difference among all treatments regarding PAV value. These results reinforce the hypothesis that the

observed abnormalities in the granules after drying (Figure 7) were not so deep as to break the granules, since if there were deep cracks, it would affect the granule's resistance, affecting the PAV. However, it is necessary to analyze the characteristics of hydrogels to confirm that there were no differences caused by "scratches".

After the rupture of the granules, there is an alignment of the leached polymers, and this alignment is described by parameter breakdown (BD - being calculated through the difference between PAV and TVA). As the BD represents the absolute difference between PAV, and TAV, it must be interpreted carefully, being more appropriated the evaluation of the Relative Breakdown - calculated from the BD difference and the PAV values (CASTANHA; MATTA JUNIOR; AUGUSTO, 2017). In this work, the starches obtained from dried potatoes have lower RBD values, due to higher TAV values (p < 0.05).

The results indicate the paste obtained from dried potatoes are slightly more consistent than those obtained from potatoes without drying (in special due to the FAV parameter). Low FAV and RSB could indicate a low rate of starch retrogradation (SHAFIE et al., 2016). Although no major differences were observed on starch granules nor molecules, this can suggest the molecules could have a difference tendency to align. This could also indicate stronger gels. However, the gel properties must also be evaluated, as discussed as follows, once the results obtained from RVA only described a partial alignment (it is important to remember that FAV is measured at 50 °C).

These results differ from those described by Duan et al. (2020), in which the pasting properties of starches obtained from dried yams differ widely from the fresh vegetable. Despite being a starch different from potato starch, an important step in Duan et al. (2020) work can influenced their results: prior to drying, their samples were blanched in boiling water, which can affect starch and their pasting properties. Therefore, a direct comparison cannot be carried out.

After obtaining the gels in the RVA, they were stored under refrigeration for 24 h: this time is necessary for the molecules to re-associate, forming the hydrogel. The firmness of the obtained potato starch gels is shown in Figure 9. No differences (p< 0.05) were observed among the starches obtained from dried potatoes (D, E15-D and E30-D) and the starch obtained from fresh potatoes (F) – possibly due to the high standard deviations. Even so, a tendency of stronger gels from dry potatoes is

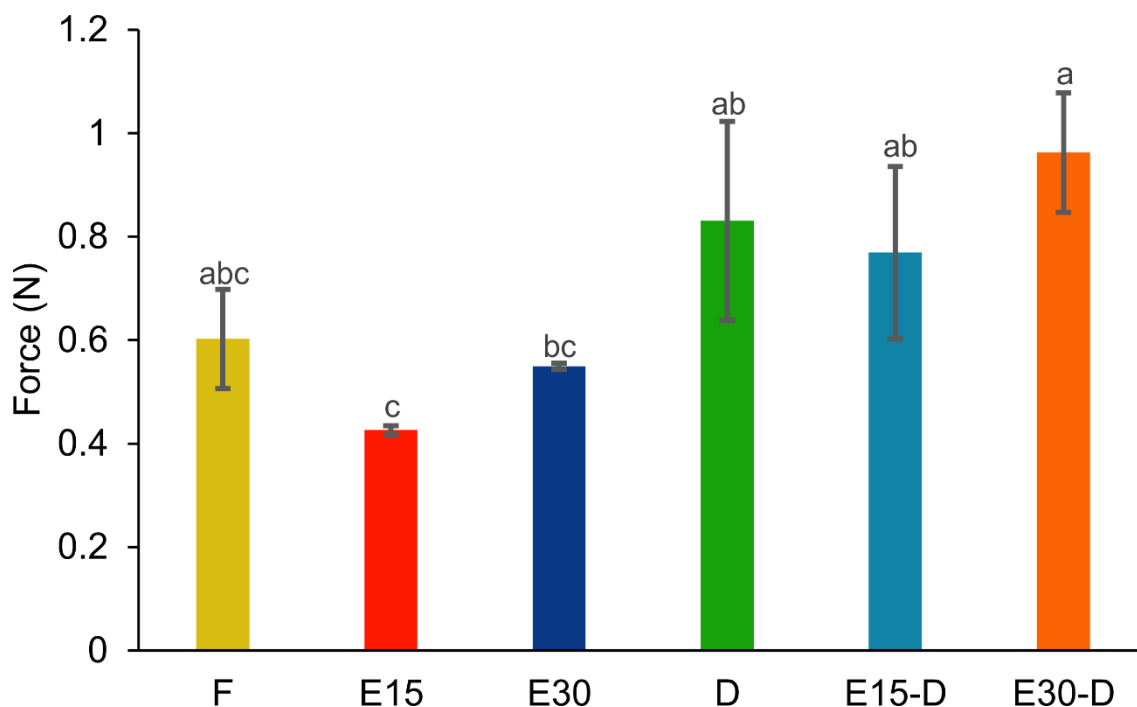observed – for instance, the treatment E30-D is stronger than the F potatoes by considering $p < 0.10$.

