Assessment of bioactive compounds and antioxidant activity of wine residues submitted to intermittent drying process

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Abstract

During wine production a large amount of waste (grape pomace) is generated. This material is considered a rich source of bioactive compounds, thus being of interest for cosmetics, pharmaceutical and food industries. However, it is susceptible to microbial degradation due to its high moisture content, and therefore drying is frequently considered an essential process for grape pomace conservation and stabilization. Nevertheless, drying conditions such as temperature and time may affect grape pomace bioactive potential. Because drying represents a high energy consumption, an alternative for reducing the energy costs is the use of intermittent operation, which operates with transient inputs of air conditions, such as the supply temperature. Intermittent drying, in addition to promoting lower energy consumption, also enables less damage to heat-sensitive materials. In the present work, modeling of the drying process of grape skins and seeds from red wine grape pomace was performed at temperatures of 40 °C, 55 °C and 70 °C, both for drying in the conventional and in the intermittent mode, with intermittences of 5 and 10 minutes. Moreover, total phenolics content (TPC), total flavonoids content (TFC) and antioxidant activity (DPPH and reducing power assays) were determined by spectrophotometric methods before and after the drying process at the proposed conditions. The identification and quantification of phenolic compounds (non-anthocyanins and anthocyanins) was carried out through LC-DAD-ESI-MS/MS analysis. Modeling results showed that, among the 8 models tested for the conventional drying, the one that best suited the experimental data, for both skin and seeds, was the Approximation of diffusion model and therefore can be used in following studies to optimize drying parameters. For the intermittent drying, experimental data could be predicted by the intermittent drying model with a global maximum deviation of 10%. Results of TPC, TFC and antioxidant activity assays showed that conventional drying had the highest impact on lowering the content of bioactive compounds both on grape skins and seeds. By the contrary, the present work showed that intermittent drying can provide grape pomace samples with higher content of bioactive compounds and higher antioxidant activity, with 10 minutes intermittence in general performing best when compared to 5 minutes intermittent period, particularly for grape seeds pomace samples.

Keywords: Intermittent drying, Modeling, Grape pomace, By-products valorization.

Resumo

Durante a produção do vinho, uma grande quantidade de resíduos (bagaço de uva) é gerada. Este material é considerado uma rica fonte de compostos bioativos, sendo de interesse para diversas indústrias. No entanto, o mesmo é suscetível à degradação microbiana devido ao seu alto teor de humidade e, portanto, a secagem é frequentemente considerada um processo essencial para a sua conservação e estabilização. No entanto, as condições de secagem, podem afetar o potencial bioativo do material. Como a secagem representa um alto consumo de energia, uma alternativa para redução dos custos é a utilização de operação intermitente, que, além de promover menor consumo de energia, possibilita menos danos aos materiais termossensíveis. No presente trabalho a modelação do processo de secagem de cascas e sementes de uva de vinho tinto foi realizada para temperaturas de 40°C, 55°C e 70°C, tanto para secagem no modo convencional quanto no modo intermitente, com intermitências de 5 e 10 minutos. Além disso, o teor de compostos fenólicos totais, o teor de flavonóides totais e a atividade antioxidante (ensaios de DPPH e poder redutor) foram determinados por métodos espectrofotométricos antes e após o processo de secagem. A identificação e quantificação dos compostos fenólicos (não-antocianinas e antocianinas) foram realizadas por LC-DAD-ESI-MS/MS. Os resultados da modelação mostraram que, para a secagem convencional, o que mais se adequou aos dados experimentais, tanto para a casca quanto para sementes, foi o modelo de Aproximação de difusão e, portanto, pode ser utilizado em estudos posteriores para otimizar os parâmetros do processo. Para a secagem intermitente, os dados experimentais puderam ser previstos pelo modelo de secagem intermitente com um desvio máximo global de 10%. Os resultados dos ensaios de compostos fenólicos, flavonoides e atividade antioxidante mostraram que a secagem convencional teve o maior impacto na redução do conteúdo de compostos bioativos tanto na casca como na semente da uva. O presente trabalho mostrou que a secagem intermitente pode fornecer amostras de bagaço de uva com maior teor de compostos bioativos e maior atividade antioxidante, com a intermitência de 10 minutos demonstrando em geral melhor desempenho quando comparada ao período intermitente de 5 minutos, principalmente para amostras de sementes de uva.

Palavras-chave: Secagem Intermitente, Modelação, Bagaço de uva, Valorização de Subprodutos.

Sumarry

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Abbreviations

HPLC..... Hich Performance Liquid Chromatography

UV-Vis. .....UV-Visible

DAD ..... Diode Array Detector

MS. .....Mass Spectometry

DPPH..... Radical 2,2-diphenyl-1-picryl-hydrazil

Pvs. ..... Vapor Pressure(kPa)

W. .....Mixing Ratio (%)

Y. ..... Moisture Content on Dry Basis (%)

y. .....Moisture Content on Wet Basis (%)

Yabs .....Absolute Moisture ($g/m^{3)}$

MR .....Moisture Ratio (g_{wv}/g_{da})

p.....Pressure of water vapor in the air (kPa)

ps .....Saturation Pressure (kPa)

t.....Time (min)

T_{exp} ..... Temperature at the outlet of the experimental heater (°C)

T_{cal} ..... Temperature estimated by the models (°C)

$\dot{Q}$ .....Heat exchange performed (W)

$\dot{W}$ .....Work rate of the system (J)

$\dot{m}_i$ ..... Mass rates entering the system (g/min)

$\dot{m}_o$ .....Mass rates leaving the system (g/min)

$\frac{mv_i^2}{2}$ .....Kinetic Energy of the system's input (J)

$\frac{mv_o^2}{2}$ .....Kinetic Energy of the system's output (J)

mgz_i .....Potencial Energy of the system's input (J)

mgz_o .....Potencial Energy of the system's output (J)

A_s ..... Surface Area (m^2)

T ..... Temperature of the sample (°C)

T_{room} ..... Room Temperature (°C)

m_{sample} .....Mass of the material(g)

c_p ..... Heat Capacity of the sample at constant pressure (mPa.s)

ΔT .....Temperature Variation of the material (°C)

m_{sample} ..... Sample's mass (g)

m_{dry} .....Mass of the dry material (g)

χ^2 .....Reduced chi-square (abs)

$RMSE$ .....Root-Mean Square Error (abs.)

EF .....Efficiency of the model (abs.)

No .....Number of Observations (abs.)

Nc ..... Number of Model's Constants (abs.)

NMSE.....Normalized Mean Square Error (abs.)

MSE..... Mean-Square Error (abs.)

TFC..... Total Flavonoids Content (mg_{ce}/g_{dr})

TPC..... Total Phenolic Content (mg_{GAE}/g_{dr})

RP ..... Reducing Power (EC_{50})

1 Introduction

The wine industry is a worldwide consolidated business. One of the leading producers and exporters of this product is Portugal, which is the 8th largest wine exporter in the world, with an approximate revenue of 778,7 million euros in the year of 2017 (Beres et al., 2017).

However, in the winemaking process a large amount of waste is obtained. For every 100 liters of wine produced 31,7 kilograms of waste are generated, which includes skins, stems and seeds (Campos, 2005). The grape pomace, if not properly disposed, represents a potential environmental problem and is often used as an undervalued product, namely as fertilizers or as animal food (Silva et al., 2018). Another option is the use of those residues for the production of ethanol or grape oil, which stands out for being a rich source of phenolic compounds, known for their antioxidant, anti-aging, anti-inflammatory and anti-microbiological capabilities. Therefore, the use of this by-product by the food, cosmetics and pharmaceutical industries has been growing over the last years (Carmona et al., 2018).

A recurring problem is the storage of grape pomace, which easily degrades due to its high moisture content, thus frequently requiring the use of the drying process. Moreover. the by-product must be also stabilized before extracting the compounds of interest and, to this end, drying is the most commonly used process. Drying stabilizes the raw material by reducing the moisture content present inside the material, decreasing the available water and, consequently, reducing the proliferation of fungi and bacteria, as well as internal reactions that degrade its quality (Defendi et al., 2016). In the case of oil extraction, it also decreases the amount of solvent used in the subsequent extraction processes (Kajihara et al., 2013).

Conventionally, drying is performed by subjecting the material to the drying air under fixed drying conditions, such as temperature and air flow rate, until it reaches the desired moisture content. However, it is estimated that drying accounts for about 60% or more of the energy costs involved in the entire agro-food production process (Silva et al., 2000). This is because this process requires high heat and mechanical energy for heating and drying air movement (Defendi, 2015).

An alternative for reducing the energy costs of the drying process is the use of intermittent operation, which operates with transient inputs of air conditions, such as the

supply temperature. Intermittent drying, in addition to promoting lower energy consumption, also enables less damage to heat-sensitive materials, being beneficial for products in which internal moisture diffusion is the prevalent phenomenon that controls drying rates (Chua et al., 2003). Most agricultural products have internal water diffusion as the phenomenon that controls drying rates, a factor that can be observed by decreasing rates since the beginning of the process (Defendi et al., 2016).

The fact that intermittent drying is less aggressive to the material to be dried, directly affects the levels of phenolic compounds as well as the antioxidant activity of grape pomace (Carmona et al., 2018). These compounds are sensitive to high temperatures and can easily be degraded if proper care is not taken during process application. Some authors found that at temperatures below 60 °C the phenolic content did not change significantly, but at higher temperatures the levels of these compounds decreased abruptly (Carmona et al., 2018). However, other authors realized that from the temperature of 45 °C there was already a decrease in the levels of phenolic compounds (Rajah et al., 2014; Silva et al.,2016). In contrast, other authors have reported that exposure of material to high temperatures for short periods of time may increase the level of phenolic compounds. The inconsistency in the results found in these and other studies demonstrates the need for a deeper investigation of this subject. In this sense, mathematical modeling is an essential tool, since it aims to predict the behavior of the material in relation to the drying conditions imposed on it. It can help engineers and researchers select and optimize drying conditions, thus being extremely important for minimizing energy consumption and, simultaneously, to decrease the quality degradation of the dried material (Xu et al., 2017).

2 State of the art

2.1 Wine and by-products production

Grape is one of the most cultivated foods in the world, having represented in 2016 a production of about 77 million tons. It is an extremely versatile food as it can be consumed raw, dried, as ingredient in different dishes or used for the manufacture of derived products, such as wine and juices. Most of this production is, however, directed to wine production, with world production being about 27 billion liters per year (Amyenio et al., 2014). The three main wine producers in 2014 were France, Italy and Spain, respectively (FAOSTAT, 2014) (Fig.1).

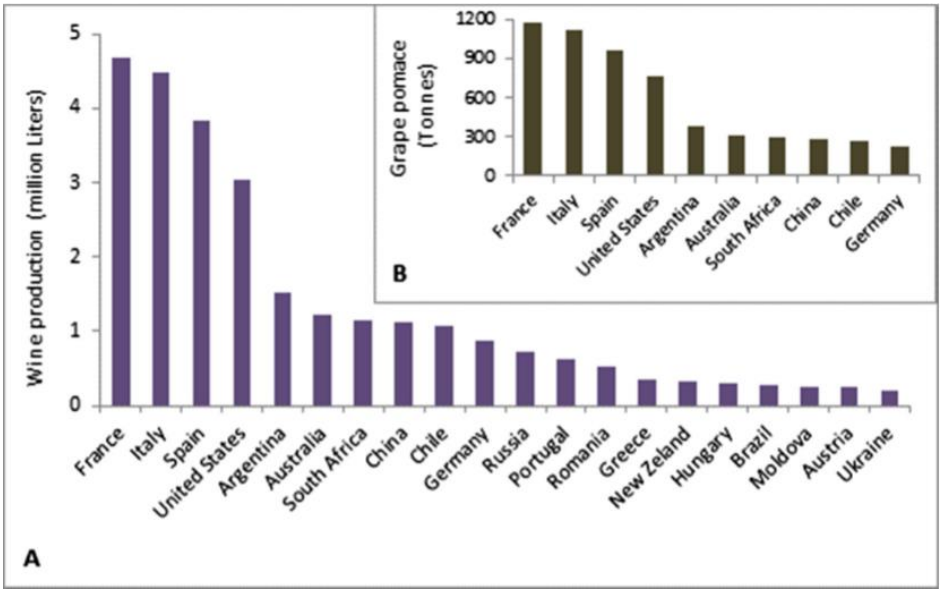


Fig.1. Production of wine around the world (adapted from Beres et al., 2017).

The amount of produced winery by-products depends on several factors, such as the pressing process and the variety of used grape, as well as the fermentation steps. By weight, grape pomace represents about 20-30% of grapes, being basically made up of peels, seeds and stems (Dwyer et al, 2014). This by-product is often portrayed as an environmental problem due to its negative impact when incorrectly disposed and is often used as a fertilizer or animal feed (Silva et al., 2018).

However, grape pomace is rich in phenolic compounds, which are associated with significant bioactive properties, in particular antioxidant activity. Previous studies showed that approximately 70% of phenolic content is preserved in grape pomace after processing (González-Centeno et al, 2010; Dwyer et al, 2014). These data represent a

great potential for the use of grape pomace in the food industry as a food supplement, as well as in the pharmaceutical and cosmetics industries (Carmona et al., 2018).

According to Campos (2005), among the compounds with antioxidant properties found in grape pomace, one of the main and most relevant is resveratrol, a polyphenol also present in red wine. Its antioxidant activity protects blood cholesterol from oxidation, slowing and minimizing the atherosclerosis process. In addition, resveratrol inhibits lipid peroxidation and decreases the risk of heart and hyperlipidemic diseases. This compound has also been described to have anti-inflammatory effects and to act against cancer and the formation of wrinkles (Campos, 2005). Besides phenolic compounds, grape pomace is also rich in other interesting compounds such as linoleic acid, which is an essential fatty acid that has important functions in the body (Campos, 2005).

Figure 2 shows the composition, in different fractions, of grape pomace divided into seedless pomace (containing residual pulp, skin and stems) and seeds. The seedless pomace is rich in fiber and phenolic compounds, mainly anthocyanins, which are known for their antioxidant capacity. The seeds, besides being rich in fiber and flavonols, another type of phenolic compounds, also enable the extraction of oil, which is rich in unsaturated fatty acids and phenolic compounds (Bail et al, 2008; Hanganu et al, 2012).

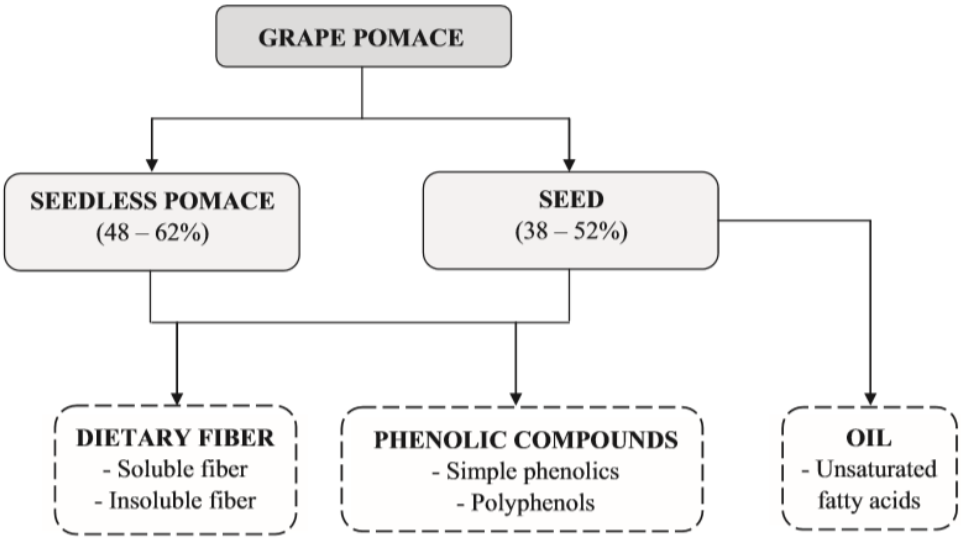


Fig.2. Composition of grape pomace (adapted from Beres et al., 2007)

2.1.1 Phenolic compounds

According to Haminiuk et al. (2012) phenolic compounds represent one of the most important, numerous and well distributed groups in the plant kingdom. So far, different phenolic compounds have been shown to have several bioactive properties including antioxidant, antimicrobial, anti-allergic, anti-inflammatory properties, among many others that are often associated with health benefits, through the consumption of fruits and vegetables.

Red wine is a known source of phenolic compounds, however only 30-40% of the phenolic compounds are extracted during the wine production process, depending on the type of grape and the method used for extraction. Therefore, there is still a high amount of phenolic compounds remaining in the wine by-products, especially in grape pomace (Ky et al., 2014).

Phenolic compounds are widely distributed within the different grape components, with the concentration on the skins, seeds, pulp and stems depending on the variety of grape but also on the edaphoclimatic factors (climate, soil, etc.) affecting the vineyards each year. Despite these variations, normally, there are about 10% or less of the extractable phenolic compounds in the pulp, 60-70% in the seeds and 28-35% in the skins (Shi et al., 2003).

Rockenbach et al. (2011) observed higher concentrations of phenolic compounds in the seeds than in the skins for all grape varieties studied. The authors also observed that the higher the levels of total phenolic compounds, the greater the antioxidant activity. This is in good agreement with previous studies demonstrating that, usually, the level of total phenolic compounds is associated with the by-product's antioxidant properties (Peixoto et al., 2018; Silva et al., 2018).

One of the most used methods for determining total phenolic compounds is the Folin-Ciocalteau spectrophotometric method, which is based on oxidation-reduction reactions between phenolic compounds and metal ions. In a first stage, the extraction of the compounds to be tested is carried out, with the main objective of obtaining a complete extraction. Then, the Folin-Ciocalteau reagent is reduced by the phenolic compounds extracted from the samples, forming a blue complex. In the end, a spectrophotometric analysis allows the quantification of the phenolic compounds based on the use of a calibration curve, generally obtained using gallic acid (Silveira, 2013).

In order to determine the profile of phenolic compounds, in turn, chromatographic methodologies are usually used. This aims at the individual separation of several constituents of a mixture, whether it is intended to identify, quantify or simply obtain a pure substance. This separation occurs by passing a mixture through a stationary phase, having a fluid (designated as the mobile phase) as a medium, knowing that these two will be miscible (Kenndler, 2004).

Among the different types of chromatography, high performance liquid chromatography (HPLC) is the most relevant one for the analysis of phenolic compounds. In this technique the mobile phase is liquid under pressure, passing through a column that contains a stationary phase, being an efficient and fast process (Silveira, 2013). For the detection and identification of the eluted compounds, different detectors can be used, such as refractive index, fluorescence, UV-Visible (UV-Vis), and diode array detector (DAD). The latter has advantages over UV-Vis, since it allows to monitoring all wavelengths simultaneously and the selection of the best for each of the compounds under analysis, increasing the sensitivity of the system. On the other hand, the UV-Vis detector only allows the selection of a single wavelength, which may not be suitable for all compounds (Silveira, 2013). Nevertheless, for the analysis of phenolic compounds in particular, the use of mass spectrometry (MS) detectors coupled to liquid chromatography has been considered as a pivotal tool since it combines the separation capacity of the chromatographic technique with the selectivity and sensitivity of MS allowing for the identification of compounds.

2.1.2 Antioxidant Activity

There are several methods to assess, *in vitro*, the antioxidant activity of biologically active substances, ranging from chemical tests with lipid substrates to more complex tests using cells or tissues and the most diverse instrumental techniques. According to Carocho et al. (2013), no single method can provide unequivocal results, with the use of more than one method being advised. Among those, some are considering screening methods, based on the use of synthetic free radicals, such as the scavenging assay of the radical 2,2-diphenyl-1-picryl-hydrazil (DPPH), or are based on lipid peroxidation, such as the β-carotene bleaching assay (Alves et al., 2010; Carocho et al., 2013). In the former, the DPPH molecule is characterized as being a stable free radical due to the displacement of the unpaired electron throughout the molecule. This

assay is based on the measurement of the antioxidant capacity of a given substance or extract in sequestering the DPPH radical, reducing it to hydrazine. When a substance that acts as an electron and hydrogen atom donor is added to a DPPH radical solution, hydrazine is obtained and simultaneously the color changes from violet to pale yellow. The antioxidant activity is determined based on the measurement of the absorbance at 517 nm. The β-carotene bleaching assay allows to evaluate the ability of a particular substance to prevent oxidation of β-carotene, protecting it from free radicals generated during the peroxidation of linoleic acid. The reaction can be monitored spectrophotometrically by the loss of β-carotene color at 470 nm, with immediate reading after the addition of the emulsion to the sample and thereafter at 15 min intervals, for a total time of 2 h (Alves et al., 2010).