Figure 9. Gel firmness from the starches extracted from potatoes before drying (F, E15, E30), and starches extracted from dried potatoes (D, E15-D, E30-D). Different letters represent significant statistical difference ($p < 0.05$) among treatments.

Once any important difference was observed in starch molecules (Figure 7), the observed trend (slightly stronger gels and pastes from starches obtained from dried potatoes) can be possibly associated with the remained ghosts. The starch ghosts are defined as gelatinized starch granule envelopes after the majority of internal starch polymers have been released, being associated with the traces of protein bounded in granules and influencing pasting and gel properties (HAN; HAMAKER, 2002). Therefore, probably it is not only coincidence a correlation between the superficial imperfection in dried granules (Figure 7) and the trend for stronger gels (Figure 9).

Similarly, there were also no differences between starches obtained after pre-treatment (E15 and E30) in relation to fresh potatoes (F, $p > 0.10$), although a tendency of weaker gels are suggested for the starches obtained after pre-treatment in relation to those obtained from dried potatoes.

Even though, the obtained result is interesting since both behaviors would be interesting from an industrial perspective: obtaining starches with any difference from

the control or obtaining stronger gels. This makes drying an option for preserving potatoes whose starch would be used with application in gels.

In summary, drying showed some effects on the starch granule surface and in some pasting properties parameters. However, these effects were small, and did not changed the overall starch properties profile. Consequently, the proposed treatments can be used to prolonging the stability of potatoes tubers, without impacting their starch properties.

6. CONCLUSIONS

In the present study, convective drying was proposed to extend the shelf life of potatoes focused on the subsequently starch extraction. Pre-treatments with ethanol were carried out for 15 and 30 min. Then, the drying kinetics, rehydration and starch structure and properties were studied.

Firstly, we observed the ethanol pre-treatment reduced the drying time up to 55%. No crust formation (defects in the drying process) was observed in the treatments (D, E15-D and E30-D).

There were no changes in the starch molecular profile of the obtained starches. However, "scratches" were observed in the starch granules obtained from dried potatoes. Even so, there were no changes in the Maltese cross, indicating that there was no gelatinization during drying.

Pasting and gel properties indicated small variation between dried potato starches and that from fresh and pre-treated samples, indicating that drying had little effect on starch properties. However, the observed differences were very small and did not changed the overall starch properties profile.

This result is highly interesting, as it indicates that drying using ethanol pre-treatment can be used to accelerate convective drying process and extend the shelf life of potatoes without impact their starch.

We conclude by confirming the hypothesis presented at the beginning of this study: convective drying of potato slices with ethanol pre-treatment did not change the structural and starch gel properties and it is a possibility of preservation of this raw material.

7. SUGGESTIONS FOR FUTURE RESEARCH

In future research, other starch sources, drying techniques and pre-treatments must be evaluated. Each starch source and drying approach has specific characteristics, the study of different raw materials can provide better understand about the correlation of mechanisms of mass transfer and starch properties.

REFERENCES

ALVANI, K. et al. Physico-chemical properties of potato starches. **Food Chemistry**, v. 125, n. 3, p. 958–965, 1 abr. 2011.

BERTOFT, E. Analysing starch Molecular structure. In: SJOO, M.; NILSSON, L. (Eds.). . **Starch in food: Structure, function and applications**. Second edi ed. Finland: 2004. p. 916.

CANTERI, M. H. G. et al. ATR-FTIR spectroscopy to determine cell wall composition: Application on a large diversity of fruits and vegetables. **Carbohydrate Polymers**, v. 212, p. 186–196, 15 maio 2019.