2.1.3 Grape pomace applications

Grape pomace extracts can be used in the pharmaceutical, food and cosmetics industries either in liquid, concentrated or powder form. Some studies have investigated the possibility of using it as a preservative either due to its high antioxidant ability to prevent lipid oxidation of fish-based products or to its antibacterial capacity (Beres et al., 2017).

Grape pomace can also be used in the food industry as a food supplement, to enrich beverages, or even as a substitute of synthetic antioxidants. Garrido et at. (2014) investigated the use of grape pomace as a natural source of antioxidant compounds in pork burgers. Lipid oxidation, color stability and market acceptance of the product were evaluated and it was concluded that grape pomace extracts have the potential to be used as natural preservatives in the food/meat industry.

Regarding the cosmetic industry, studies have been carried out evaluating the potential for using grape pomace as an anti-aging agent in cosmetics. Currently, there are already available several different products on the market that include grape polyphenols as ingredients, such as facial creams, facial serum, anti-aging creams and anti-wrinkle creams, among others (Beres et al., 2017).

2.1.4 Grape seed oil

Grape seed oil is well known and widely marketed in some countries, mainly incorporated in the formulation of cosmetics (Beres et al., 2017). However, recent studies also point to the potential use of grape seed oil in other areas, as in the pharmaceutical and food industries, due to its high content in fatty acids, phenolics and its interesting antioxidant capacity. In fact, several studies reported that phenolic compounds are present in higher amounts in seeds compared to other components of the grape pomace (stems and skins), representing about 70% of the total concentration of phenolic compounds (Shinagawa et al., 2015).

Usually, oil extraction is performed using solid-liquid extraction with hexane as a solvent. This technique has high yield rates (around 95%), but it presents some disadvantages, such as the use of organic solvents and its loss during the extraction process. Hexane is considered an air pollutant and, due to its toxicity, the obtained product needs to be refined. Due to environment concerns and to promote greater safety, the possibility of using other solvents, to reduce the emission of volatile organic compounds in the atmosphere, or other greener approaches has been studied. Among those, the most frequently suggested is cold pressed extraction, a classic method for oil recovery allowing, in general, achieving a better quality of the product compared to solvent extraction. Nevertheless, its extraction rate is relatively low (Beres et al., 2017).

Lately, the demand for grape oil by the cosmetics, food and pharmaceutical industries is increasing, as vegetable oils are part of the human diet, and there is a growing demand for new sources of lipophilic compounds that can replace animal fat. (Shinagawa et al., 2015).

Recent research demonstrated that the consumption of grape seed oil is associated with different health benefits, as it has hepatoprotective, neuroprotective properties and the ability to reduce liver cholesterol, presenting a high potential to be incorporated in the pharmaceutical industry (Ismail et al., 2015) . Thus, grape seed oil comes as an alternative to create new opportunities to the wine industry, promoting lower production costs and representing a new source of food for human consumption (Shinagawa et al., 2015). Grape seed oil is rich in polyunsaturated fatty acids and can be used in meat products, improving its nutritional quality by reducing calories and cholesterol, without significantly affecting the taste of the final product (Choi et al., 2010). Besides its use in the food industry, as mentioned, the cosmetic industry has also

denoted a great interest in using this type of oil as ingredient in different formulations. In addition, the feasibility of using grape seed oil as a source for biodiesel production and other by-products (namely wine marc) for bioethanol production have already been proposed as a possible alternative and a good solution for waste control in the winery industry (Fernández et al., 2010).

2.2 Drying process applied to foods

Drying is an extremely important unit operation for the conservation of the quality of several materials, as well as for increasing its useful life during its storage. Drying reduces the moisture content, reducing the water available for the proliferation of fungi and bacteria, for its respiration (which causes weight loss and generates heat) and for the occurrence of biochemical reactions that promote self-product degradation (Silva et al., 2000).

Generally, the moisture of most food products is reduced until reaching the level of 10-15%, depending on the material to be dried, so that the growth of microorganisms present in the food is inhibited, thus avoiding loss of quality (Moraes, 2006).

Puzzi (2000) pointed out that the production of many foods is periodic, but the demand from agro-industries and trade is constant. In this sense, foods that are obtained, for example in two-months harvest, are frequently requested throughout the year. Therefore, drying process may be needed to extend product's useful life, despite there may be some losses in the nutritional properties. This process is also associated with other advantages, such as reducing the weight and volume (important for storage) and making packaging and transportation easier and cheaper (Moraes, 2006). Finally, drying allows for the product being available to be sold throughout the year, during any season.

Incropera & Dewitt (1992) claim that the conditions during the drying process of agricultural products are considered isothermal and the transfer of water restricted to the material surface only. However, knowledge of the behavior of water molecules within the product is essential for a better understanding of the drying process of agricultural products. Moisture can move in different ways within the material during the drying process, including by liquid diffusion, capillary diffusion, surface diffusion, hydrodynamic flow, steam diffusion and thermal diffusion (Martinazzo et. al., 2007).

Drying can be performed naturally, using the heat of the sun to carry out the process. This operation, however, may not be sufficient for the material to reach the ideal moisture levels to be stored for long periods of time, may take a long time and if the food is not appropriately protected from environmental conditions, food safety concerns may arise.

Thus, mechanical drying, in which a mass of heated air passes through the material to be dried, is generally performed (Puzzi, 2000). According to Mujumdar (2006), industrial sectors consume about 12% of all energy involved in manufacturing processes. Thus, drying systems directly affect the environment, with a predominant participation in the emission of greenhouse gases and, consequently, in acid rain and in the destruction of stratospheric ozone. An alternative for lowering energy costs and increase the quality of the dried material relies on the use of intermittent operation, which makes it possible to optimize the transfer of heat and mass in the material.

2.2.1 Important drying variables

The conventional drying process uses hot air for heat transfer and consequent mass transfer within the material. The air's ability to remove water from the material depends mainly on its temperature and relative moisture (Celestino, 2010). During the drying process, moisture is removed from the material by the movement of water inside the material, due to the difference in water vapor pressure between the surface of the product to be dried and the drying air (Silva et al., 2000).

To better understand the drying process, some important definitions according to Perry and Green (1998) are given, as follows:

Internal diffusion. In the drying process, liquid or vapor mass is transported inside a solid due to concentration gradients. This transport is defined as internal broadcast.

Water vapor pressure (Pvs). It is the pressure exerted by the water vapor. For each air temperature, there is an amount of steam that the air can carry without the steam becoming liquid. The higher the air temperature, the greater the amount of vapor present in the air.

Mixing ratio (W). It is the relationship between the weight of water vapor and the unit of dry air, that is, it is the proportion of steam present in dry air.

Moisture content. Amount of moisture per unit mass of the dry or wet solid.

Critical moisture content. Upon drying at a constant temperature, there is an average moisture content, defined as critical moisture content.

Moisture content on dry basis (Y). Moisture content of the wet solid, represented by the ratio of mass of water to mass of dry solid:

$$Y = \frac{m_{water}}{m_{ss}} \quad (1)$$

Moisture content on wet basis (y). Moisture content of the wet solid, represented by the ratio of mass of water to mass of wet solid:

$$y = \frac{m_{water}}{m_{ss}+m_{water}} \quad (2)$$

Balance moisture content. Limit of moisture content up to which the material can dry under certain conditions of temperature and air moisture.

Absolute moisture (Yabs). Relationship between the mass of water vapor present in a defined mass of dry air.

Moisture Ratio (MR). Defined as the relationship between the partial pressure of water vapor in the air (p) and the pressure of water vapor under equilibrium conditions (ps: saturation pressure), according to the expression below:

$$MR = \frac{p}{p_s} \quad (3)$$

2.2.2 Drying kinetics

The drying kinetics corresponds to the rate with which the food looses moisture and is controlled both by the drying conditions, such as the temperature, speed and relative moisture of the drying air, and by the characteristics of the food, such as particle size, arrangement and height of materials (Celestino, 2010). Figure 3 represents the way that moisture behaves throughout the drying process.

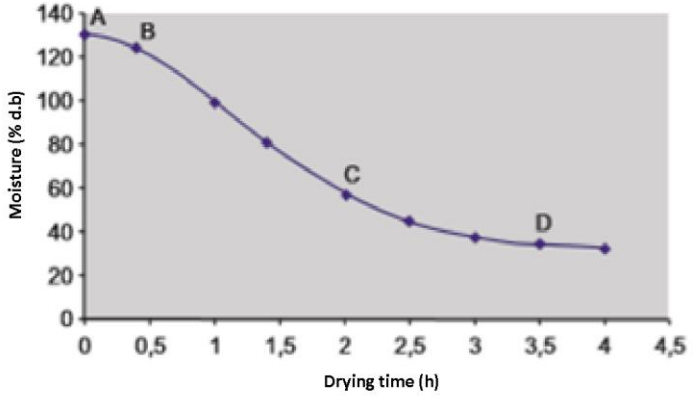


Fig.3. Drying kinetics (adapted from Celestino, 2010)

As in Figure 3, the AB segment corresponds to the period in which the food adapts to the drying conditions. The BC segment represents the moment when the water in the food has no resistance to leave it, when there is the greatest reduction in the moisture content of the material, because that's when the material has the highest moisture. Point C represents critical moisture, where an increase in internal resistance occurs. From point D onwards, the moisture of the food decreases until it reaches the equilibrium moisture for the exposed temperature and moisture conditions. The drying process stops when the material reaches equilibrium moisture (Celestino, 2010).

Akpinar et al. (2003) in their study on the drying of red peppers carried out experiments at temperatures of 55, 60 and 70 °C. The moisture variation over the drying time is shown in Figure 4. Based on the obtained results, the authors concluded that the moisture decreases over the drying time and, for higher temperatures, the drying rates are initially higher, but soon decrease until they become the same or even lower than those at lower temperatures. This increase in the initial drying rate is explained by the greater potential for heat transfer between the air and the slices of red pepper, favoring the evaporation of water from the slices of red pepper.

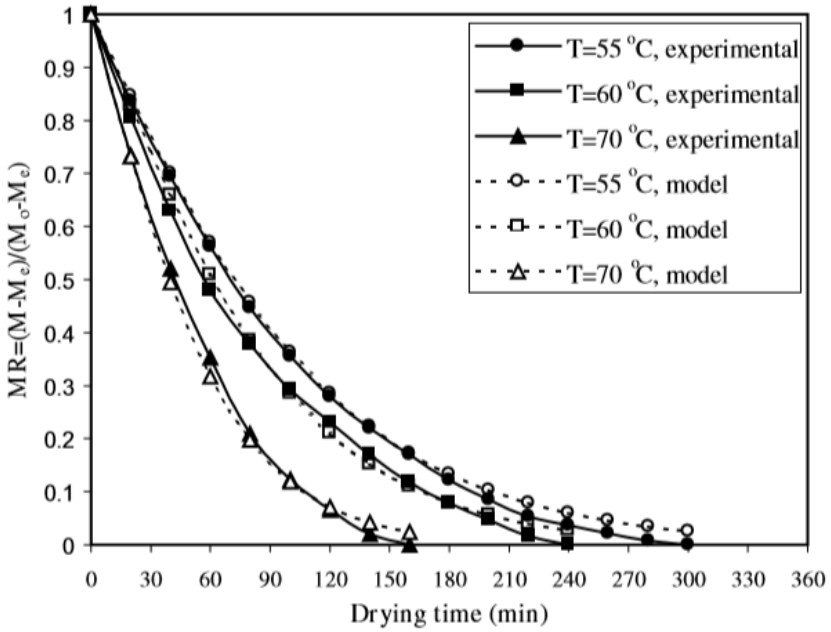


Fig.4. Moisture variation depending on the actual drying time and the drying time predicted by the adjusted diffusion model (adapted from Akpinar et al., 2003)

Wang et al. (2007) studied the mathematical modeling of apple pomace drying, carrying out experiments at temperatures of 75, 85, 95 and 105 ° C and observed that the moisture rate decreases continuously as the drying progresses, as there is less water available inside the material. They also observed that the diffusivity effect increases as the temperature increases. The proportions of moisture versus drying time of the apple pomace at the selected temperatures are shown in Figure 5. Among the proposed temperatures, the one that showed the greatest potential for energy optimization of the apple pomace drying process was the interval between the temperatures of 85 and 95 ° C, as the change of 10 °C from 85 ° C to 95 ° C was the one that had the best effect on drying time.

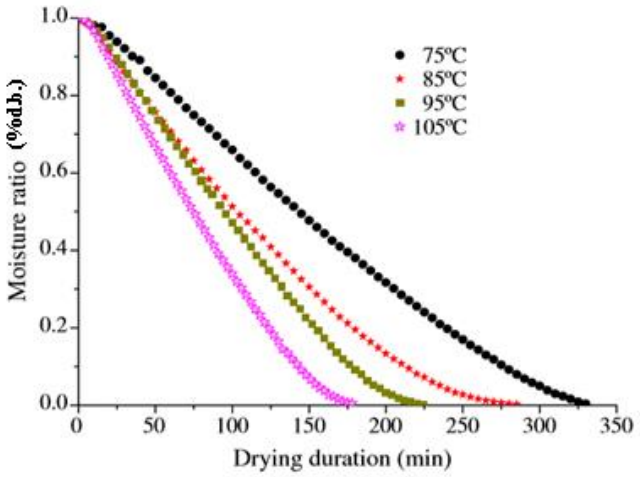


Fig.5. Thin-layer drying curves of apple pomace at different temperatures (adapted from Wang et al., 2007).

2.2.3 Drying methods

The drying methods applied to foods are mainly divided into natural drying and artificial drying. Natural drying is a low-cost process, widely used in underdeveloped and/or developing tropical regions. The movement of air is done by the action of the wind and solar energy is the one that provides the energy necessary for moisture evaporation (Silva et al., 2000). Dried foods using the natural method have a stronger color than artificially dried foods, but greater nutritional losses occur (Celestino, 2010).

According to Silva et al. (2000), although some products manage to reach the ideal moisture content for storage through natural drying, the product is exposed to pest attack, plant tipping and the weather, which cause greater losses in quality of product. Another disadvantage is the need to occupy the field for long periods of time, delaying soil preparation operations for new crops.

In artificial drying, there is human interference, accelerating and optimizing the process. Heat is produced artificially in greenhouses or sheds that are designed and prepared for this purpose, or using appropriate drying equipment. The temperature, moisture and speed of the drying air are also controlled, making the method faster and requiring a smaller drying area. However, this method requires capital and specialized labor (Moraes, 2006).

Different types of drying used in the industry and their respective operating principles are described as follows (Aghbashlo et al., 2013):

Batch or tray drying. Tray dryers are the most commonly used dryers for drying low tonnage products. It consists of a stack of trays or several piles of trays located in a large insulated chamber into which the hot air is blown with properly designed fans and guide vanes.

Continuous or industrial drying. The previous method (batch drying) has many advantages, including simple, low-cost chambers, low labor costs and easy removal and unloading procedures. However, a continuous dryer allows achieving better efficiency and final products with higher quality while consuming less energy.

Heat pump assisted drying systems. Heat pumps are facilities for elevating the temperature of low grade heat energy to a more useful level using a relatively small amount of high grade energy. They have been known as energy efficient equipment when used in conjunction with drying operations. The heat pump dryers have many advantages over conventional hot air drying including the ability to recover energy from the exhaust gas and the capability to control the drying gas temperature and moisture. A heat pump drying system consists mainly of two subsystems: a heat pump system and a drying system.

Fluidized bed drying. Fluidized bed is a drying method widely used for wet particulate and granular materials that can be fluidized. It can also be used in masses and suspensions, which can be fluidized in inert beds. The main advantages of this method arises from the easiness of mixing solids, high rates of heat and mass transfer and easy material transport.

Freeze drying. This method is adequate for heat sensitive materials such as certain bioactive compounds, pharmaceuticals, and foods, for which heating is not recommended, even at moderate temperatures. In freeze drying, the solvent (generally water) is eliminated as a vapor by sublimation from the frozen products being dried in a vacuum chamber. This method presents several advantages over hot-air drying such as reduced loss of flavor and aroma.

Spray drying. This technique is considered the most important when dehydrating a liquid or slurry such as milk or eggs, being extensively used in different areas, in particular in the food industry. The spray drying process is composed of following stages: (a) pumping the liquid to the atomization device; (b) atomizing the liquid throughout a nozzle; (c) drying the generated droplets in hot drying media; and (d) separating the dried particles from the exhaust air.

Vacuum drying. This method is mainly applied to the dehydration of heat-sensitive wet material by using a reduced pressure environment and reducing the boiling point of the liquid to be removed

2.3 Intermittent drying

As previously mentioned, drying, when done mechanically, is a process that has high energy costs (Silva et al., 2000). An alternative to conventional drying is intermittent drying, which unlike the traditional way, provides the air system with transient conditions (flow, temperature or pressure) in order to obtain the best operational conditions for the process. It has been shown that by applying transient conditions to the process, it is possible to reduce the drying time and consequently reduce the energy consumption involved in the process (Putranto et al., 2011).

The drying rate is controlled by the rate of moisture migration from the interior of the solid to the surface where the liquid evaporates. Therefore, in order to optimize energy consumption and improve product quality, it is important to combine the amount of energy required by the product during drying with the external energy supplied in several possible ways to find the best drying conditions. According to Chua et al. (2003), for foods whose drying is controlled by the diffusion of heat and moisture within the grain, intermittent drying is beneficial, and most agricultural products have this characteristic.

Kowalski and Pawlowski (2011) studied the drying of wood and ceramic materials in order to assess the quality of these materials in view of the type of drying used as well as different drying conditions. According to these authors, intermittent drying offers better energy efficiency due to reduced heat input, less effective drying time and less air consumption, in addition to improving product quality as a result of reducing the stresses induced by drying. This can be explained because intermittent drying consists of decreasing the drying rate just before the material starts to damage, increasing the drying rate only when there is no danger of crack formation. The results obtained showed that by modeling the temperature, lower energy consumptions are obtained and by modeling the air moisture it is possible to obtain a material with better final quality. In addition, it was also demonstrated that using intermittent drying it is possible to achieve a better quality without major differences in the drying time.

Aquerreta (2007) studied the influence of drying and temperature modulation on rice quality. Both studies evidenced that it is possible to maintain the physiological quality of the rice seeds through the modulation of the temperature. Additionally, Aquerreta (2007) evaluated the energy consumption involved in the process, and concluded that a reduction can be obtained by modulating the temperature of the drying air.

Villela (1991) studied the effects of intermittent drying on the quality of corn seeds and observed that this approach not only promoted the maintenance of the material's quality but also provided a reduction in the incidence of fungi and bacteria, allowing the product to be stored by longer periods of time. Similar results were obtained by Oliveira and Rocha (2007) regarding the process of intermittent drying of beans, since the authors concluded that this drying mode has greater energy efficiency and makes it possible to obtain a better final product quality.

Chua et al. (2000a) studied the drying of guavas and observed that, for similar drying times, better results in terms of the material quality and maintenance of ascorbic acid can be achieved through temperature modeling. The results showed that ascorbic acid content can increase up to 20% when using intermittent drying. In another work, Chua et al (2000b) demonstrated that throughout the application of intermittent drying it was possible to decrease the color variation of potato, guava and banana by 87%, 75% and 67%, respectively.

According to Defendi (2015), intermittent drying can be performed in several ways according to the properties of the drying air, such as temperature and flow, or the system as pressure is modulated. The present work will focus on the step operation (Figure 6), which is characterized by having a modulation based in two temperatures, alternating between them until the desired moisture is reached. Figure 6 illustrates the types of modeling related to intermittent drying.

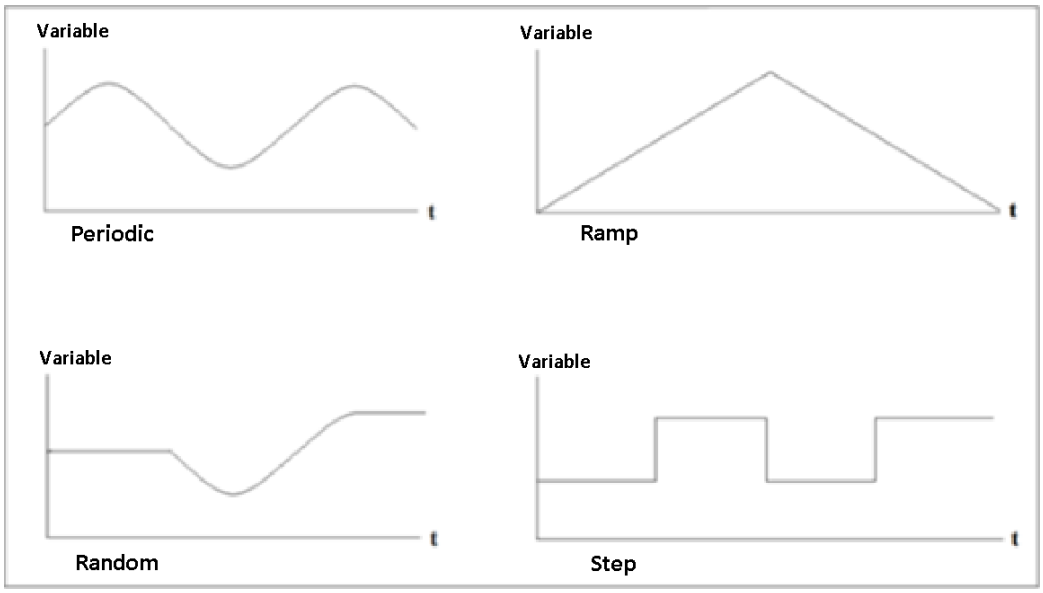


Fig.6. Types of Intermittent Drying (adapted from Defendi, 2015).