CASTANHA, N.; MATTA JUNIOR, M. D. DA; AUGUSTO, P. E. D. Potato starch modification using the ozone technology. **Food Hydrocolloids**, v. 66, p. 343–356, 1 maio 2017.

CHEN, X. D. Food drying fundamentals. In: DONG CHEN, XIAO AND MUNJUMBAR, A. S. (Ed.). . **Drying Technology in Food Processing**. 1 edition ed. Ansari Road, Daryaganj, New Delhi: Wiley-Blackwell, 2014. p. 322.

CHEN, X. D.; PATEL, K. C. Biological change during food drying process. In: CHEN, X. D.; MUJUMDA, A. S. (Eds.). . **Drying Technology in Food Processing**. Oxford: Blackwell Publishing Ltd, 2008. p. 93.

CHOU, S. K.; CHUA, K. J. New hybrid drying technologies for heat sensitive foodstuffs. **Trends in Food Science and Technology**, v. 12, n. 10, p. 359–369, 1 out. 2001.

COPELAND, L. et al. Form and functionality of starch. **Food Hydrocolloids**, v. 23, n. 6, p. 1527–1534, 1 ago. 2009.

CORRÊA, J. L. G. et al. The Influence of Ethanol on the Convective Drying of Unripe, Ripe, and Overripe Bananas. **Drying Technology**, v. 30, n. 8, p. 817–826, jun. 2012.

DERMESONLOUOGLOU, E.; CHALKIA, A.; TAOUKIS, P. Application of osmotic dehydration to improve the quality of dried goji berry. **Journal of Food Engineering**, v. 232, p. 36–43, 1 set. 2018.

DUAN, X. et al. Drying treatments on Chinese yam (Dioscorea spp.) prior to wet milling influence starch molecular structures and physicochemical properties. **Food Hydrocolloids**, v. 102, p. 105599, 1 maio 2020.

DUBOIS, M. et al. Colorimetric Method for Determination of Sugars and Related Substances. **Analytical Chemistry**, v. 28, n. 3, p. 350–356, 1 mar. 1956.

FENG, Y. et al. Improvement of the catalytic infrared drying process and quality characteristics of the dried garlic slices by ultrasound-assisted alcohol pretreatment. **LWT**, v. 116, p. 108577, 1 dez. 2019.

FUNEBO, T. et al. Microwave and convective dehydration of ethanol treated and frozen apple - physical properties and drying kinetics. **International Journal of Food Science and Technology**, v. 37, n. 6, p. 603–614, 1 ago. 2002.

GIRI, S. K.; PRASAD, S. Drying kinetics and rehydration characteristics of microwave-vacuum and convective hot-air dried mushrooms. **Journal of Food Engineering**, v. 78, n. 2, p. 512–521, jan. 2007.

GROMMERS, H. E.; KROGT, D. A. VAN. Potato Starch: Production, modifications and uses. In: BEMILLER, J.; WHISTLER, R. (Eds.). . **Starch: Chemistry and Technology**. Trird ed. 2009. p. 212–239.

HAN, X.-Z.; HAMAKER, B. R. Association of Starch Granule Proteins with Starch Ghosts and Remnants Revealed by Confocal Laser Scanning Microscopy. **Cereal Chemistry Journal**, v. 79, n. 6, p. 892–896, nov. 2002.

JOBLING, S. Improving starch for food and industrial applications. **Current Opinion in Plant Biology**, v. 7, n. 2, p. 210–218, 1 abr. 2004.

JULIANO, B. O. A simplified assay for millied-rice amylose. **Cereal Foods World**, 1971.

LIU, Q. Understanding Starches and Their Role in Foods. In: CUI, S. W. (Ed.). . **Food carbohydrates : chemistry, physical properties, and applications**. Boca Raton, FL: 2005. p. 309–349.

LIU, Q. et al. Physicochemical properties of dry matter and starch from potatoes grown in Canada. **Food Chemistry**, v. 105, n. 3, p. 897–907, 1 jan. 2007.

LLAVATA, B. et al. Innovative pre-treatments to enhance food drying: a current review. **Current Opinion in Food Science**, v. 35, p. 20–26, 1 out. 2020.

MARTÍNEZ, P. et al. Physicochemical, functional and morphological characterization of starches isolated from three native potatoes of the Andean region. **Food Chemistry: X**, v. 2, p. 100030, 30 jun. 2019.