2.4 Drying of grape pomace

As previously mentioned, in the wine production process, large quantities of by-products are produced, which end up becoming both an economic and an environmental problem due to difficulties in storage, processing or disposal. Grape pomace, the by-product produced in greater quantity in the wine industry, is considered rich in natural bioactive compounds, mainly phenolic compounds, therefore becoming the focus of several studies (Carmona et al., 2018).

Because grape pomace is susceptible to microbial degradation and its freezing is not feasible for industry, drying of the grape pomace is a good alternative (Carmona et al., 2018). In addition, this approach allows stabilizing the material that can be latter used to extract the desired compounds.

Rajah et al. (2014), when studying the effect of the drying process on the intensification of phenolic compounds recovery from grape pomace, observed that for temperatures up to 100 °C the drying process has a negative effect on the yields and bioactive properties of the extracts obtained by accelerated solvent extraction. However, after this temperature and up to 140 °C, the polyphenols extracts of dry grape pomace exhibited higher antioxidant activity, which can be related to a specific mixture of polyphenols with synergistic effects between the different compounds.

Larrauri et al. (1997), observed that for drying temperatures below 60 °C, there were no significant changes in the polyphenolic content, color and antioxidant activity of red grape pomace skins. Haas et al. (2016) demonstrated that significant variations in phenolic concentrations occur after dehydration. In samples submitted to air drying at 45°C during 4h and 55 min or lyophilization, a decrease in the content of polymerized and total polyphenols was observed when compared to drying at 55 and 65°C for shorter periods.

In their study, Carmona et al. (2018) obtained results that demonstrated that for drying carried out at 40°C with controlled drying conditions, such as air temperature and air flow, there is an improvement in the quality of the product, being not only beneficial, but also advisable. In all the samples of grape pomace studied, the antioxidant activity and phenolic compounds showed improvements in comparison to fresh samples, increasing the potential of exploiting grape pomace as a powerful natural resource that can be used as an antioxidant ingredient in functional foods, as well as other uses in the cosmetic and pharmaceutical industry.

Tseng et al. (2012), who studied the effect of different types of drying and storage on the retention of bioactive compounds in grape pomace, observed that drying in the oven at 40°C and drying in room air are highly acceptable, considering the amount of retention of bioactive compounds and their much lower cost compared to freeze drying, suggesting that they can be used in commercial drying applications of large quantities of wine by-products.

2.5 Mathematical modelling

Mathematical modeling is one of the most important tools for the development of drying processes and technology. With it, it is possible to predict how the process will behave, helping researchers and engineers to choose and optimize the drying process itself. These models are generally constituted by a set of differential algebraic, partial and ordinary equations, which are implemented using methods of spatial discretization, such as finite differences or line method, which results in nonlinear problems (Bonfigli et al., 2017).

Over the years, several mathematical models have been developed, but the most commonly used are the models proposed by Page, Newton and Midilli (Xu et al., 2017). Table 1 shows the main mathematical models used to describe the drying process,

where *a*, *b*, *c*, *g*, *h* and *n* are empirical constants of the drying models, k, k_0, k_1 are empirical constants in the drying models, MR is the moisture ratio and *t* is the time in minutes.

Table 1. Main mathematical models used to describe the drying process (adapted from Akpinar et al., 2003).

Model no.	Model name	Model
1	Newton	$MR = \exp(-kt)$
2	Page	$MR = \exp(-kt^n)$
3	Modified Page	$MR = \exp[-(kt)^n]$
4	Henderson and Pabis	$MR = a\exp(-kt)$
5	Logarithmic	$MR = a\exp(-kt) + c$
6	Two terms	$MR = a\exp(-k_0 t) + b\exp(-k_1 t)$
7	Wang and Singh	$MR = 1 + at + bt^2$
8	Approximation of diffusion	$MR = a\exp(-kt) + (1-a)\exp(-kbt)$
9	Verma et al.	$MR = a\exp(-kt) + (1-a)\exp(-gt)$
10	Modified Henderson and Pabis	$MR = a\exp(-kt) + bexp(-gt) + cexp(-ht)$
11	Two-term exponential	$MR = a\exp(-kt) + (1-a)\exp(-kat)$
12	Hii et al.	$MR = a\exp(-kt^n) + b\exp(-gt^n)$
13	Midilli et al.	$MR = a\exp(-kt^n) + bt$

Mathematical modeling of the process is important because it describes how the material's moisture varies depending on the drying time. This allows the process to be described by a mathematical equation and parameters to be adjusted, parameters that characterize the drying kinetics according to its main variables. Thus, it is not necessary to collect data every time a drying process needs to be evaluated (Defendi et al., 2016). According to Midilli et al. (2002) there are three types of mathematical modeling used to describe the kinetics of the drying process of agricultural products: the theoretical model, which considers only the internal resistance that the material presents in relation to the transfer of heat and water with hot air, and the semi-theoretical and empirical models, which consider only the external resistance provided to the temperature and relative moisture of the drying air.

According to Banga et al. (2003) due to the complexity of the underlying mechanisms, the uncertainties about the measurement of material properties and the

difficulty of obtaining reliable results, rigorous and detailed modeling is a difficult task. Therefore, it is common to associate the proposed models with the experimental data through empirical relationships, which comprise the main mass transfer coefficients for a certain range of conditions involved in the process, in order to obtain a more accurate description of the process.

Goneli et al. (2014) in their study on the drying and modeling of mastic leaves, observed that the model that best fitted to the drying kinetics of the material was the one proposed by Midilli, using statistical tools to compare the adjusted models, such as the values of the coefficient of determination and the relative average error, in addition to the calculation of the values of the standard deviation of the estimate. According to the authors, this fact would be related to the fast loss of water from the material during the initial stages of the process, generating a drying curve more sharp and characterized by this model. Corrêa et al. (2010), in their study on drying and mathematical modeling of coffee, also found that the model proposed by Midilli was the one that best fits the experimental data on the drying of coffee fruits. The same occurred in the study promoted by Reis et al. (2011) on mathematical modeling of drying Cumari pepper from Pará.

Wang et al. (2007), in their study on the mathematical modeling of drying apple pomace, found that the logarithmic model was the one that best suited the drying kinetics of the study material. They also observed that of the temperatures studied (75, 85, 95 and 105 °C), the interval between 85 ° C and 95 ° C was the one with the greatest potential for energy optimization, as it corresponded to the interval where the greatest increase in drying rates occurred.

In turn, when studying the drying of beans, Corrêa et al. (2007) concluded, based on statistical parameters, that the models of Page, Midilli, Henderson and modified Pabis, Two terms and Approximation of diffusion, among the tested series, are the ones that best represent the bean drying phenomenon. Among those, the traditional Page model was selected to describe the drying kinetics of beans in thin layer due to its simplicity.

Regarding the drying of grape pomace, and according to Celma et al. (2009), the most relevant aspects for the drying process are the mathematical modeling of both the process and the equipment used. For the model to be accurate, it is necessary to know the drying behavior of the product, as well as statistical regressions and correlations, in order to obtain a set of equations that allow an adequate description of

the system. In their study on mathematical modeling of drying grape pomace, Celma et al. (2009) found that the Midilli model was the one that best suited the process, having used statistical parameters to compare the used models. Ferreira et al. (2012) also studied the mathematical modeling of grape pomace and, after adjusting the models presented in Table 2, concluded that the model that best described the drying process of this material was the modified Page model. Motta et al. (2017), in turn, observed that when implementing fractional calculation in mathematical modeling, there was a better description of the drying process of grape pomace by classical mathematical models, such as that of Page. This occurs, mainly due to the fact that, many times, the process occurs anomalously, not obeying Fick's second law of diffusion, making the drying curves not having a completely exponential behavior.

The cases mentioned above demonstrate the importance of knowing the characteristics of each material and its consequent drying kinetics, since each product behaves in a unique way in the process, and even the same product can be represented by different models depending on the drying conditions imposed on the products themselves.

3 Objectives

The main purpose of this study is to apply intermittent drying in order to maximize the preservation of the quality of the material in terms of antioxidant activity and bioactive compounds. This work also aims to assess and compare the conventional operation versus to the intermittent drying method, applied to drying of grape pomace components. The dried samples will be assessed for their composition in bioactive compounds and antioxidant activity. Moreover, this work also aims at performing the mathematical modeling of grape pomace drying process, both in conventional and intermittent operation. Overall, this study will allow to observe how drying affects the levels of phenolic compounds and the antioxidant activity of grape pomace.

4 Materials and methods

4.1 Drying experiments

4.1.1 Materials

The pomace sample (seeds, skins and stems) was provided by the company Adega Cooperativa de Silgueiros. For drying experiments, a greenhouse oven with external regulation of air temperature and a timer for time control were used. The quantification of the mass of the samples was carried out on a semi-analytical balance with an accuracy of 10^{-2} grams. Aluminum containers were used to handle the samples. A Combined RH and Temperature probe (Delta Ohm, HP3217R) was used inside the oven to measure air velocity and verify that it was similar among experiments. A mercury thermometer was also used to measure the ambient temperature.

4.1.2 Determination of the absolute moisture content of the samples

A monolayer of seeds and skins were placed separately in three glass petri dishes, taking note of the masses of the containers before and after adding the material. Subsequently, the samples were introduced in the oven, where they remained for a period of 24 hours at a temperature of 105 °C ± 2 °C, in order to establish the moisture content, on a dry and wet basis. After 24 hours, the petri dishes masses were measured to determinate the amount of evaporated water. Figure 7 shows the oven used in the experiments.

Fig.7. Laboratory oven (BINDER ED 23)

4.1.3 Conventional and intermittent drying

Before being subjected to the drying process, the sample was manually separated into seeds and skins (the stems were discarded because they corresponded to a small fraction of the total residues and, according to the literature, they did not present considerable levels of compounds). After separation, the seeds and skins were dried separately in duplicate at temperatures of 40, 55 and 70 °C for a total period of 2 hours. The samples were dried using both conventional and intermittent methods, the latter being carried out with tempering periods of 5 and 10 minutes.

During drying process, periodic measurements were made every 5 minutes using a semi-analytical balance, in order to observe the variation in the moisture content of the seed over time. Therefore, when the drying method was intermittent with a period of 10 minutes, the samples remained 10 minutes in the oven, then 10 minutes on the bench, with the variation of the sample mass being measured every 5 minutes.

In each experiment, small samples, about 5 g, were taken to the oven before and after the drying process in order to determine the initial and final average of moisture content. This procedure was similar to the one previously described for determining the absolute moisture content of the samples. The room temperature was also measured in each experiment.

4.2 Mathematical modeling

4.2.1 Conventional Drying

Table 2 shows typical mathematical models adjusted for the conventional drying method. They were adjusted with the experimental data of moisture content on dry basis obtained in the laboratory, which is related to the amount of water evaporated in the process over time.

Table 2. Mathematical models adjusted to the conventional drying method (adapted from Akpinar et al., 2003).

Model no.	Model name	Model
1	Newton	$MR = \exp(-kt)$
2	Page	$MR = \exp(-kt^n)$
3	Henderson and Pabis	$MR = a\exp(-kt)$
4	Logarithmic	$MR = a\exp(-kt) + c$
5	Two terms	$MR = a\exp(-k_0 t) + b\exp(-k_1 t)$
6	Approximation of diffusion	$MR = a\exp(-kt) + (1-a)\exp(-kbt)$
7	Hii et al.	$MR = a\exp(-kt^n) + b\exp(-gt^n)$
8	Midilli et al.	$MR = a\exp(-kt^n) + bt$

$a, b, c, g, h, n, k, k_0 \; and \; k_1$ are empirical constants of drying models, *MR* is the moisture ratio described by $(Ys-Ys_e)/(Ys_0-Ys_e)$ and *t* is the time in minutes. *Ys* is the moisture of the sample, Ys_e is the equilibrium moisture of the sample at the proposed drying temperature and Ys_0 is the initial moisture of the sample.

The parameters were adjusted by minimizing the objective function (sum of least squares) represented by the Equation 4 below:

$$\phi = \sum(Ys_{exp} - Ys_{cal})^2 \quad (4)$$

Ys_{exp} is the sample overall moisture content in dry basis along the drying time and Ys_{cal} is the overall moisture content in dry basis calculated by each mathematical model. The quality of the adjustment was evaluated by statistical parameters that will be explained in section *'4.2.3'*.

4.2.2 Intermittent drying

Modeling for the intermittent drying method with tempering periods of 5 and 10 minutes was conducted considering both mass and energy balance equations (Equations 5 and 6).

$$\frac{dYs}{dt} = -K(Ys - Ys_e) \quad (5)$$

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \dot{m}_i \left(u_i + \frac{v_i^2}{2} + gz_i\right) - \dot{m}_o \left(u_o + \frac{v_o^2}{2} + gz_o\right) \quad (6)$$

$\frac{dE}{dt}$ represents the variation of system energy over time; $\dot{Q}$ is the heat exchange performed; $\dot{W}$ is the work rate of the system (which may be axis work, border displacement or electrical work); $\dot{m}_i$ and $\dot{m}_o$ are the mass rates entering and leaving the system, respectively; u_i and u_o represent the internal energy involved in the input and output; $\frac{v_i^2}{2}$ and $\frac{v_o^2}{2}$ are the kinetic energies and gz_i and gz_o are the potential energies of the system's input and output.

The variation in the mass of water in the material is equivalent to the rate of evaporated water, with *K* being a global mass transfer coefficient given by $k_s A / m_{ss}$ (A is the mass exchange area, which is the surface area of the material , m_{ss} is the mass of dry solid).

The mass and energy balances, represented by the system of two differential equations, were solved simultaneously. The K parameter was determined by solving the models and minimizing the objective function in Equation 4, similarly to the models for conventional drying.

The energy E of the system is described by Equation 7:

$$E = U + KE + PE \quad (7)$$

In which *U* is the internal energy, *KE* is the kinetic energy and *PE* is the potential energy of the material. As the material is stagnant and due to temperature variations, the variation of the internal energy is much greater than the variation of the kinetic and potential energies. In addition, *PxV* work is added to the *U* resulting in *H*. Therefore, the energy balance equation results in equation 8:

$$\frac{dU}{dt} = \dot{Q} - \dot{m}_{ev} h_{ev} \quad (8)$$

$\frac{dU}{dt}$ is the variation of the system internal energy over time, the term $\dot{m}_{ev} h_{ev}$ is the energy that leaves the system and h_{ev} is the enthalpy of the vapor of water, whose values were taken from the literature (Shapiro et al., 2013).

Assuming that heat transfer occurs only by convection (non-significant transfers by radiation and conduction), it can be described by Newton's law of cooling (Equation 9):

$$\dot{Q} = -hA_s(T - T_{air}) \quad (9)$$

In which h is the convective coefficient; A_s is the surface area; T is the temperature of the sample and T_{air} is the air temperature in contact with the samples. The value of h was estimated for natural convection from the literature (Incropera et al., 1992).

The internal energy variation is represented by the Equation 10:

$$\Delta U = m_{sample} c_p \Delta T \quad (10)$$

ΔU is the change in internal energy; m_{sample} is the mass of the material; c_p is the heat capacity at constant pressure of the sample and ΔT is the temperature variation suffered by the material. The internal energy is calculated as a function of c_v , but as the material is in a solid state, the values of c_p and c_v are similar.

Substituting the equations presented previously in the energy balance equation, we have (Equation 11):

$$\frac{dm_{sample} c_p T}{dt} = hA_s(T_{air} - T) - \dot{m}_{ev} h_{ev} \quad (11)$$

This equation can describe the intermittent drying method with tempering periods of 5 and 10 minutes. Considering that the specific heat of the grain is constant (Equation 12):

$$\frac{dm_{sample} T}{dt} = \frac{hA_s(T_{room} - T)}{c_p} - \frac{\dot{m}_{ev} h_{ev}}{c_p} \quad (12)$$

The sample's mass (m_{sample}) can be represented by the Equation 13 below:

$$m_{sample} = (1 + Y_s) m_{dry} \quad (13)$$

Where Y_s is the sample's overall moisture content in dry basis.

Substituting the m_{sample} equation in Equation 13, we have (Equation 14):

$$\frac{d(1+Y_s)m_{dry}T}{dt} = \frac{hA_s(T_{air}-T)}{c_p} - \frac{\dot{m}_{ev}h_{ev}}{c_p} \quad (14)$$

The mass of the completely dry material, m_{dry}, is constant, then (Equation 15):

$$\frac{d(1+Y_s)T}{dt} = \frac{hA_s(T_{air}-T)}{c_p m_{dry}} - \frac{\dot{m}_{ev}h_{ev}}{c_p m_{dry}} \quad (15)$$

The mass rate of water evaporated from the sample can be represented as follows (Equation 16):

$$\dot{m}_{ev} = \frac{m_{sample}|t_i - m_{sample}|t_{i+1}}{t_{i+1}-t_i} \quad (16)$$

In the Equation (16) above, a numerator i is used, which has the function of assisting in programming, for example, t_i is the time in which the current mass rate of evaporated water was calculated and t_{i+1} the time in which the next mass rate of evaporated water was calculated. The system of ordinary differential equations was solved by the Euler numerical method with step size for the time of 0.01 seconds.

Substituting Equation (14) in the Equation (16), we have (Equation 17):

$$\dot{m}_{ev} = \frac{m_{dry}(1+Y_{s\,i}) - m_{dry}(1+Y_{s\,i+1})}{t_{i+1}-t_i} \quad (17)$$

Finally, simplifying, we obtain (Equation 18):

$$\dot{m}_{ev} = \frac{m_{dry}(Y_{s\,i} - Y_{s\,i+1})}{t_{i+1}-t_i} \quad (18)$$

Equation (4) was minimized to adjust K parameter based on experimental data by solving simultaneously equations 5 and 6. Parameter K was adjusted as a linear equation as a function of temperature.

4.2.3 Statistical analysis of models fitting

The criteria for the best models fitting, regarding both mathematical models proposed for conventional and intermittent drying, was assessed by the following statistical parameters (Equations 19-21):

$$\chi^2 = \frac{\sum(Ys_{exp} - Ys_{cal})^2}{No - Nc} \tag{19}$$

$$RMSE = \left(\frac{1}{No}\sum(Ys_{cal} - Ys_{exp})^2\right)^{\frac{1}{2}} \tag{20}$$

$$EF = \frac{\sum\left(Ys_{exp} - \overline{Ys}_{exp}\right)^2 - \sum\left(Ys_{cal} - Ys_{exp}\right)^2}{\sum\left(Ys_{exp} - \overline{Ys}_{exp}\right)^2} \tag{21}$$

χ^2 is the reduced chi-square, $RMSE$ is the root-mean-square error, EF is the efficiency of the model, No is the number of observations, Nc the number of model constants and $\overline{T}_{exp}$ is the value of the experimental average temperature. The subs *cal* and *exp* represent respectively correlated and experimental data. According to Meisami-asl el al (2010), the value of the reduced chi-square represents the square root of the deviation between the experimental data and those calculated by the model and determines how good the fit was. Therefore, the lower the value for χ^2, the better the adjustment. The value of $RMSE$ represents the deviation between the experimental values and those estimated by the model. EF, in turn, is related to the model's ability to describe the system. Therefore, the ideal value for $RMSE$ is zero and 1,0 for the EF value.

In addition to the parameters mentioned above, the parameters Mean-Square Error (MSE) and Normalized Mean Square Error (NMSE) (Sarbishei, 2011; Chani-Cahuana, 2018) presented below were also used (Equations 22-23):

$$MSE = \frac{1}{N}\sum_{k=0}^{N-1} E\left(\left|X[k] - X_{fixed}[k]\right|^2\right) \tag{22}$$

$$NMSE = \frac{RMSE}{Ys_{max} - Ys_{min}} \tag{23}$$

Where N is the number of observations. The min and max subscripts represent the maximum and minimum values for the experimental data.

4.3 Chemical Analyses

4.3.1 Extraction of phenolic compounds

After being dried, part of the sample was crushed in a mill, model IKA A11 BASIC, and stored at -20 ° C in a plastic container for later use. Figure 8 shows the analytical mill used for sample preparation. The samples obtained from the company (non-dried) were also submitted to the same procedure.

Fig.8. Analytical mill (IKA A11BASIC)

The extraction of phenolic compounds was done using approximately 2 g of sample. In the extraction of the compounds present in the grape skin, the sample was mixed with 100 ml of ethanol: water (80:20, v/v), and the extraction was carried out under agitation for 1 hour, at room temperature and protected from light. After that time, the mixture was sonicated in an ultrasound bath for 5 minutes. Subsequently, it was filtered with a N° 4 buckner filter. The residue obtained was extracted again, repeating the procedure described above. After adding both solutions obtained, if they were turbid, they were centrifuged at 6000 rpm for 5 minutes. Then, the ethanol was removed at 40 ° C under reduced pressure using a rotary evaporator (Buchi). After that,

the extract was frozen and lyophilized. The residue obtained was dissolved again in the respective extraction solvents and used after adequate dilution.

For the extraction of phenolic compounds from grape seeds, before performing the extraction with the 80% ethanol solution, the sample was defatted using 40 mL of hexane. The extraction was performed by agitating the mixture for 30 minutes at room temperature and protected from light. After this time, the mixture was filtered with a N° 4 buckner filter. The residue was then extracted using a methodology similar to the one described previously.

Figure 9 shows the rotary evaporator used in this study:

Fig.9. Rotary evaporator, (Buchi), used in the preparation of extracts.

After lyophilization, 25 mg of each sample was weighed and placed in a 10 mL volumetric flask and ethanol: water solution was added to the desired volume, thus obtaining a 2.5 mg/mL stock solution. Serial dilutions were made to obtain the concentrations C1 = 1.25 mg/mL, C2 = 0.625 mg/mL, C3 = 0.3125 mg/mL, C4 = 0.1563 mg/mL, C5 = 0.0781 mg/mL, C6 = 0.0390 mg/mL, C7 = 0.0195 mg/mL.

4.3.2 Determination of bioactive compounds

4.3.2.1 Total phenolic compounds

The determination of the total phenolic compounds content of the hydroethanolic extract of grape seeds and skins was performed by spectrophotometry in a microplate reader (Epoch 2, Biotek), using the reagent Folin–Ciocalteu. To obtain the

calibration curve, an ethanolic solution of Gallic acid was used as standard compound, with concentrations of 0.005; 0.01; 0.05; 0.1 and 0.25 mg/mL. Ethanol was used as blank.

In a test tube 200 μL of extract from each sample or standard was mixed with 1000 μL of Folin-Ciocalteu reagent (1:10 v/v, in water) and 800 μL of sodium carbonate (75 g/L). The tubes were taken to the vortex for 15 seconds and placed to rest in the dark for 30 minutes at 40 ° C, for color development. Simultaneously, a blank was prepared using ethanol instead of sample. After incubating, the tubes were centrifuged at 6000 rpm for 2 minutes. Then the contents of each test tube were transferred to a 96 wells microplate using a micropipette.

Finally, the absorbance was measured at 765 nm using a microplate reader (Epoch2, Biotek) and the concentration in terms of total phenolic compounds was calculated using the standard curve obtained with gallic acid. The results were expressed in mg equivalent of gallic acid per gram of extract (mg GAE/g extract).

Figure 10 shows the microplate reader (Epoch2, Biotek), which was used to read the absorbance of bioactive compounds and antioxidant activity, while Figure 11 presents the test tubes and microplate evidencing the reaction with gallic acid standard.

Fig.10. Microplate reader (Epoch2, Biotek)

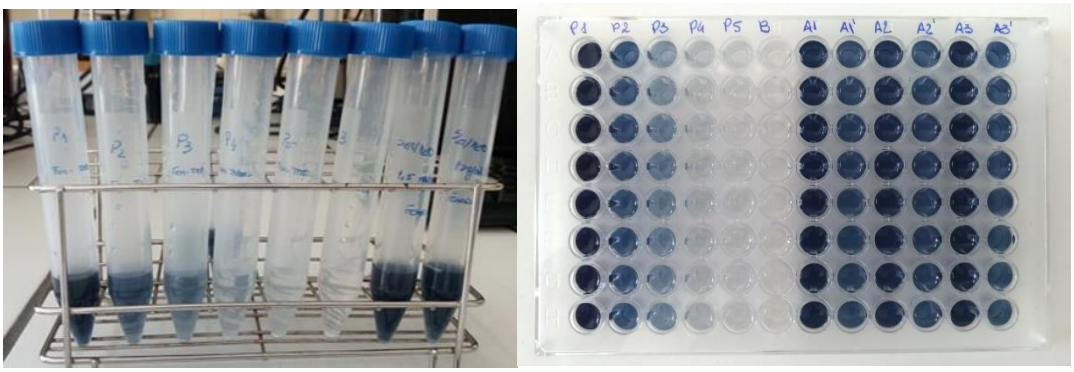


Fig.11. Standards prepared with Gallic acid for the determination of total phenols.

4.3.2.2 Total flavonoid content

The determination of total flavonoids content was performed using Catechin as standard. To obtain the calibration curve, different solutions were prepared with concentrations of 0.01; 0.025; 0.05; 0.1; 0.25 and 0.5 mg/mL. Ethanol was used as blank.

A total of 500 µL of the extract solution, standard or ethanol, was mixed in 15 ml falcon tubes with 2 mL of distilled water and 150 µL of $NaNO_2$ solution (5%, m/v). The tubes were vortexed for 15 seconds and left for 6 minutes in the dark. Then, 150 µL of $AlCl_3$ solution (10%, m/v) was added and the tubes were vortexed for 15 seconds and left to stand for another 6 minutes in the dark. Subsequently, 2 mL of the NaOH solution (4%, m/v) and 200 µL of distilled water were mixed, vortexed for 15 seconds and left to stand for another 15 minutes in the dark.

Finally, if the solution was turbid or with suspended particles, it was centrifuged at 6000 rpm for 2 minutes. After that, the samples were transferred to a microplate with the aid of a micropipette and an absorbance was read at 510 nm using a microplate reader (Epoch2, Biotek).

The concentration of total flavonoids content was calculated using a standard curve obtained with catechin, the values being expressed in catechin equivalents per gram of extract (mg CE/g of extract).

Figure 12 shows an image with the final appearance of catechin standards, in test tubes, as well as the samples placed on the microplate for reading.

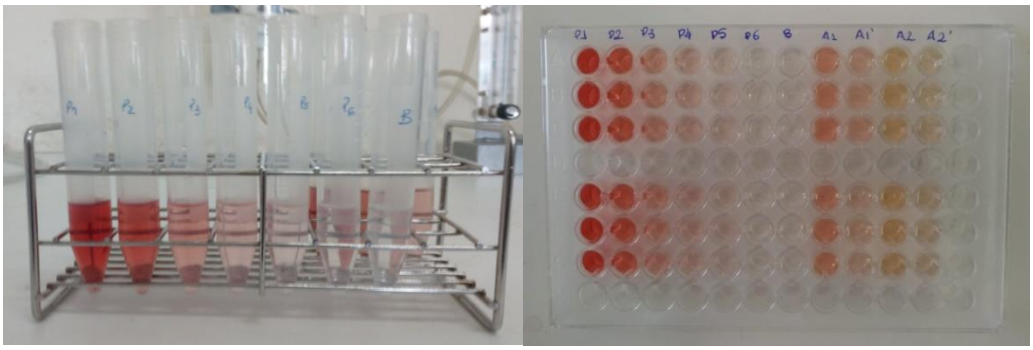


Fig.12. Standards prepared with catechin for the determination of total flavonoids.

4.3.3 Determination of Antioxidant Activity

4.3.3.1 Reducing power

To determine the reducing power, dilutions of C2 to C7 of the hydroethanolic extract of grape seeds and skins were used.

A total of 500 µL of each dilution and ethanol (Blank) were placed in 15 ml falcon tubes. Then, 500 µL of sodium phosphate buffer solution (200 mmol/L, pH 6.6) and 500 µL of potassium ferrocyanide (1% w/v) were added to each tube. Each tube was homogenized and placed in the oven at 50 ° C for a period of 20 minutes. Subsequently, 500 µL of trichloroacetic acid (10% w/v) were added and the tubes were centrifuged at 6000 rpm for 2 minutes. After centrifugation, 1 mL of solution was removed from each tube into a new tube, and 1 mL of deionized water and 200 µL of iron chloride (0.1% w/v) were also added. After homogenized, the solutions were transferred in triplicate to a microplate and their absorbance were read at 690 nm using a microplate reader (Epoch2, Biotek).

Finally, the concentration of the extract solution corresponding to 0.5 of absorbance (EC50) was calculated by interpolation from the absorbance graph as a function of the concentration of the sample. All extracts were analyzed at least in duplicate, with triplicate measurements.

Figure 13 shows the samples on the microplate for reading.

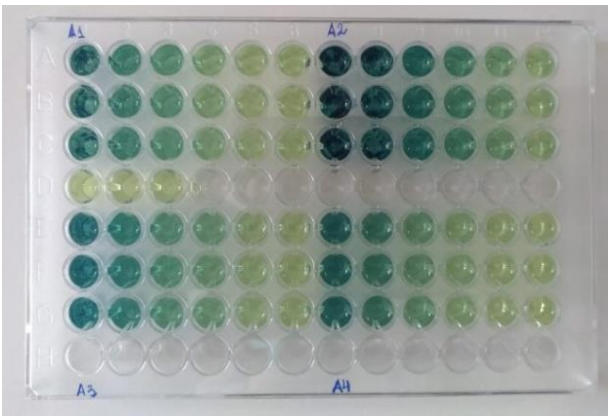


Fig.13. Determination of the reducing power.

4.3.3.2 Capture of the DPPH radical

The determination of antioxidant activity by the DPPH method was performed using the microplate reader. For the analysis, dilutions C1 to C7 of the hydroethanolic extract of grape seeds and skins were prepared.

A total of 30 μL of each of the different concentrations of extract and ethanol were mixed with 270 μL of ethanolic solution of DPPH (6 x 10^{-5} mol/L), homogenized and the mixture obtained was placed in the dark for 1 hour.

After the time, the solutions were transferred in quadruplicate to a microplate and their absorbance was read at 517 nm using a microplate reader (Epoch2, Biotek).

Free radical scavenging activity (RSA) was calculated as a function of the percentage of DPPH discoloration using Equation 24:

$$\%\, captation = \left[\frac{Abs_{DPPH} - Abs_{sol}}{Abs_{DPPH}}\right] x\ 100 \qquad (24)$$

Where Abs_{sol} represents the absorbance of the solution in the presence of extract at a certain concentration and Abs_{DPPH} represents the absorbance of the DPPH solution (blank reaction). The minimum concentration of antioxidant required to reduce the initial concentration of radical scavenging activity (EC50) by 50% was calculated by interpolation from the RSA percentage graph as a function of the sample concentration. All extracts were analyzed at least in duplicate, with quadruplicate measurements.

In Figure 14 there is a photograph with the samples of the hydroethanolic extract placed on a microplate for reading.

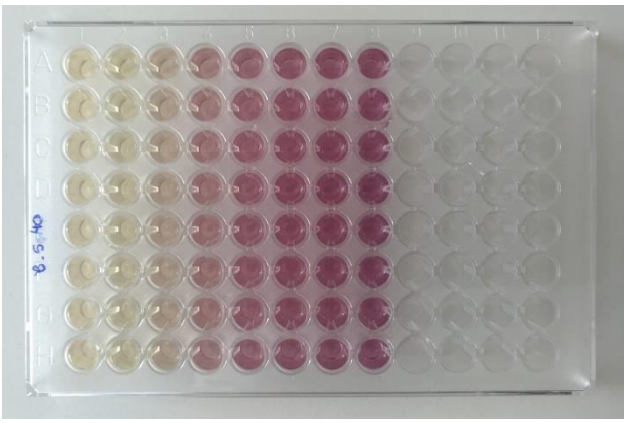


Fig.14. Determination of% DPPH capitation for hydroethanolic extract.

4.4 Analysis of the phenolic compounds by LC-DAD-ESI-MS/MS

4.4.1 Non-anthocyanin compounds

The extracts were analysed using a Dionex Ultimate 3000 HPLC instrument (Thermo Scientific, San Jose, CA, USA) equipped with a diode-array detector and coupled to a mass detector (LC-DAD-ESI/MSn). The chromatographic system consisted of a quaternary pump, an autosampler maintained at 5ºC, a degasser, a photodiode-array detector, an automatic thermostatic column compartment. The chromatographic separation was carried out on a Waters Spherisorb S3 ODS-2 C18, (3 μm, 4.6 mm × 150 mm, Waters, Milford, MA, USA) column thermostatted at 35 °C. The solvents used were: (A) 0.1% formic acid in water, (B) acetonitrile. The elution gradient established was isocratic 15% for 5 min, 15% B to 20% B over 5 min, 20-25% B over 10 min, 25-35% B over 10 min, 35-50% for 10 min, and re-equilibration of the column, using a flow rate of 0.5 mL/min. Double online detection was carried out in the DAD using 280, 330 and 370 nm as preferred wavelengths and in a mass spectrometer (MS) connected to HPLC system via the DAD cell outlet.

The mass spectrometer was operated in negative ion mode using Linear Ion Trap LTQ XL mass spectrometer (ThermoFinnigan, San Jose, CA, USA) equipped with an ESI source. Typical ESI conditions were nitrogen sheath gas 50 psi, spray voltage 5 kV, source temperature 325 °C, capillary voltage -20 V, and the tube lens offset was kept at voltage of -66 V. The full scan covered the mass range from m/z 100 to 1500. The collision energy used was 35 (arbitrary units). Data acquisition was carried out with Xcalibur® data system (ThermoFinnigan, San Jose, CA, USA).

The phenolic compounds were identified by comparing their retention times, UV-vis and mass spectra with those obtained with standard compounds, when available. Otherwise, compounds were tentatively identified comparing the obtained information with available data reported in the literature. For quantitative analysis, a calibration curve for each available phenolic standard was constructed based on the UV signal. For the identified phenolic compounds for which a commercial standard was not available, the quantification was performed through the calibration curve of another compound from the same phenolic group. The results were expressed as mg per g of extract.

4.4.2 Anthocyanin compounds

Chromatographic separation was achieved with a Waters Spherisorb S3 ODS-2 C18 (3 μm, 4.6 mm × 150 mm, Waters, Milford, MA, USA) column working at 35 °C. The solvents used were: (A) 0.1% trifluoroacetic acid (TFA) in water, (B) acetonitrile. The gradient elution followed these parameters: 10% B for 3 min, from 10 to 15% B for 12 min, 15% B for 5 min, from 15 to 18% B for 5 min, from 18 to 30% B for 20 min, from 30 to 35% B for 5 min, and from 35 to 10% B for 10 min. The resulting total run time was 60 minutes, followed by column reconditioning of 10 minutes, using a flow rate of 0.5 mL/min. Double online detection was carried out in the DAD using 520 nm as the preferred wavelength and in a mass spectrometer (MS) connected to HPLC system via the DAD cell outlet. MS detection was performed in positive mode, using a Linear Ion Trap LTQ XL mass spectrometer (Thermo Finnigan, San Jose, CA, USA) equipped with an ESI source. Nitrogen served as the sheath gas (50 psi); the system was operated with a spray voltage of 4.8 kV, a source temperature of 320 °C, a capillary voltage of 14 V. The tube lens offset was kept at a voltage of 75 V. The full scan covered the mass range from *m*/*z* 100 to 1500. The collision energy used was 20 (arbitrary units). Data acquisition was carried out with Xcalibur® data system (Thermo Finnigan, San Jose, CA, USA).

The identification of the anthocyanin compounds was performed using standard compounds, when available, by comparing their retention times, UV-vis and mass spectra; and also, comparing the obtained information with available data reported in the literature giving a tentative identification. For quantitative analysis, a calibration curve for each available phenolic standard was constructed based on the UV signal. For the identified anthocyanin for which a commercial standard was not available, the

quantification was performed through the calibration curve of the most similar available standard. The results were expressed as mg/g of extract.

4.5 Statistical Analysis

For all chemical analysis, the standard deviation of the data was calculated based on Equation 25 below:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{N}} \quad (25)$$

Where $\bar{x}$ is the average of the values obtained, N is the number of observations and x_i is the value of the observation.

For statistical analysis, the SISVAR software (v.5.7) was used, in which an analysis was performed using the Tukey Test (95% of significance level).

5 Results and discussion

5.1 Drying experiments

5.1.1 Conventional drying

Average values obtained for each statistical parameter were calculated and the values related to the quality of the adjustment for conventional models for the grape seeds are summarized in Table 3. The best statistical values closest to ideality are highlighted. All kinetic drying graphics obtained by adjusting the models for the conventional drying of grape seeds are shown in Annexes A-C of this work.

Table 3. Average of the statistical parameters for conventional drying of grape seeds.

Model name	χ^2	**NRM**	**MSE**	***EF***	***RMSE***
Approximation of diffusion	$4.33745x10^{-05}$	$8.133x10^{-03}$	$3.82x10^{-05}$	0.9992	$5.2x10^{-03}$
Hii et al	$4.38246x10^{-04}$	$1.80x10^{-02}$	$3.37x10^{-04}$	0.9881	$1.2x10^{-02}$
Henderson and Pabis	$3.91697x10^{-04}$	$2.617x10^{-02}$	$3.60x10^{-04}$	0.9957	$1.7x10^{-02}$
Logarithmic	$1.88048x10^{-04}$	$1.67x10^{-02}$	$1.65x10^{-04}$	0.9905	$1.1x10^{-02}$
Midilli et al	$3.50353x10^{-04}$	$2.00x10^{-02}$	$2.99x10^{-04}$	0.9907	$1.3x10^{-02}$
Newton	$6.26895x10^{-04}$	$3.45x10^{-02}$	$6.16x10^{-04}$	0.9945	$2.2x10^{-02}$
Page	$6.04062x10^{-05}$	$9.467x10^{-03}$	$5.56x10^{-05}$	0.9938	$6.1x10^{-03}$
Two terms	$3.85792x10^{-04}$	$2.487x10^{-02}$	$3.24x10^{-04}$	0.9974	$1.6x10^{-02}$

Although all the models presented a good fit, based on results, the model that best fit the experimental data was the Approximation of diffusion model. Figure 15 presents the kinetic drying curves predicted by this model in comparison to experimental data for all drying temperatures.

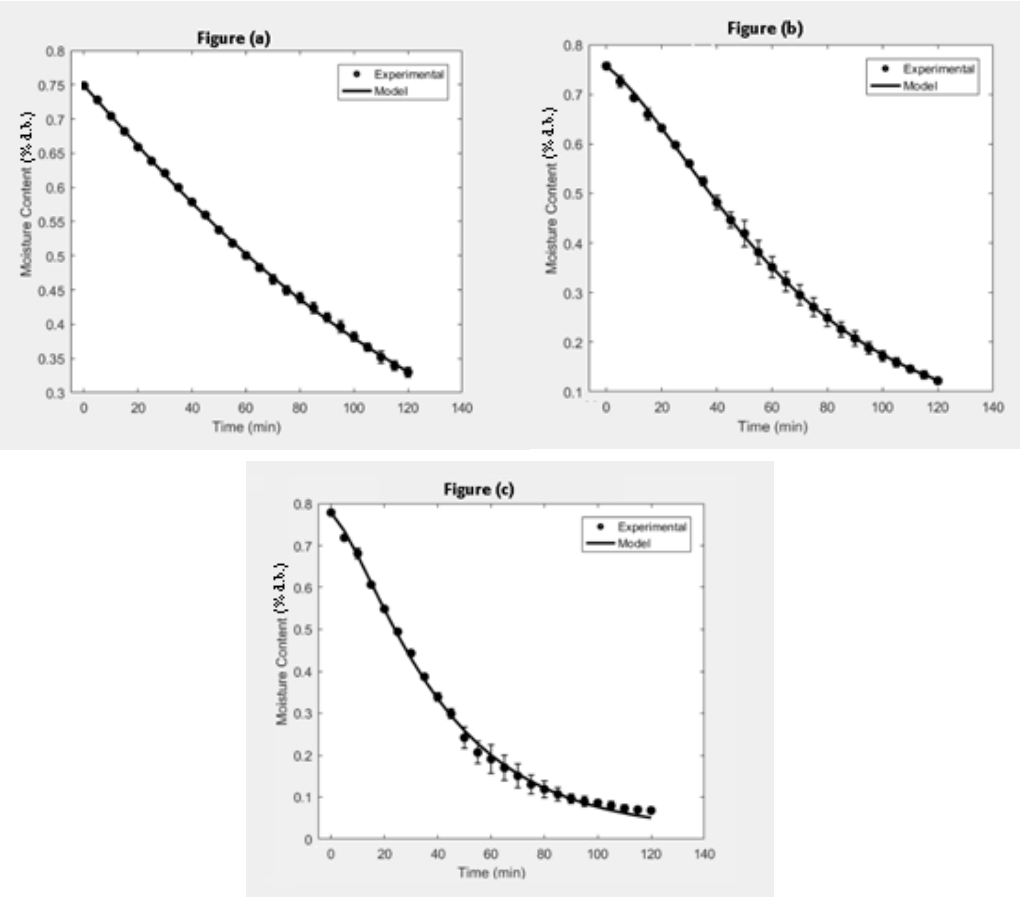


Fig.15. Moisture content for conventional drying of grape seeds estimated by Approximation of diffusion model at 40°C (a), 55°C (b) and 70°C (c), respectively.