MORAES, F. DE. Redução da atividade de água. In: AUGUSTO, P. E. D. (Ed.). . **Principíos de tecnologia de alimentos**. 1. ed. Rio de Janeiro: 2018. p. 409.

MUJUMDAR, A. S.; DEVAHASTIN, S. FUNDAMENTAL PRINCIPLES OF DRYING. In: **Guide to Industrial Drying: Principles, Equipments & New Developments**. 3 rd ed. 2004. p. 349.

NODA, T. et al. Physicochemical properties and amylopectin structures of large, small, and extremely small potato starch granules. **Carbohydrate Polymers**, v. 60, n. 2, p. 245–251, 6 maio 2005.

PAGE, G. E. **Factores ingluencing the maximum rates of air drying shelled corn in thin layers**. [s.l.] Purdue University, 1949.

PANDEY, O. P.; MISHRA, B. K.; MISRA, A. Comparative study of green peas using with blanching & without blanching techniques. **Information Processing in Agriculture**, v. 6, n. 2, p. 285–296, 1 jun. 2019.

PELEG, M. **An Empirical Model for the Description of Moisture Sorption CurvesJournal of Food Science**, 1988.

RATTI, C. **Hot air and freeze-drying of high-value foods: A reviewJournal of Food Engineering**Elsevier Ltd, , 2001.

ROJAS, M. L.; AUGUSTO, P. E. D. Ethanol pre-treatment improves vegetable drying and rehydration: Kinetics, mechanisms and impact on viscoelastic properties. **Journal of Food Engineering**, v. 233, p. 17–27, 1 set. 2018a.

ROJAS, M. L.; AUGUSTO, P. E. D. Ethanol and ultrasound pre-treatments to improve infrared drying of potato slices. **Innovative Food Science and Emerging Technologies**, v. 49, p. 65–75, 1 out. 2018b.

ROJAS, M. L.; AUGUSTO, P. E. D.; CÁRCEL, J. A. Ethanol pre-treatment to ultrasound-assisted convective drying of apple. **Innovative Food Science and Emerging Technologies**, v. 61, p. 102328, 1 maio 2020.

ROJAS, M. L.; SILVEIRA, I.; AUGUSTO, P. E. D. Improving the infrared drying and rehydration of potato slices using simple approaches: Perforations and ethanol. **Journal of Food Process Engineering**, n. February, p. 1–7, 2019.

ROJAS, M. L.; SILVEIRA, I.; AUGUSTO, P. E. D. Ultrasound and ethanol pre-treatments to improve convective drying: Drying, rehydration and carotenoid content of pumpkin. **Food and Bioproducts Processing**, v. 119, p. 20–30, 1 jan. 2020.

SAGUY, I. S.; MARABI, A.; WALLACH, R. New approach to model rehydration of dry food particulates utilizing principles of liquid transport in porous media. **Trends in Food Science and Technology**, v. 16, n. 11, p. 495–506, 1 nov. 2005.

SANTOS, P. H. S.; SILVA, M. A. Kinetics of L-ascorbic acid degradation in pineapple drying under ethanolic atmosphere. **Drying Technology**, v. 27, n. 9, p. 947–954, 18 ago. 2009.

SARIFUDIN, A. et al. Pore characteristics and structural properties of ethanol-treated starch in relation to water absorption capacity. **LWT**, p. 109555, 10 maio 2020.

SHAFIE, B. et al. Characterization and classification of whole-grain rice based on rapid visco analyzer (RVA) pasting profile. **International Food Research Journal**, v. 23, n. 5, p. 2138–2143, 2016.

SHI, J.; LE MAGUER, M. OSMOTIC DEHYDRATION OF FOODS: MASS TRANSFER AND MODELING ASPECTS. **Food Reviews International**, v. 18, n. 4, p. 305–335, 31 dez. 2002.

SILVA, M. A.; BRAGA, A. M. P.; SANTOS, P. H. S. Enhancement of fruit drying: the ethanol effect. **Proceedings of the 18th International Drying Symposium (IDS 2012)**, November, p. 11–15, 2012.

SILVA, M. G.; CELEGHINI, R. M. S.; SILVA, M. A. Effect of ethanol on the drying characteristics and on the coumarin yield of dried guaco leaves (Mikania laevigata schultz BIP. Ex Baker). **Brazilian Journal of Chemical Engineering**, v. 35, n. 3, p. 1095–1104, 1 jul. 2018.