Analogously for the conventional drying of grape skins, Table 4 shows the average of the statistical parameters obtained by each adjustment. The best fitting values are highlighted. All kinetic drying graphics obtained by adjusting the models for the conventional drying of grape skins are shown in Annexes D-F of this work.

Table 4. Average of the statistical parameters for conventional drying of grape skins.

Model name	χ^2	**NRM**	**MSE**	***EF***	***RMSE***
Approximation of diffusion	$1.2514x10^{-04}$	$8.433x10^{-04}$	$1.10x10^{-04}$	0.9991	$9.567x10^{-03}$
Hii et alx	$6.2600x10^{-04}$	$1.356x10^{-02}$	$4.87x10^{-04}$	0.9965	$1.63x10^{-02}$
Henderson and Pabis	$8.0726x10^{-04}$	$4.463x10^{-02}$	$7.37x10^{-04}$	0.9946	$2.52x10^{-02}$
Logarithmic	$1.5090x10^{-04}$	$9.533x10^{-03}$	$1.33x10^{-04}$	0.9989	$1.10x10^{-02}$
Midilli et alx	$3.0354x10^{-04}$	$1.320x10^{-02}$	$2.55x10^{-04}$	0.9969	$1.34x10^{-02}$
Newton	$1.2139x10^{-03}$	$2.630x10^{-02}$	$1.179x10^{-04}$	0.9915	$3.13x10^{-02}$
Page	$1.4249x10^{-04}$	$9.233x10^{-03}$	$1.31x10^{-04}$	0.9989	$1.05x10^{-02}$
Two terms	$5.1644x10^{-04}$	$1.570x10^{-02}$	$4.31x10^{-04}$	0.9967	$1.84x10^{-02}$

Based on these statistical parameters, the model that best fit the experimental data was also the Approximation of diffusion model. The graphic showing the comparison between the moisture content values of the material calculated by this model and the data obtained experimentally is shown in Figure 16. These results indicate that those models can be applied as auxiliar equations to simulation and design purposes.

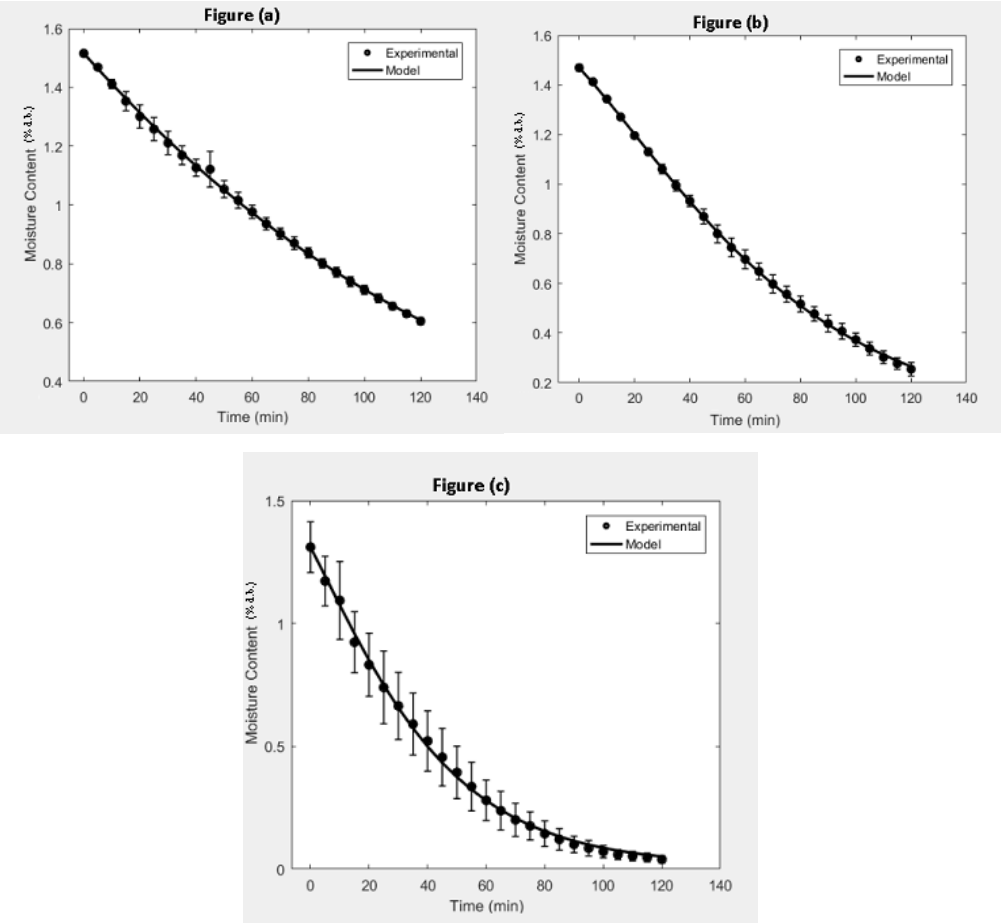


Fig.16. Moisture content for conventional drying of grape skins estimated by Approximation of diffusion model at 40°C (a),55°C (b) and 70°C (c), respectively.

5.1.2 Intermittent drying

Table 5 shows the averages of the statistical parameters related to the adjustment of the proposed intermittent drying model for grape seeds based on experimental data and the values obtained for the minimized objective function. These statistical parameters indicate that the proposed model resulted in a good fitting for both tempering periods.

Table 5. Average of the statistical parameters for intermittent drying of grape seeds.

Parameter	5 min	10 min
EF	0.993367	0.979497
χ^2	1.29×10^{-04}	1.30×10^{-04}
$RMSE$	9.49×10^{-03}	9.97×10^{-03}
ϕ	0.034487	0.011463

Figure 17 shows the graphs of the sample's moisture variation at a drying temperature of 70°C with the intermittences of 5 and 10 minutes (X is the moisture in % dry basis). All the graphics obtained by the modeling of the intermittent drying of grape seeds are disposed in the *Annex G* at the end of this work.

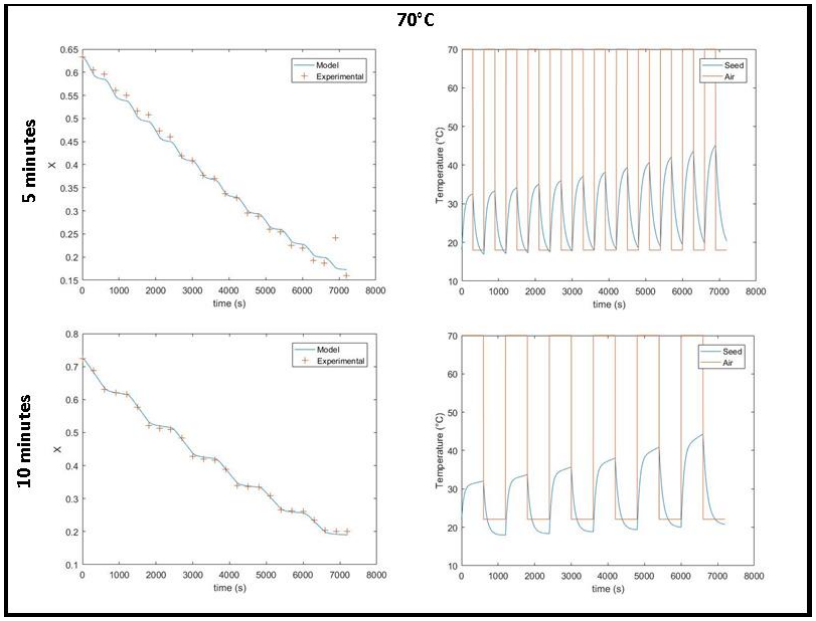


Fig.17. Moisture content for intermittent drying of grape seeds at 70°C with 5 and 10 minutes intermittence.

In Figure 17 it is possible to observe how the material's moisture and its temperature vary according to the proposed intermittency.

With the values obtained for the statistical parameters at each temperature and in both intermittence times (5 and 10 minutes) it's possible to observe that the adjusted model described better the drying with a intermittence of 5 minutes. A graph showing the experimental values of the moisture content of the grape seeds in comparison to the moisture content values predicted by the model is shown below in Figure 18. It can be inferred by this graphic that experimental data could be predicted by the intermittent drying model with a global maximum deviation of 10%

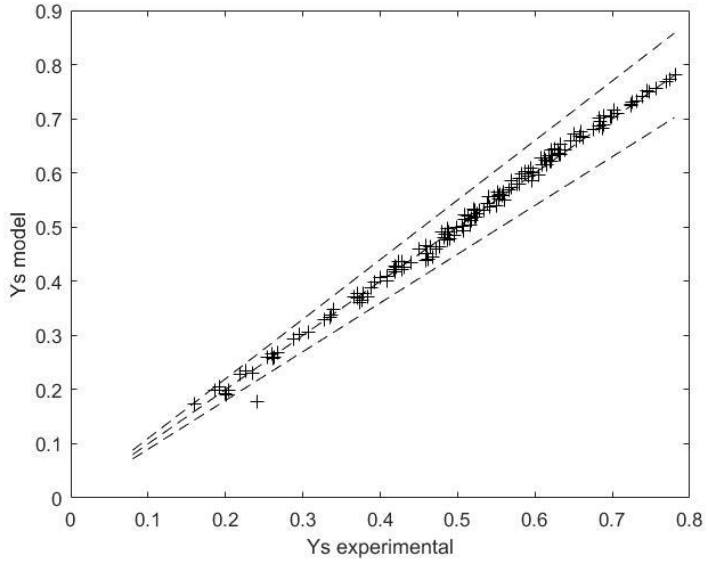


Fig.18. Material moisture proposed by the model versus Experimental material moisture.

The averages values obtained for the statistical parameters are relatively low, but could be improved. This is due to the fact that some of the experimental data show great variation in relation to the others, resulting in a worse adjustment to the model. This can be caused by human faults during the process or also by faults related to the equipment used, such as lack of calibration, malfunction, among others.

Table 6 presents the averages of the statistical parameters for the intermittent drying of grape skins and the values obtained for the minimized objective function. The parameters have similar values, what indicates that for both intermittences, the adjustment was satisfactory.

Table 6. Average of the statistical parameters for intermittent drying of grape skins.

Parameter	5 min	10 min
$\boldsymbol{EF}$	0.987514	0.987191
$\boldsymbol{\chi^2}$	7.22×10^{-04}	8.21×10^{-04}
$\boldsymbol{RMSE}$	2.25×10^{-02}	2.47×10^{-02}
ϕ	0.023262	0.023167

Figure 19 shows the graphs of the moisture variation of the sample at a drying temperature of 70°C with the intermittences of 5 and 10 minutes (X is the moisture in % dry basis). The graphics obtained for each condition are presented in *Annex H*.

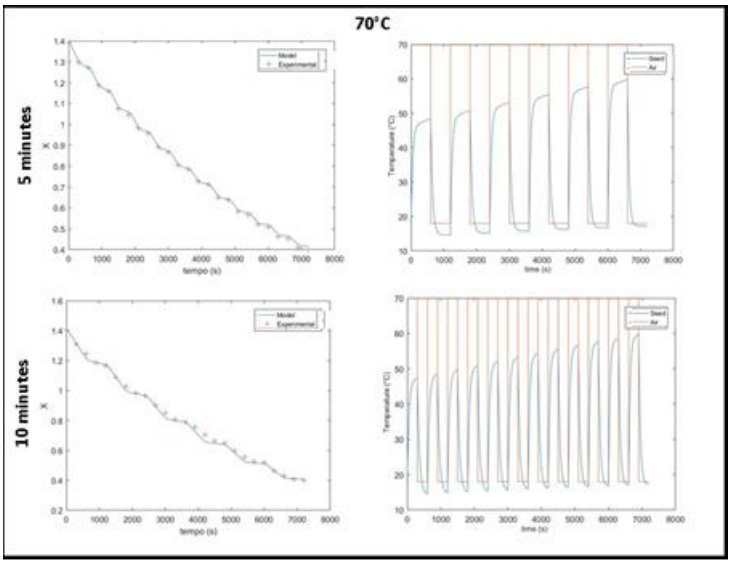


Fig.19. Moisture content for intermittent drying of grape skins at 70°C with 5 and 10 minutes intermittence.

It is possible to observe that for both intermittences the values obtained for the statistical parameters at each temperature and in both intermittence times (5 and 10 minutes) have similar values. In both cases the adjustment was satisfactory, but the 5-minute intermittence better suited the model. Figure 20 shows the material moisture calculated by the model in detriment to the moisture obtained experimentally. Evidencing that the experimental data could be predicted by the intermittent drying model with a global maximum deviation of 10%.

It is also possible to observe from all these results that drying air temperature variation impacts on samples drying kinetics. Figures 17 and 19 shows that drying curves presented higher slope when samples were in contact with hot air, leading to higher drying rates in comparison to drying rates when samples were in contact with air at room temperature. During these tempering periods, there is a small quantity of evaporated water, which can be observed by low slope values. However, those tempering periods are important to provide samples inner water stabilization, when there is water diffusion from center to sample's surface. This can lead to a reduction of process energy consumption in comparison to conventional operation, because the time samples are in contact with hot air are reduced and drying process are mainly controlled by diffusion of water inside samples for crops products. In addiction to that, it was verified that samples final moisture content were similar to both conventional and intermittent drying data for experiments conducted at the same hot air temperature, even

if drying curves for intermittent operation presented oscillations and conventional operation drying curves presented exponential patter without oscillations.

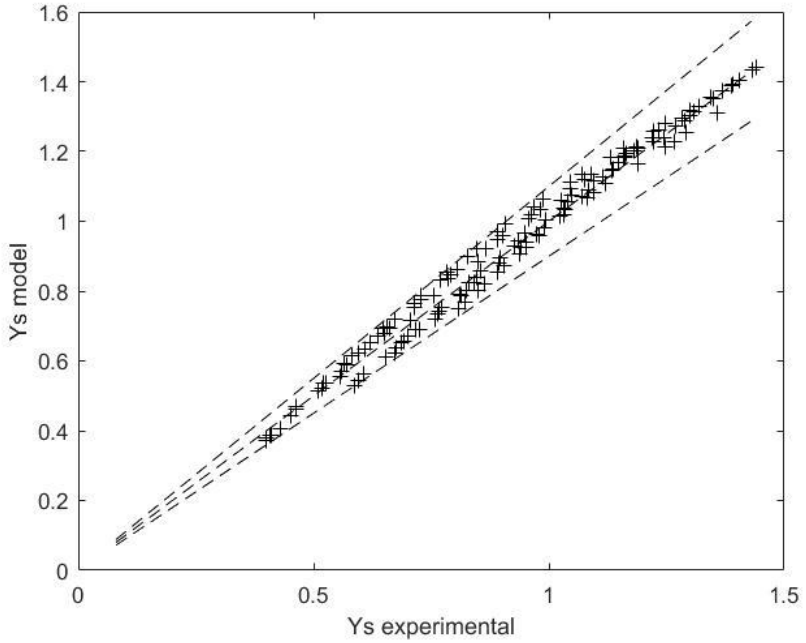


Fig.20. Material moisture proposed by the model versus Experimental material moisture.

5.2 Chemical Analysis

5.2.1 Extraction of phenolic compounds

In this work, approximately 2g of each sample submitted to drying processed was extracted with an hydroethanolic solution. Therefore, the values of moisture were determined for each sample (Table 7) and taken into account for calculations to minimize the interference of the moisture difference in each sample and in each type of drying performed.

Table 8 presents the values of the mass of the dry material for each of the drying modes for grape skins and grape seeds, as well as the sample mass after lyophilization and the yield of each extraction:

Table 7. Moisture content on wet basis of grape skin and seeds after the drying process.

Drying Mode	Final Moisture content on wet basis (%) - SKIN	Final Moisture content on wet basis (%) - SEEDS
Non-dried Sample	58.5363	43.4996
Conv. 40°C	32.3177	21.7683
Conv. 55°C	20.2358	10.8827
Conv. 70°C	3.7960	6.3825
Drying Mode	**Final Moisture content on wet basis (%) - SKIN**	**Final Moisture content on wet basis (%) - SEEDS**
5 min Int. 40°C	44.7248	34.1019
5 min Int. 55°C	35.8822	26.8093
5 min Int. 70°C	28.5172	13.3793
10 min Int. 40°C	40.0898	31.4562
10 min Int. 55°C	37.0317	27.1663
10 min Int. 70°C	25.8808	29.6904

Table 8. Extraction of phenolic compounds from grape skin and seeds.

Drying mode	Mass for extraction(g)	Mass of dry material (g)	Mass after lyophilization (g)	Yield (%)
Grape Skin				
Non-dried Skin	2.0244	0.8394	0.1567	6.1823
Conv. 40°C	2.0076	1.3588	0.1838	9.1552
Conv. 55°C	2.0097	1.6030	0.1190	5.9213
Conv. 70°C	2.0097	1.9334	0.2574	12.8079
5 min Int. 40°C	2.0271	1.1205	0.0513	2.5327
5 min Int. 55°C	2.0211	1.2959	0.1953	9.6611
5 min Int. 70°C	2.029	1.4504	0.1651	8.1375
10 min Int. 40°C	2.0101	1.2043	0.1810	9.0045
10 min Int. 55°C	2.018	1.2707	0.2105	10.4311
10 min Int. 70°C	2.0007	1.4829	0.2329	11.6409
Grape Seeds				
Non-dried Seeds	2.0238	1.2533	0.7081	0.1044
Conv. 40°C	2.0246	1.7896	1.4000	0.1071
Conv. 55°C	2.0727	1.8016	1.6055	0.13143
Conv. 70°C	2.0946	1.7791	1.6655	0.0881
5 min Int. 40°C	2.0487	1.312	0.8646	0.1077
5 min Int. 55°C	2.0336	1.8711	1.3695	0.13785
5 min Int. 70°C	2.0096	1.9536	1.6922	0.1297
10 min Int. 40°C	2.0116	1.6371	1.1221	0.1189
10 min Int. 55°C	2.0246	1.7302	1.2602	0.1908
10 min Int. 70°C	2.0073	1.3988	0.9835	0.09034

5.2.2 Determination of bioactive compounds

5.2.2.1 Total phenolic compounds

Drying methods and process conditions impact on the stability of phenolic compounds because high temperatures can lead to degradation of phenolic compounds and affect antioxidant activity of grape pomace (Carmona et al, 2018). Table 9 shows the average of the values of total phenolic compounds of grape skin and seeds in mg_{GAE} per gram of dry residue ($mg_{GAE}\ g_{dr}^{-1}$) as well as the standard deviation and the statistical analysis of each experiment. The data were separated by temperature for better comparison.

Table 9. Content of total phenolic compounds of grape skin and seeds extracts.

Drying Temperature	Drying Mode	mg_{GAE}/g_{dr}	Standard Deviation	Statistical analysis
Grape Skin				
-	Non-dried Skin	149.7	0.6	a6
	Conventional	90.8	0.8	a2
40°C	5 min Intermittent	130	2	a5
	10 min Intermittent	94	2	a2
	Conventional	75	2	a1
55°C	5 min Intermittent	101	2	a3
	10 min Intermittent	113	1	a4
	Conventional	68.8	0.7	a1
70°C	5 min Intermittent	92	1	a2 a3
	10 min Intermittent	99	4	a2 a3
Grape Seeds				
-	Non-dried Seed	359	4	a8
	Conventional	111.1	0.8	a3
40°C	5 min Intermittent	174	3	a4
	10 min Intermittent	230.4	0.3	a6
	Conventional	78.2	0.1	a1
55°C	5 min Intermittent	91.6	0.1	a2
	10 min Intermittent	202	1	a5
	Conventional	92.8	0.7	a2
70°C	5 min Intermittent	161.8	0.2	a4
	10 min Intermittent	281	5	a7

The values of total phenolic compounds (TPC) in grape skin ranged from 149.74 mg_{GAE}/g_{dr} for the non-dried sample to 68.8 mg_{GAE}/g_{dr} for the conventional drying at 70°C. It can be observed in Table 9 that the sample with the highest concentration is the non-dried (in natura) one, as expected. This is because the material has not undergone any

heat treatment and degradation of phenolic compounds during the drying is mainly due to thermal effects in high temperatures above 40°C (Carmona el al., 2018). Besides that, for all drying temperatures, the conventional mode was the one who returned the lowest values and for the highest temperatures (5 and 70°C) the 10-minute intermittent drying performed better possibly because it was less aggressive to the material.

Through statistical analysis it is possible to observe that, for grape skin, the conventional drying methods at temperatures of 55 and 70°C are not significantly different for the Tukey test with a significance level of 95%. The conditions that presented the highest TPC values are statistically different from each other.

The TPC levels in grape seeds ranged from 358.87 mg_{GAE}/g_{dr} for the natural sample to 78.16 mg_{GAE}/g_{dr} for samples submitted to conventional drying at 55°C. For all drying temperatures, the drying mode that represented the best value was the intermittent method with 10-minutes of intermittence. This difference was accentuated with the increase of the drying temperature, demonstrating how the intermittent method is less aggressive to the material submitted to the process. The conventional method, on the other hand, was the one that returned the worst values of antioxidant activity which can be implied by the higher time that samples are in contact with hot air. Besides temperature, this can possibly be related also to the fact that the oven used was ventilated, thus increasing the possibility of oxidation phenomena.

Statistical analysis for grape seeds indicated that most of the drying methods used are significantly different from each other and this factor is extended to the values highlighted in Table 9.

Figure 21 shows the effect of drying air temperature and drying mode on total phenolic compounds of grape skin.

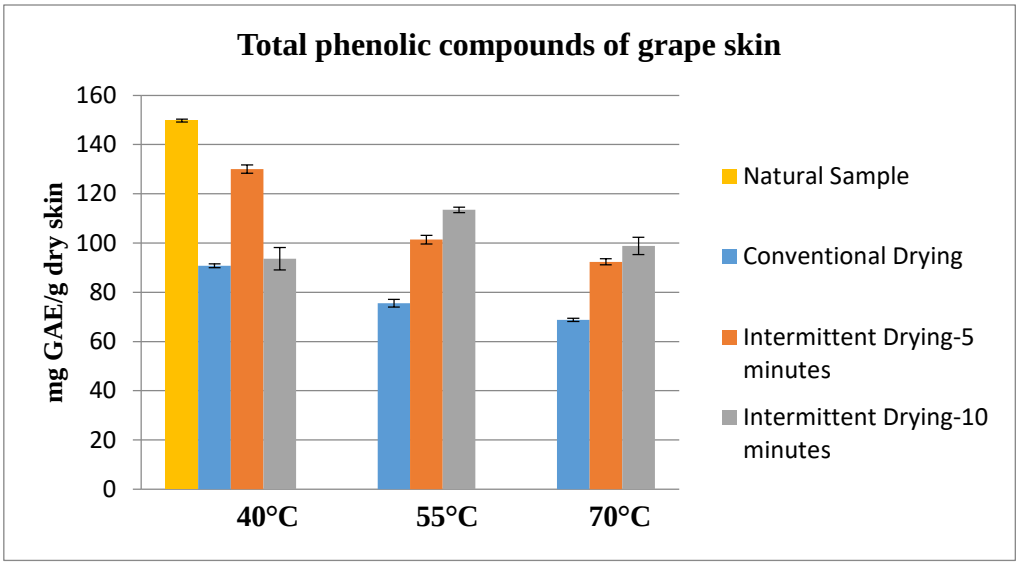


Fig.21. Effect of drying air temperature and drying mode on total phenolic compounds (TPC) of grape skin.

The drying process reduces the levels of TPC for all types of drying. However, it is worth mentioning that there was a better preservation of these levels for intermittent drying at a temperature of 40°C and 5 minutes of intermittence (for grape skin) and 70°C and 10 minutes of intermittence (for grape seeds). The increase in drying temperature caused a decrease in TPC for the conventional and intermittent drying with 5 minutes of intermittence, while for a 10-minute of intermittence there was a better preservation of TPC levels from 40 to 55°C and then further degradation from 55 to 70°C, which may have been caused by some practical or laboratory error. In addition, TPC was lower at conventional drying, regardless of the applied drying temperature. The intermittent drying mode is less aggressive because it alternates the exposure time to the drying air temperature and the ambient temperature, resulting in a final product with better quality and consequently higher concentrations of phenolic compounds.

Figure 22 shows how the drying method affects the TPC levels of grape seeds. Through the analysis of Figure 22 it is possible to observe that the conventional drying method is the one that presented higher degradation on TPC levels. The intermittent drying methods are the most affected by the increase in temperature used in the process and in all cases the TPC level of the sample decreases from 40 to 55°C and increases from 55 to 70°C.

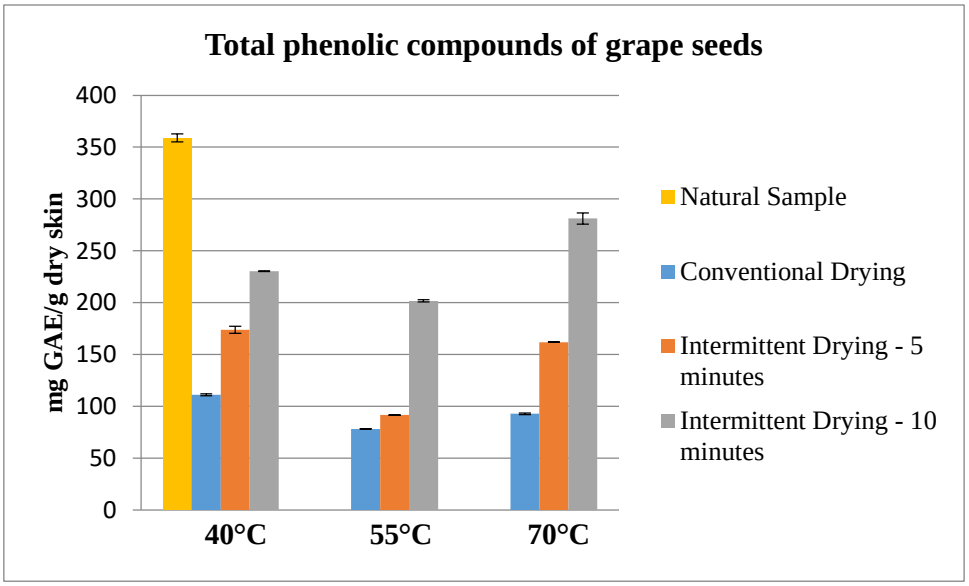


Fig.22. Effect of drying air temperature and drying mode on total phenolic compounds (TPC) of grape seeds.

In general, for both types of samples (skins and seeds) the intermittent method was the one that returned the highest preservation of TPC levels in comparison to in natura samples data. It was also observed that the higher the drying temperature applied, the higher the difference between the intermittent and the conventional TCP levels.

5.2.2.2 Total flavonoid content

Flavonoids are very important for their associated health benefits due to their antioxidant properties. Some authors have reported that flavonoids such as rutin and quercetin shows potent antioxidant activity (Xu et al., 2017). The average of the total flavonoid content (TFC) of grape skin is presented in Table 12 in mg_{CE} per gram of dry residue ($mg_{CE}\ g_{dr}^{-1}$). The data were separated by temperature and the drying conditions that returned a higher concentration of total flavonoid content are highlighted.

The TFC in grape skin were in the range 38.5 $mg_{CE}.g_{dr}^{-1}$, for the sample dried at 70°C by conventional mode, to 72 $mg_{CE}.g_{dr}^{-1}$, for non-dried samples. As observed for the TPC, for all drying temperatures, the conventional drying method was the one that was most aggressive to the material, consequently returning the lowest TFC values.

Among the drying conditions that returned the best values, the drying performed with 5 minutes of intermittence at 40°C was not significantly different from the average values obtained by in natura samples. At temperatures of 55 and 70°C the highlighted

values are not significantly different from each other, however they are significantly different from the value at 40°C.

Table 10. Content of total flavonoid content of grape skin and seeds extracts.

Drying Temperature	Drying Mode	mg_{CE}/g_{dr}	Standard Deviation	Statistical analysis
Grape Skin				
-	Non-dried Skin	72	2	a5
	Conventional	48.01	0.09	a2 a3
40°C	5 min Intermittent	67	3	a5
	10 min Intermittent	53.3	0.7	a3 a4
	Conventional	39.3	0.6	a1
55°C	5 min Intermittent	49	1	a2 a3 a4
	10 min Intermittent	49.2	0.9	a2 a3 a4
	Conventional	38.5	0.3	a1
70°C	5 min Intermittent	43	2	a1 a2
	10 min Intermittent	56.2	0.3	a4
Grape Seeds				
-	Non-dried Seed	186	9	a6
	Conventional	70	2	a1 a2 a3 a4
40°C	5 min Intermittent	102.8	0.8	a4 a5
	10 min Intermittent	77.2	0.4	a3 a4 a5
	Conventional	41.2	0.6	a1 a2
55°C	5 min Intermittent	85.8	0.9	a3 a4 a5
	10 min Intermittent	79.6	2.8	a2 a3 a4 a5
	Conventional	34	1	a1
70°C	5 min Intermittent	55.9	0.2	a1 a2 a3
	10 min Intermittent	99	6	a4 a5

TFC values in grape seeds ranged from 186.01 mg_{CE}/g_{dr} for the non-dried seed to 34.34 mg_{CE}/g_{dr} for the conventional drying at 70°C. For all drying temperatures the conventional drying was the one that most affected the TFC levels, returning the lowest values. For milder temperatures (40 and 55°C), the drying method that proved to be the most effective retaining the TFC levels was the one with 5 minutes of intermittence while for higher temperatures (70°C) with 10 minutes of intermittence was responsible for presenting a better TFC level preservation.

Tukey Test (95% of significance level) indicated that highlighted conditions for grape seeds, as highlighted in Table 10 are not significantly different from each other.

Figure 23 presents comparative data showing the effect of drying air temperature and drying mode on total flavonoids content. The drying method that was most affected

by the increase in the temperature was the drying method with 5 minutes of intermittence, which showed the biggest reduction. The conventional drying method and the 10-minute of intermittence method were less affected, but the 10-minute intermittent method stood out considerably at 70°C, showing to be the best option for higher temperatures.

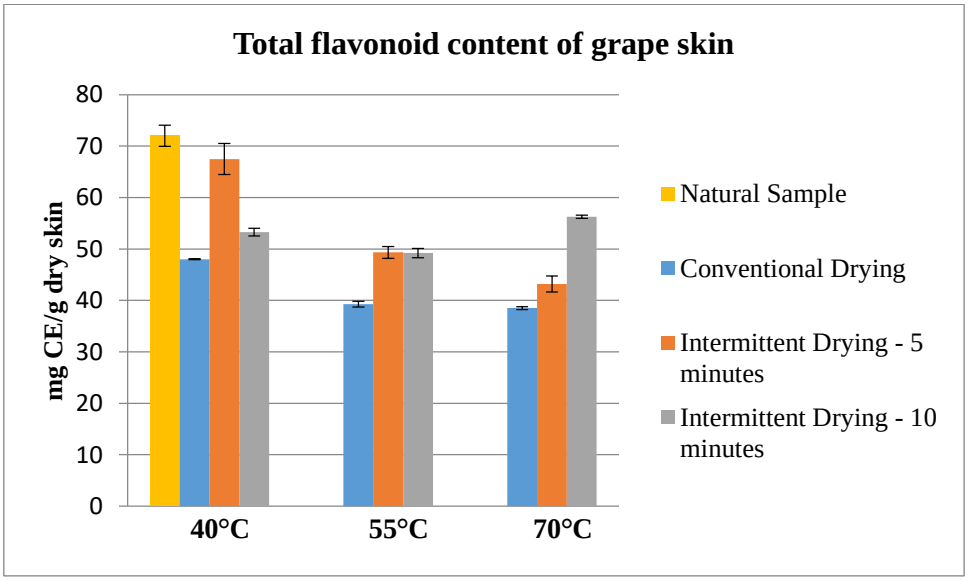


Fig.23. Effect of drying air temperature and drying mode on total flavonoids content (TFC) of grape skin.

Figure 24 shows the effect of temperature and drying mode on the TFC levels of grape seeds:

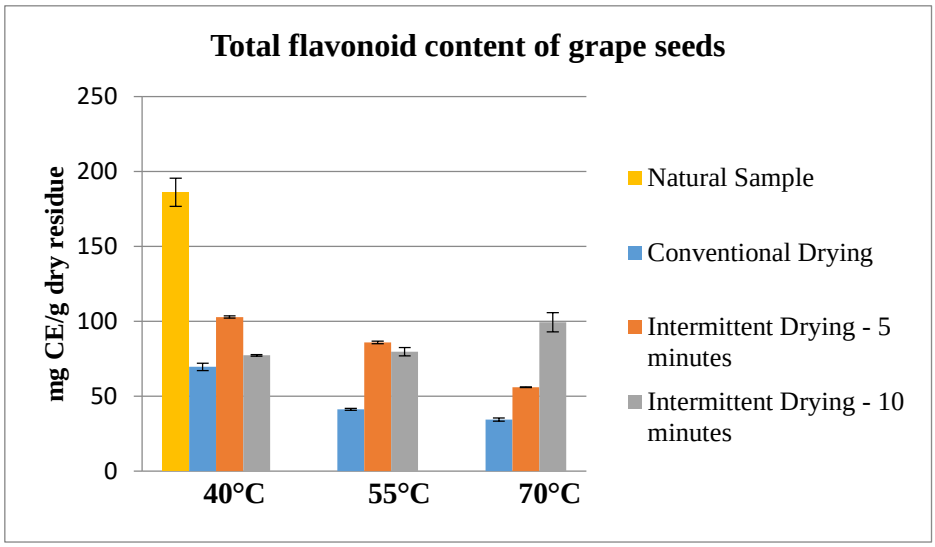


Fig.24. Effect of drying air temperature and drying mode on total flavonoids content (TFC) of grape seeds.

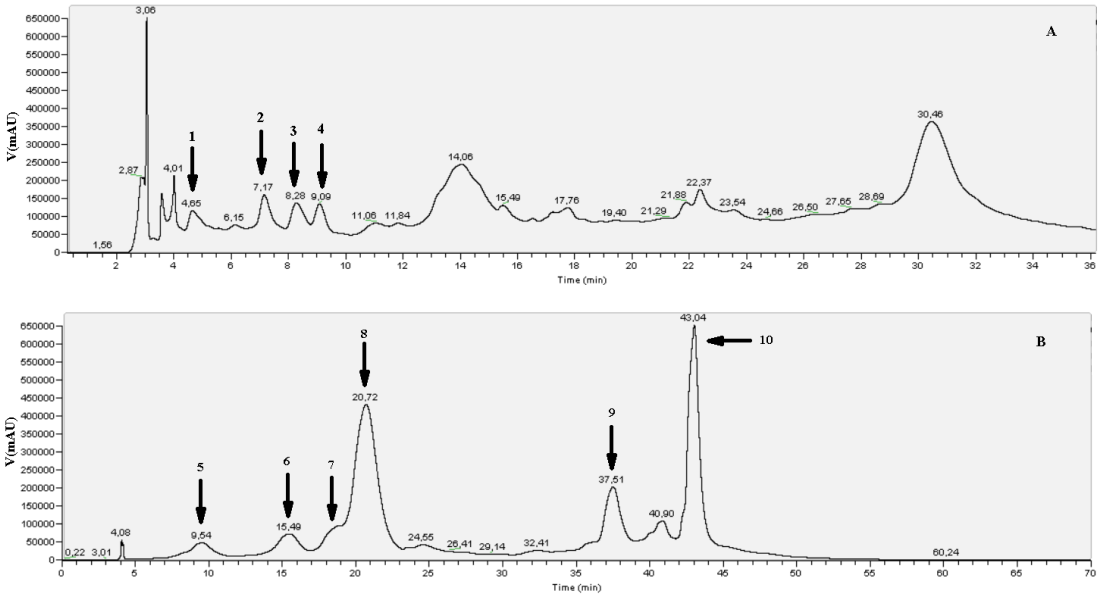
It can be observed significant difference between the in natura sample and the ones submitted to drying. The conventional and 5-minute of intermittence methods decreased the TFC levels with the increase of drying temperature, while the opposite occurs with the 10-minute of intermittence method.

In general, the intermittent method returned a better preservation of bioactive compounds of the final product for grape skins and seeds. This quality preservation is observed by the higher levels of TFC. It is also clear that with the increase in the drying temperature, the increase in the flashing period also benefits the quality of the final product.

5.3 Analysis of the phenolic compounds by LC-DAD-ESI-MS/MS

Ten and thirteen phenolic compounds (non-anthocyanin and anthocyanin) were tentatively identified in the ethanol/water (20:80, v/v) extracts prepared from grape skins and grape seeds, respectively (Table 11). The identified compounds comprised seven flavan-3-ols (catechin and epicatechin derivatives), six anthocyanins (malvidin, petunidin and peonidin derivates) and four hydroxicinnamic acid derivatives.

Figure 25 presents an exemplificative chromatogram evidencing the phenolic profile of the hydroethanolic extracts obtained from grape pomace skins and seeds.



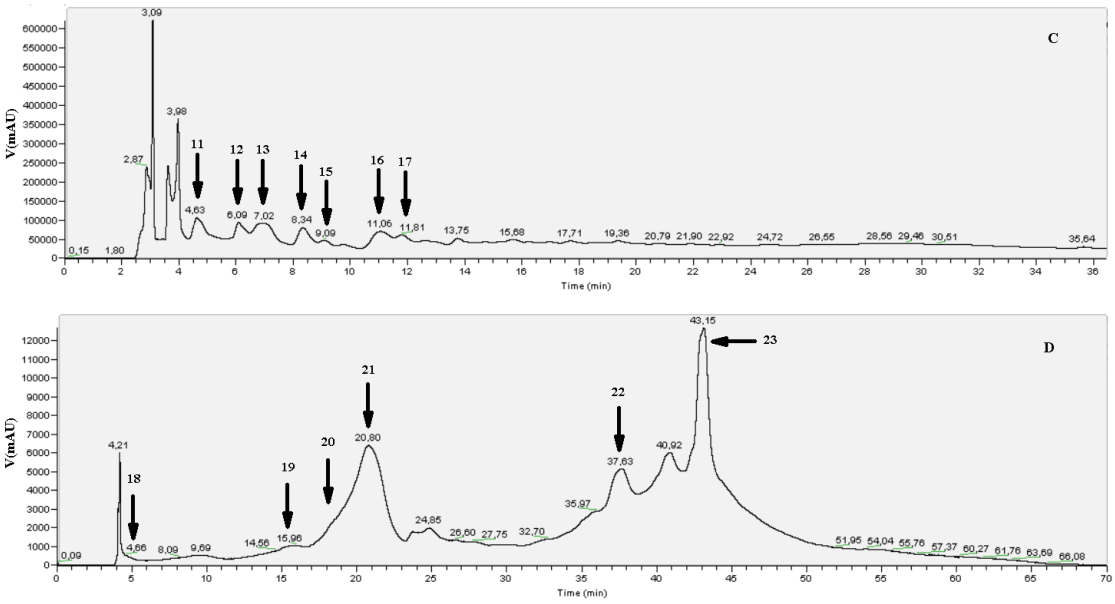


Fig. 25. Exemplificative HPLC chromatograms showing the non-anthocyanin phenolic profile recorded at 280 nm (A) and anthocyanin profile recorded at 520 nm (B) of the hydroethanolic extract of the grape skin, and non-anthocyanin phenolic profilerecorded at 280 nm (C) and anthocyanin profile recorded at 520 nm (D) of the hydroethanolic extract of the grape seeds.

Table 11 presents the retention time (Rt), wavelengths of maximum absorption (λmax), mass spectral data and tentative identification of the phenolic compounds (non-anthocyanin and anthocyanin) in the hydroethanolic extracts of grape pomace.

Peaks 1, 2, 3 and 11 were identified as phenolic acids derivatives. Peaks 1 and 11 ($[M-H]^-$ at *m/z* 341) presented MS^2 fragments at *m/z* 179 (-162 u) being both tentatively identified as caffeic acid hexoside. Similarly, two *p*-coumaric acid hexosides (peaks 2 and 3) were also tentatively identified, because both presented a pseudomolecular ion $[M-H]^-$ at *m/z* 325 and a unique MS^2 fragment at *m/z* 163 (*p*-coumaric acid), corresponding to the loss of an hexosyl moiety (162 u).