SIMPSON, R. et al. Understanding the success of Page's model and related empirical equations in fitting experimental data of diffusion phenomena in food matrices. **Trends in Food Science and Technology**, v. 62, p. 194–201, 1 abr. 2017.

SONG, Y.; JANE, J. Characterization of barley starches of waxy, normal, and high amylose varieties. **Carbohydrate Polymers**, 2000.

TAO, Y. et al. Applications of water blanching, surface contacting ultrasound-assisted air drying, and their combination for dehydration of white cabbage: Drying mechanism, bioactive profile, color and rehydration property. **Ultrasonics Sonochemistry**, v. 53, p. 192–201, 1 maio 2019.

TATEMOTO, Y. et al. Drying characteristics of food materials injected with organic solvents in a fluidized bed of inert particles under reduced pressure | Kopernio. **Journal of Food Engineering**, v. 158, p. 80–85, 2015.

THOMAS, D. J.; ATWELL, W. A. Starch analysis Methods. In: PRESS, E. (Ed.). **Starches**. Minnesota: 1999. p. 94.

THOMSON, J. XLII. On certain curious motions observable at the surfaces of wine and other alcoholic liquors . **The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science**, v. 10, n. 67, p. 330–333, nov. 1855.

VASANTHAN, T. et al. Starch from Alberta potatoes: Wet-isolation and some physicochemical properties. **Food Research International**, v. 32, n. 5, p. 355–365, 1 jun. 1999.

WANG, Q.; CUI, S. W. Understanding the Physical Properties of Food Polysaccharides. In: CUI, S. W. (Ed.). . **Food carbohydrates : chemistry, physical properties, and applications**. 1 st ed. Boca Raton, FL: 2005. p. 432.

WANG, X. et al. Effect of vacuum and ethanol pretreatment on infrared-hot air drying of scallion (Allium fistulosum). **Food Chemistry**, v. 295, p. 432–440, 15 out. 2019.

APPENDIX A. Simple abstract / Resumo simples / Resumen sencillo

Simple Abstract (English)

Starch is a very important natural ingredient for several industries. Some roots and tubers, such as potatoes and cassava, are source of starch, but these vegetables are high perishable due to high water content. Processing can be an alternative to increase stability, such as using drying. However, drying requires long time at high temperatures, which can negatively impact the starch quality. In this work, ethanol was used as a simple pre-treatment prior to drying of potatoes. Our results showed that drying process was improved with the application of ethanol, without negative impact on starch properties. Consequently, our proposal is a simple and effective method to preserve potatoes, avoiding degradation and increasing value added by obtaining starch.

Resumo simples (Português)

O amido é um ingrediente muito importante para diversas indústrias. Algumas raízes e tubérculos, como a batata e a mandioca, são fonte de amido, mas esses vegetais são altamente perecíveis devido ao alto teor de água. O processamento, como a secagem, pode ser uma alternativa para aumentar a estabilidade desses vegetais. Entretanto, a secagem requer muito tempo em altas temperaturas, o que pode impactar negativamente a qualidade do amido. Neste trabalho, o etanol foi utilizado como um pré-tratamento simples antes da secagem de batatas. Nossos resultados mostraram que a secagem foi melhorada com a aplicação de etanol, sem impacto negativo nas propriedades do amido.Consequentemente, nossa proposta é um método simples e eficaz de conservar a batata, evitando a degradação e aumentando o valor agregado com a obtenção do amido.

Resumen sencillo (Español)

El almidón es un ingrediente natural muy importante para varias industrias. Algunas raíces y tubérculos, como las papas y la yuca, son fuente de almidón, pero estos vegetales son muy perecederos debido al alto contenido de agua. El procesamiento puede ser una alternativa para aumentar la estabilidad, como uso del secado. Sin embargo, el secado requiere mucho tiempo a altas temperaturas, lo que puede afectar negativamente la calidad del almidón. En este trabajo, se utilizó etanol como un pretratamiento simple antes del secado de las papas. Nuestros resultados mostraron que el proceso de secado se mejoró con la aplicación de etanol, sin impacto negativo en las propiedades del almidón. En consecuencia, nuestra propuesta es un método simple y efectivo para conservar la papa, evitando su degradación y aumentando el valor agregado mediante la obtención de almidón.