Peaks 4 and 12-17 were identified as flavan-3-ols. Peaks 12 and 14 were positively identified as (+)-catechin and (−)-epicatechin, respectively, by comparison with commercial standards taking into account their retention time, mass and UV–vis spectra. Peak 13 and 17 ($[M-H]^-$ at *m/z* 577) presented MS^2 fragments at *m/z* 451, 425, and 407 (-126 mu, -152 mu and -152-18 mu, respectively) and also *m/z* 289 and 287, coherent with the loss of two (epi)catechin units, being therefore tentatively identified as B-type (epi)catechin dimers. On the other hand, peaks 4 and 15 ($[M-H]^-$ at *m/z* 865) and 16 ($[M-H]^-$ at *m/z* 1153), were assigned as B-type (epi)catechin trimers and tetramer, respectively (Peixoto et al., 2018).

Table 11. Retention time (Rt), wavelengths of maximum absorption (λmax), mass spectral data and tentative identification of phenolic compounds (non-anthocyanin and anthocyanin) in the hydroethanolic extracts of grape pomace.

Peak	Rt (min)	λ_{max}	$[M-H]^-$ (m/z)	MS^2(m/z)	Tentative identification
			Grape Skin		
Non-anthocyanin compounds					
1	4.7	326	341	179(100), 135(23)	Caffeic acid hexoside
2	7.2	311	325	163(100), 119(25)	*p*-Coumaric acid hexoside
3	8.3	312	325	163(100), 119(25)	*p*-Coumaric acid hexoside
4	9.1	278	865	577(50). 451(30), 425(100), 407(38), 289(20)	β-Type (epi)catechin trimer
Anthocyanin compounds					
5	9.6	522	465	303(100)	Peonidin-3-*O*-glucoside
6	15.5	523	479	317(100)	Petunidin-3-*O*-glucoside
7	18.6	519	463	331(100)	Malvidin-O-pentoside
8	20.6	525	493	331(100)	Malvidin-3-O-glucoside
9	37.5	527	535	331(100)	Malvidin-3-*O*-acetyl-glucoside
10	42.8	530	639	331(100)	Malvidin-3-*O*-*p*-coumarouylglucoside
			Grape Seeds		
Non-anthocyanin compounds					
11	4.7	326	341	179(100), 135(23)	Caffeic acid hexoside
12	6.1	280	289	245(100), 205(26). 179(12)	(+)-Catechin
13	6.9	280	577	451(30), 425(100), 407(38), 289(20)	β-Type (epi)catechin dimer
14	8.4	280	289	245(100), 205(14), 179(8)	(-)-Epicatechin
15	9.1	278	865	577(48), 451(33), 425(100), 407(45), 289(20)	β-Type (epi)catechin trimer
16	11.1	279	1153	865(34), 577(60), 451(30), 425(100), 407(28), 289(20)	β-Type (epi)catechin tetramer
17	11.8	280	577	451(40), 425(100), 407(19). 289(10)	β-Type (epi)catechin dimer
Anthocyanin compounds					
18	9.6	522	465	303(100)	Peonidin-3-*O*-glucoside
19	15.5	523	479	317(100)	Petunidin-3-*O*-glucoside
20	18.6	519	463	331(100)	Malvidin-O-pentoside
21	20.6	525	493	331(100)	Malvidin-3-O-glucoside
22	37.5	527	535	331(100)	Malvidin-3-*O*-acetyl-glucoside
23	42.8	530	639	331(100)	Malvidin-3-*O*-*p*-coumarouylglucoside

The remaining compounds (peak 5-10) corresponded to the anthocyanin compounds. Peaks 5, 6 and 8 were positively identified as peonidin-3-*O*-glucoside, petunidin-3-*O*-glucoside, and malvidin-3-*O*-glucoside, by comparison with commercial standards, taking into account the chromatographic characteristics. The peaks 7, 9 and 10 were were identified taking into account the identifications performed by Kammerer, Kljusuric, Carle, & Schieber (2005), being tentatively identified as malvidin glycoside derivatives.

Tables 12 and 13 presents the quantification of the phenolic compounds present in all extracts. Flavan-3-ols were the main family of non-anthocyanin compounds present in the hydroethanolic extracts of grape skin. Regarding anthocyanins, the major compounds were malvidin derivatives. For the grape seeds samples, catechin and epicatechin were the most abundant molecules. As expected, anthocyanins in grape seeds samples presented concentrations significantly smaller than the ones in grape skin samples. Some differences were observed compared to the anthocyanins reported previously by Peixoto et al. (2018) in grape pomace, which can be related to different grape cultivars and edaphoclimatic conditions associated to the grape's growth.

For grape skin samples, anthocyanin compounds were the most affected by the increase of the drying temperature. The drying method that had the most impact on total compounds content was the conventional one, which is in good agreement with the results obtained for TPC determinations, used as fast screening assay. Also, in both methods, the 10 min intermittence treatment showed a good preservation of compounds. Nevertheless, while the Folin assay evidenced a reduced effect when drying at 40 ºC with 5 min intermittence, the same was not obtained for the individual compound's quantification.

For the grape seeds sample, a lower content of phenolic compounds was obtained for the in natura samples, which was not expected. This result can be possibly related either to some damage of the sample during storage or to the fact that the same extract as obtained for non-anthocyanins was used extraction instead of performing the extraction with methanol containing 0.5% trifluoroacetic acid, as previously described (Gonçalvez et al., 2017; Peixoto et al., 2018).

Table 12. Quantification of phenolic compounds (non-anthocyanin and anthocyanin) in the hydroethanolic extracts of grape skin (mg/$g_{extract}$ ± standard deviation).

Peak	Compound	Non-dried Sample	Conventional			Intermittent – 5 minutes			Intermittent – 10 minutes		
			40°C	55°C	70°C	40°C	55°C	70°C	40°C	55°C	70°C
1	Caffeic acid hexoside	0.068±0.001	0.054±0.001	0.096±0.001	0.13±0.01	0.054±0.001	0.139±0.001	0.078±0.001	0.035±0.001	0.0669±0.001	0.0939±0.001
2	*p*-coumaric acid hexoside	0.45±0.02	0.21±0.01	0.328±0.001	0.23±0.01	0.43±0.02	0.407±0.001	0.42±0.02	0.24±0.01	0.2384±0.001	0.26±0.01
3	*p*-coumaric acid hexoside	0.42±0.02	0.22±0.01	0.32±0.01	0.24±0.01	0.39±0.01	0.41±0.01	0.38±0.01	0.237±0.001	0.231±0.01	0.27±0.01
4	β-Type (epi)catechin trimer	0.90±0.03	0.72±0.01	0.858±0.001	0.79±0.03	0.963±0.001	1.191±0.001	1.08±0.07	1.07±0.03	0.74±0.02	0.65±0.01
	Total	1.84±0.01	1.20±0.03	1.61±0.01	1.40±0.05	1.84±0.02	2.153±0.001	2.0±0.1	1.58±0.04	1.27±0.03	1.27±0.01
5	Peonidin-3-*O*-glucoside	2.71±0.01	2.21±0.01	2.5±0.1	1.29±0.02	2.66±0.01	1.98±0.06	2.34±0.07	2.20±0.03	2.24±0.03	2.44±0.02
6	Petunidin-3-*O*-glucoside	4.01±0.08	3.12±0.03	3.8±0.1	1.52±0.03	3.4±0.1	3.0±0.1	3.31±0.07	3.384±0.001	3.236±0.001	4.2±0.1
7	Malvidin-*O*-pentoside	6.1±0.2	4.45±0.04	5.4±0.2	1.63±0.05	5.4±0.4	2.91±0.08	6.0±0.4	5.2±0.2	4.9±0.2	6.6±0.2
8	Malvidin-3-*O*-glucoside	22.5±0.4	14.0±0.6	18.2±0.4	4.71±0.03	14.1±0.3	15.7±0.1	19.1±0.1	16.2±0.5	21.0±0.5	22.6±0.7
9	Malvidin-3-*O*-acetyl-glucoside	9.79±0.05	5.7±0.1	6.19±0.08	2.21±0.01	5.50±0.06	4.45±0.08	7.0±0.4	5.5±0.2	6.5±0.2	6.8±0.3
10	Malvidin-3-*O*-*p*-coumarouylglucoside	32.4±0.2	26.82±0.04	22.5±0.2	5.69±0.03	17.78±0.09	10.35±0.06	32.2±0.2	20.8±0.2	22.7±0.2	22.2±0.2
	Total	77.55±0.01	56.3±0.9	58.7±0.4	17.1±0.1	48.8±0.2	38.4±0.1	70.0±0.3	53±1	61±1	64.9±0.1

The following calibration curves were used for compound's quantification, 1: y = 388345x+406369 (caffeic acid); 2 and 3: y = 301950x+6966.7 (*p*-coumaric acid); 4: y = 84950x-23200 (catechin); 5-10: y = 151438x - 3E+06 (peonidin-3-O-glucoside)

Table 13. Quantification of phenolic compounds (non-anthocyanin and anthocyanin) in the hydroethanolic extracts of grape seeds (mg/$g_{extract}$ ± standard deviation).

Peak	Compounds	Non-dried Sample	Conventional			Intermittent – 5 minutes			Intermittent – 10 minutes		
			40°C	55°C	70°C	40°C	55°C	70°C	40°C	55°C	70°C
11	Caffeic acid hexoside	0.13±0.01	0.177±0.001	0.15±0.01	0.158±0.001	0.035±0.001	0.13±0.01	0.14±0.01	0.193±0.001	0.141±0.001	0.126±0.001
12	(+)-Catechin	0.051±0.001	0.305±0.001	0.203±0.001	0.22±0.01	0.26±0.01	0.33±0.01	0.428±0.001	0.65±0.02	0.40±0.02	0.378±0.001
13	β-Type (epi)catechin dimer	0.13±0.01	0.30±0.01	0.28±0.02	0.24±0.02	0.124±0.001	0.46±0.04	0.49±0.01	0.66±0.02	0.42±0.02	0.39±0.01
14	(-)-Epicatechin	0.09±0.01	0.409±0.001	0.22±0.02	0.28±0.01	0.324±0.001	0.37±0.01	0.53±0.02	0.78±0.02	0.44±0.02	0.48±0.03
15	β-Type (epi)catechin trimer	0.015±0.001	0.11±0.01	0.09±0.01	0.07±0.01	0.066±0.001	0.11±0.01	0.17±0.01	0.19±0.01	0.12±0.01	0.125±0.001
16	β-Type (epi)catechin tetramer	0.14±0.01	0.28±0.02	0.355±0.001	0.30±0.01	0.206±0.001	0.27±0.01	0.33±0.01	0.31±0.02	0.29±0.02	0.25±0.02
17	β-Type (epi)catechin dimer	0.075±0.001	0.21±0.01	0.194±0.001	0.18±0.01	0.116±0.001	0.19±0.01	0.279±0.001	0.263±0.001	0.225±0.001	0.220±0.001
	Total	0.63±0.02	1.80±0.01	1.49±0.01	1.44±0.01	1.13±0.02	1.85±0.06	2.38±0.01	3.05±0.03	2.02±0.03	1.97±0.05
18	Peonidin-3-*O*-glucoside	0.911±0.001	0.945±0.001	nd	0.92±0.01	0.945±0.001	1.020±0.001	2.046±0.001	1.033±0.001	0.937±0.001	1.018±0.001
19	Petunidin-3-*O*-glucoside	0.920±0.001	0.956±0.001	nd	0.94±0.01	0.958±0.001	1.056±0.001	2.100±0.001	1.129±0.001	0.975±0.001	1.057±0.001
20	Malvidin-O-pentoside	0.97±0.01	0.993±0.001	nd	0.96±0.01	0.990±0.001	1.08±0.01	2.273±0.001	1.20±0.01	1.004±0.001	1.131±0.001
21	Malvidin-3-*O*-glucoside	0.918±0.001	1.208±0.001	1.032±0.001	1.02±0.01	1.20±0.02	1.68±0.02	3.22±0.06	1.758±0.001	1.36±0.01	1.78±0.01
22	Malvidin-3-*O*-acetyl-glucoside	0.926±0.001	0.99±0.01	1.031±0.001	0.95±0.01	0.991±0.001	1.13±0.01	2.27±0.01	1.27±0.02	1.02±0.01	1.17±0.001
23	Malvidin-3-*O*-*p*-coumarouylglucoside	0.932±0.001	1.050±0.001	1.051±0.001	0.98±0.01	1.07±0.01	1.176±0.001	2.40±0.02	1.49±0.05	1.02±0.02	1.20±0.01
	Total	5.58±0.01	6.139±0.001	3.113±0.001	5.76±0.01	6.15±0.01	7.14±0.01	14.31±0.08	7.87±0.04	6.31±0.04	7.36±0.01

The following calibration curves were used for compound's quantification, 11: y = 388345x+406369 (caffeic acid); 12-17: y = 84950x – 23200 (catechin); 18-23: y = 151438x - 3E+06 (peonidin-3-O-glucoside).

5.3.1 Determination of Antioxidant Activity

Reducing power is a significant indicator of the antioxidant activity and is generally assessed based on the measurement of the reduction of Fe^{3+} to Fe^{2+} in the presence of antioxidants (Xu et al., 2017). Another frequently used assay, is based on the use of the DPPH radical, which is a stable organic free radical presenting an absorption maximum band around 515-528 nm being one of the most used reagents for the evaluation for the radical scavenging ability of an antioxidant (Xu et al., 2017). Table 14 shows the average of EC_{50} obtained for reducing power and DPPH assays in grape skin and grape seeds extracts.

Table 14. Results of reducing power and DPPH assays obtained for grape pomace extracts (mean ± standard deviation).

Drying Temperature	**Drying Mode**	**Reducing power**		**DPPH**	
		EC_{50} (mg/mL)	Statistical analysis	EC_{50} (mg/mL)	Statistical analysis
Grape Skin					
-	Natural Skin	0.19 ± 0.04	a1	0.2326 ± 0.0004	a3
	Conventional	0.287 ± 0.004	a1 a2 a3	0.347 ± 0.001	a5
40°C	5 min Intermittent	0.2817 ± 0.0006	a1 a2 a3	0.2005 ± 0.0002	a2 a3
	10 min Intermittent	0.376 ± 0.003	a3	0.288 ± 0.009	a4
	Conventional	0.25 ± 0.04	a1 a2	0.28 ± 0.02	a4
55°C	5 min Intermittent	0.29 ± 0.01	a1 a2 a3	0.223 ± 0.002	a3
	10 min Intermittent	0.26 ± 0.01	a1 a2	0.1729 ± 0.0004	a1 a2
	Conventional	0.301 ± 0.009	a2 a3	0.2056 ± 0.0004	a1 a2
70°C	5 min Intermittent	0.2664 ± 0.0009	a1 a2	0.2860 ± 0.0008	a4
	10 min Intermittent	0.230 ± 0.008	a1 a2	0.1477 ± 0.0007	a1
Grape Seeds					
-	Natural Seed	0.103 ± 0.004	a1 a2	0.058 ± 0.002	a1
	Conventional	0.165 ± 0.007	a3 a4	0.113 ± 0.003	a1 a2
40°C	5 min Intermittent	0.184 ± 0.009	a4	0.104 ± 0.003	a1 a2
	10 min Intermittent	0.0635 ± 0.0002	a1	0.0439 ± 0.0006	a1
	Conventional	0.30 ± 0.01	a6	0.16 ± 0.01	a2
55°C	5 min Intermittent	0.130 ± 0.005	a2 a3	0.094 ± 0.009	a1
	10 min Intermittent	0.092 ± 0.001	a1 a2	0.060 ± 0.002	a1
	Conventional	0.23 ± 0.01	a5	0.122 ± 0.001	a1 a2
70°C	5 min Intermittent	0.0804 ± 0.0004	a1	0.0809 ± 0.0004	a1
	10 min Intermittent	0.075 ± 0.005	a1	0.078 ± 0.004	a1

Figure 26 shows the impact of the air temperature and drying mode in the reducing power of grape skin extracts. For these samples, the reducing power EC50 values ranged from 0.19 mg/mL for the in natura sample to 0.376 mg/mL for the sample dried at 40°C with 10 minutes of intermittence. Although it was not expected this last sample being the one presenting lower antioxidant activity in this assay, it should be mentioned that statistical analysis didn't evidenced significant differences among the values obtained for several samples. In fact, only a limited influence was observed with the increase in the drying temperature since the samples showing higher antioxidant potential within each tested temperature (highlighted values in the table) were not significantly different ($p > 0.05$).

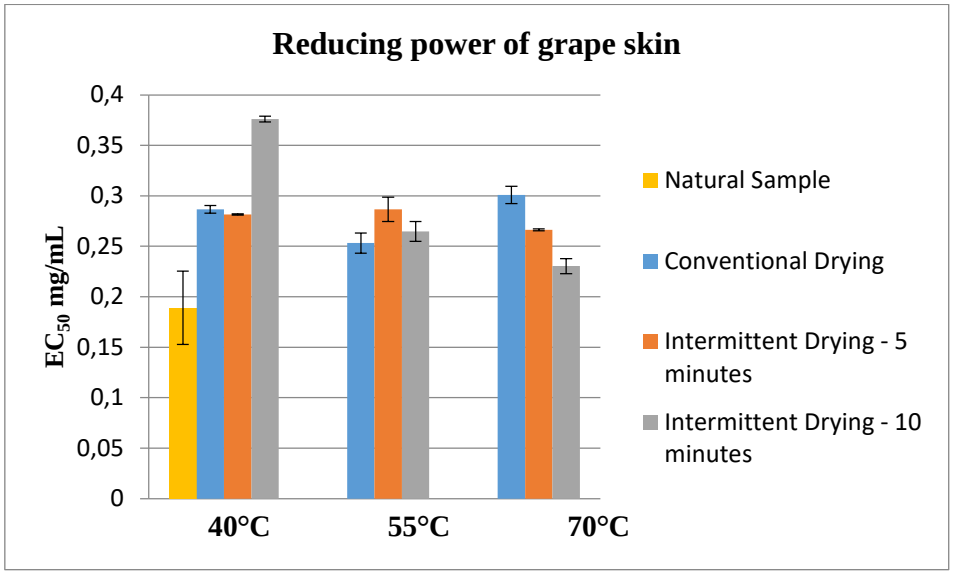


Fig.26. Effect of drying air temperature and drying mode on reducing power (RP) of grape skin.

The EC_{50} for DPPH assay in grape skin were in the range of 0.1477 mg/mL for the intermittent drying at 70°C temperature with a 10-minute intermittence to 0.347 mg/mL for the conventional drying at 40°C. In general, the conventional drying method performed worst compared to the intermittent methods since it presented values higher EC50values, particularly at 40 ºC and 55 ºC (Figure 27). The sample presenting the highest antioxidant potential in this assay was the dried skins at 70 ºC with 10 min intermittence, followed by drying at 55 ºC with 10 min intermittence and at 40 ºC with 5 min intermittence, which is in good agreement with TPC and TFC results since in general those samples presented the highest contents. While for the samples submitted to 5 min intermittence drying mode, higher drying temperatures resulted on decreased

antioxidant activity, the same behavior was not observed for the two other drying methods tested. For both conventional and 10 min intermittence methods, an increase of antioxidant potential was observed with increasing temperature. These could possibly be related to a release of bounded antioxidant compounds with higher temperature, but this hypothesis was not confirmed neither by the individual compounds analysis by LC-MS/MS or the contradicting results for 5 min intermittence drying. On the other hand, this variability can be possibly related to a lack of homogeneity in sampling, therefore suggesting the need of increasing repetitions for this determination.

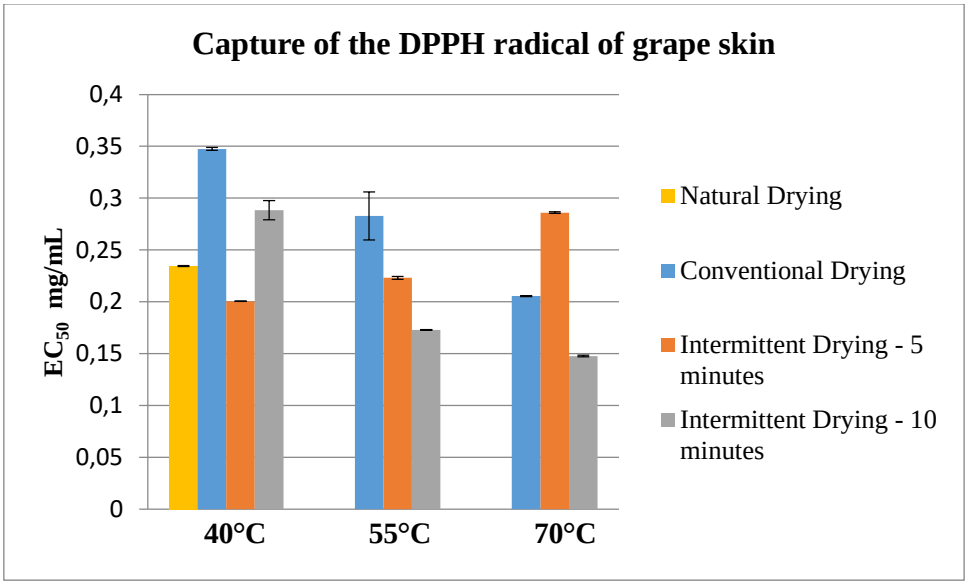


Fig.27. Effect of drying air temperature and drying mode on DPPH assay of grape skin.

For grape seeds, the obtained results indicate that for all proposed drying temperatures, the intermittent drying method was the one that presented the best final quality of the material, returning a better EC_{50} value for the reducing power assay, and consequently a greater antioxidant activity (Table 14 and Figure 28). The values ranged from 0.0635 mg/mL of EC_{50} for the 10-minutes intermittence drying at 40°C to 0.3 mg/mL of EC_{50} for the conventional drying at 55°C. Although better EC_{50} values were obtained for the 10 min intermittent drying at all the three temperatures considered (40, 55 and 70 ºC) when compared to the in non-dried sample, the performed statistical analysis showed that the obtained values are not significantly different from each other. The obtained results are in good agreement with TPC values since the seeds dried at 70 ºC and 40 ºC with intermittence of 10 minutes were the dried samples presenting higher TPC. Conventional drying, in turn, was the one that returned the worst values for the

highest temperatures (55 and 70°C), while at 40°C the result was similar to drying with an intermittency of 5 minutes.

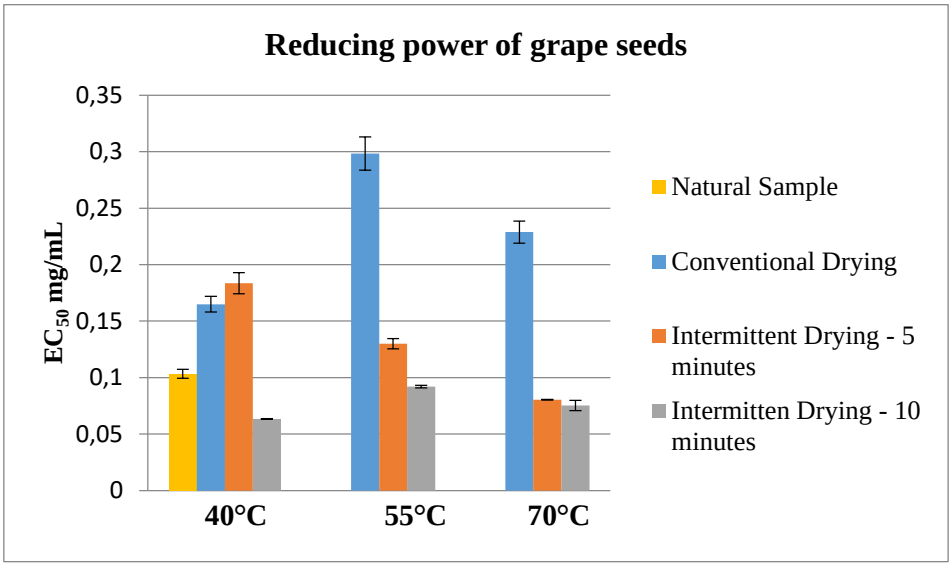


Fig.28. Effect of drying air temperature and drying mode on reducing power (RP) of grape seeds.

Similar results were obtained for the DPPH assay, for which grape seeds submitted to the 10-minute intermittent drying method stood out for presenting much better values for the DPPH test, returning lower EC_{50} values than the others (Figure 29). The values of the DPPH assay ranged from 0.0439 mg/mL for the 10-minutes of intermittence drying at 40°C to 0.17 mg/mL for the conventional drying at 55°C. The results for the conventional mode proved to be the worst for all drying temperatures, with several values showing significant differences when compared to the ones obtained with other treatments. Interestingly, the seeds dried under the conventional method were the ones presenting the lowest TPC, TFC and content of anthocyanins and non-anthocyanin phenolics, which is in good agreement with the antioxidant properties evidenced by those samples.

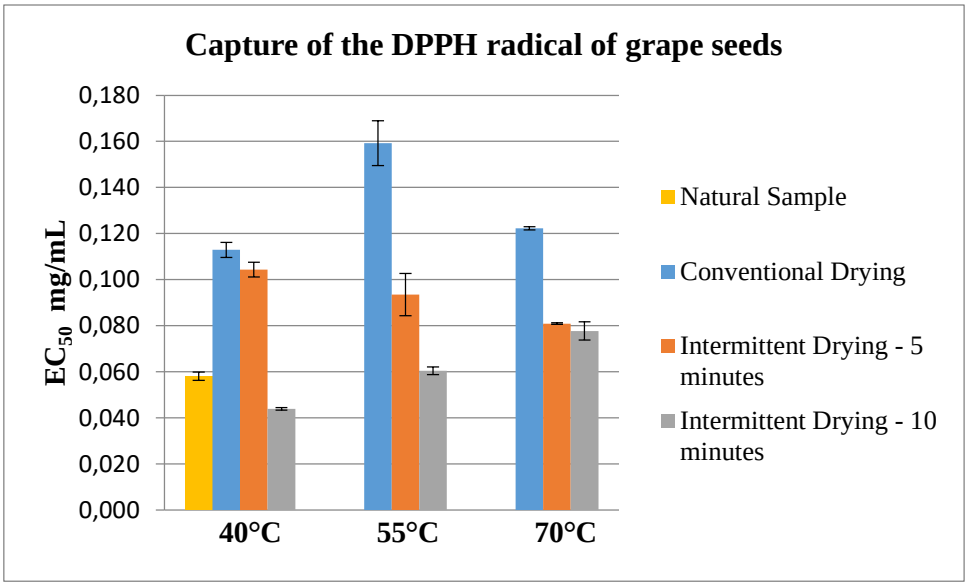


Fig.29. Effect of drying air temperature and drying mode on DPPH assay of grape seeds.

In general, both the skins and the seeds showed results that evidence the fact that intermittent drying is more effective in the matter of final quality of the material, and for higher drying temperatures, longer periods of intermittence return a better value for the DPPH radical capture test.

Particularly when compared to conventional oven drying, the intermittent drying method stood out positively, proving its effectiveness in maintaining the final quality of the material. Other authors have found similar results for other matrices, such as Oliveira and Rocha (2007) regarding the process of intermittent drying of beans, in which the authors concluded that this drying mode makes it possible to obtain a better final product quality. Chua et al. (2000a) studied the drying of guavas and observed that, for similar drying times, better results in terms of the material quality and maintenance of ascorbic acid can be achieved through temperature modeling. In another work, Chua et al (2000b) demonstrated that throughout the application of intermittent drying it was possible to decrease the color variation of potato, guava and banana.

6 Conclusions and future works

In this study, the drying of grape pomace (seeds and skin, separately) was investigated. The modeling of the drying process of grape pomace from red wine grape pomace was performed at temperatures of 40°C, 55°C and 70°C, both for drying in the conventional and in the intermittent mode, with intermittences of 5 and 10 minutes. Modeling results showed that, among the 8 models tested for the conventional drying, the one that best suited the experimental data was the Approximation of diffusion model, for both grape skin and seeds. The model for intermittent drying predicted the experimental data of both types of samples with a global maximum deviation of 10%.

The effect of air temperature (40°C, 55°C, 70°C) during the selected drying time of two hours was examined regarding the TPC, TFC, individual phenolics content and antioxidant activity of grape pomace, a waste from the wine industry that can be used to obtain added-value products such as bioactive phenolic compounds. The results suggest that intermittent drying is a promising technique for preservation of grape pomace bioactive compounds and properties. In both skins and seeds, conventional drying had the highest impact on lowering the content of bioactive compounds and antioxidant activity. Among the drying conditions assayed, for grape skin pomace both TPC and TFC suggest that drying at 40 ºC with 5 minutes intermittence allows maintaining a highest amounts of bioactive compounds, however the individual compounds quantification was not in good agreement with this finding, thus suggesting the need for further studies. For the seeds, the highest bioactive compounds content and antioxidant activity was generally observed for the highest temperature (70 ºC) with intermittent drying.

The seeds showed the highest concentrations of phenolic compounds (mainly a β-type (epi)catechin dimer), as well as highest antioxidant activity (in reducing power and DPPH assays), which is according to previous results from the literature and probably related to a higher content in catechin derivatives. On the other hand, the skins exhibited the highest amounts of anthocyanins, mainly due to the presence of malvidin derivatives. Therefore, this study showed that the bio-residues resulting from the wine industry, which are sometimes discarded, can be considered a rich source of bioactive compounds, namely phenolic compounds, with high antioxidant activity, thus potentially being of interest for other industries. Currently, in view of circular economy,

it is extremely important to add value to this type of byproduct in order to increment their use in the extraction of biomolecules for applications in food, pharmaceutical and cosmetic industries. The present work also showed that intermittent drying can provide grape pomace samples with higher content of bioactive compounds and higher antioxidant activity when compared to conventional drying performed at the same temperature.

For future works, it would be important to develop a study in relation to the energy optimization of the drying process using the data obtained in this work, developing, therefore, a model that simulates which drying conditions return less energy consumption, taking place a comparison between intermittent and conventional drying methods.

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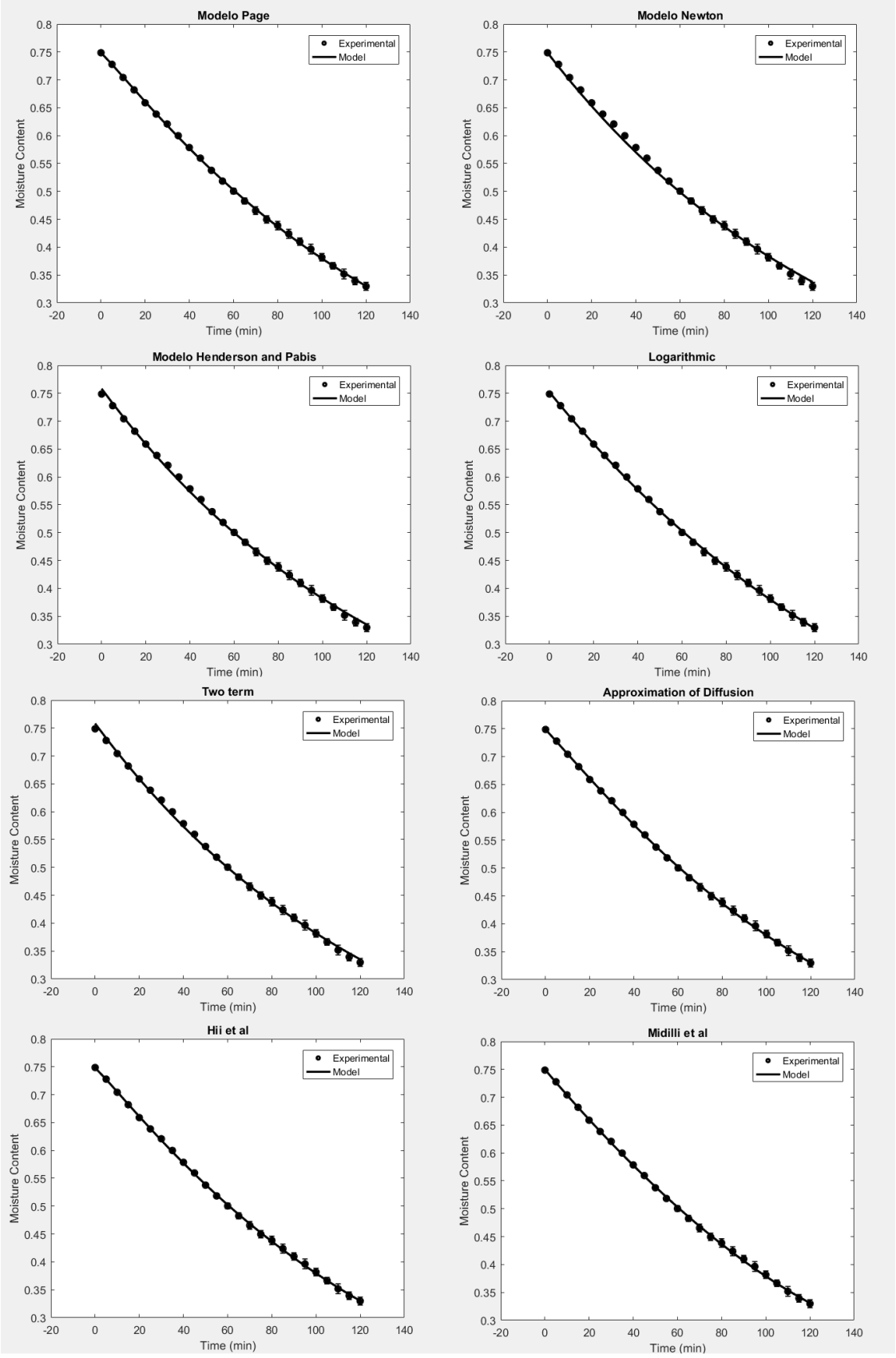
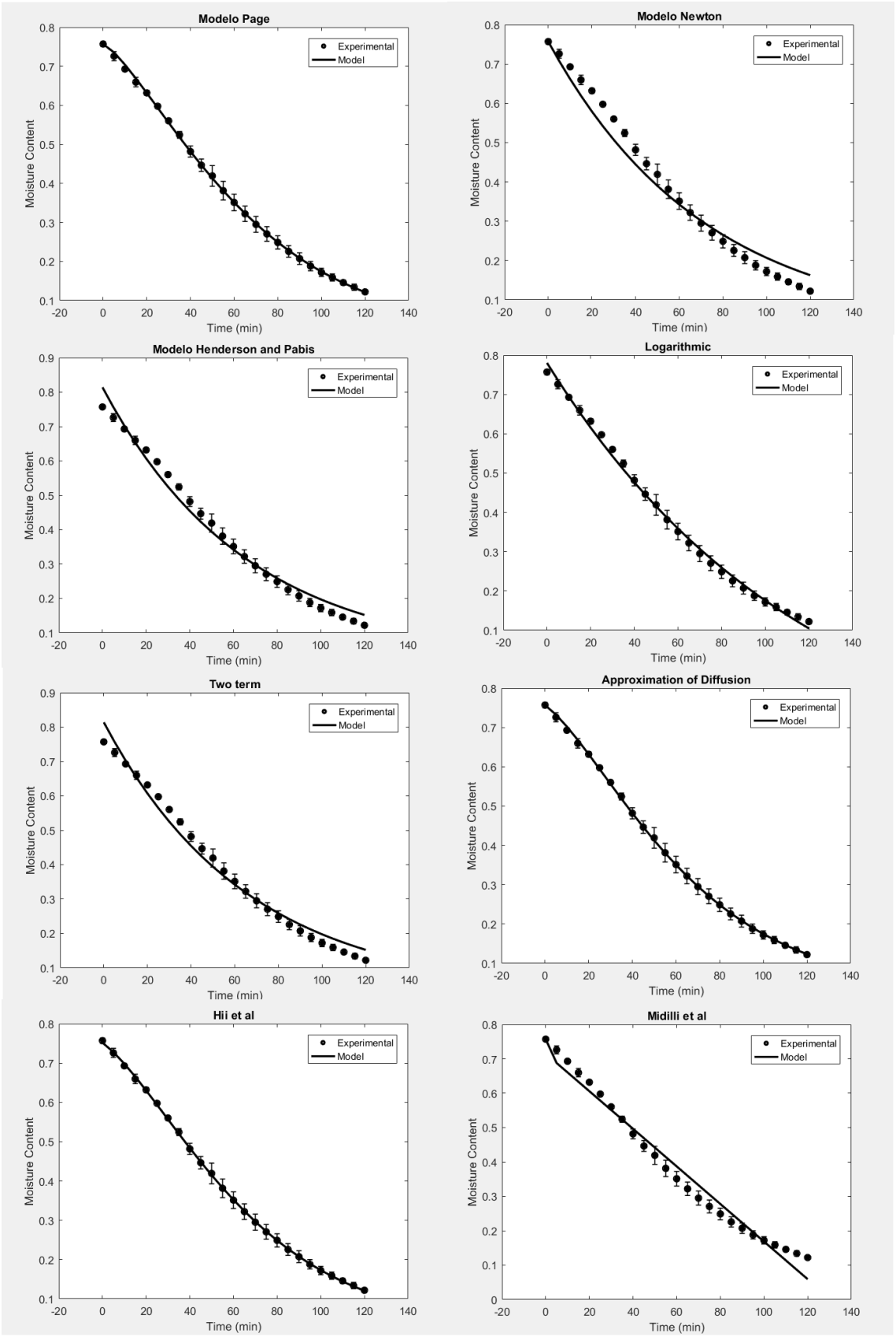
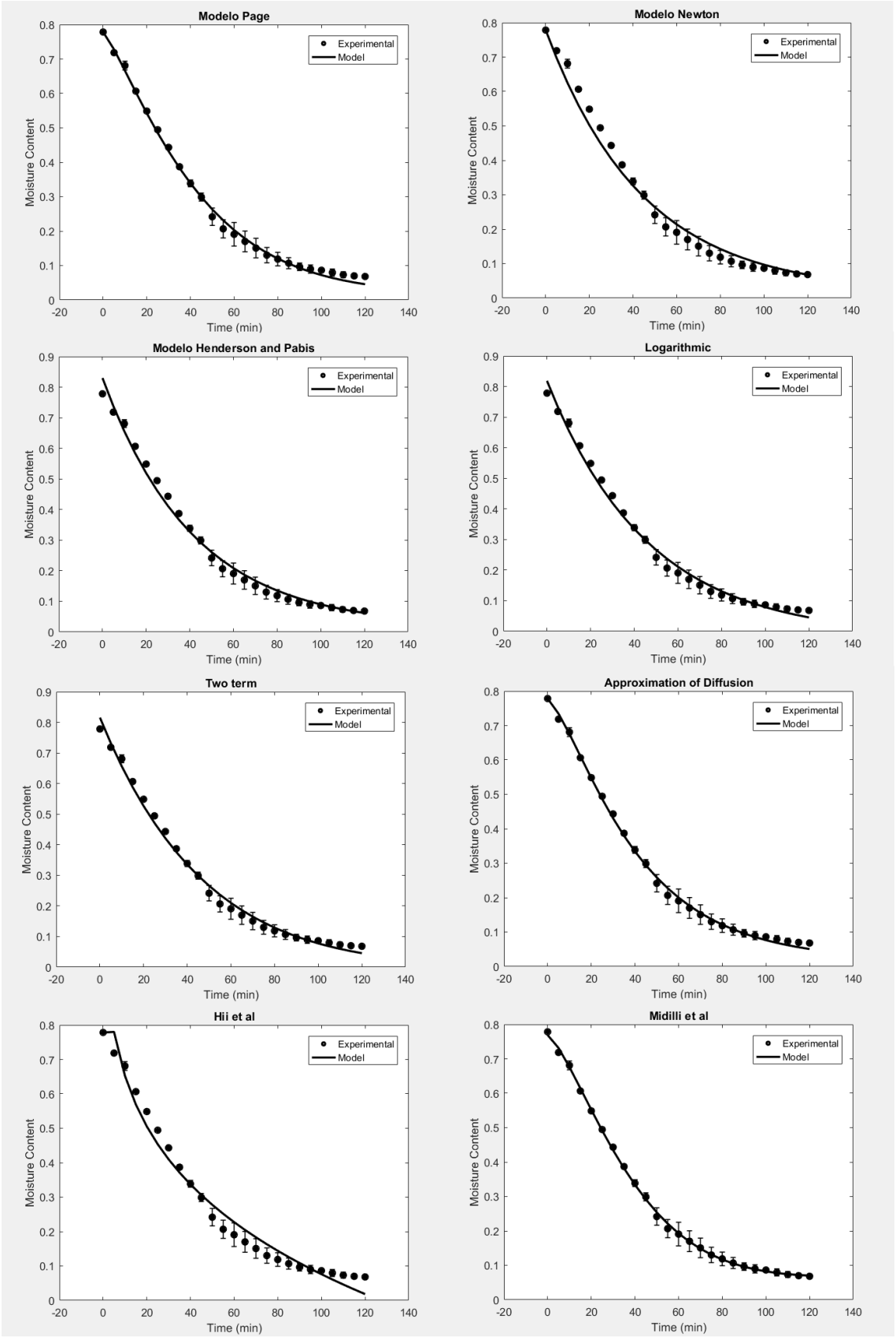
ANNEX A. Modeling of conventional drying of grape seeds at 40°C.



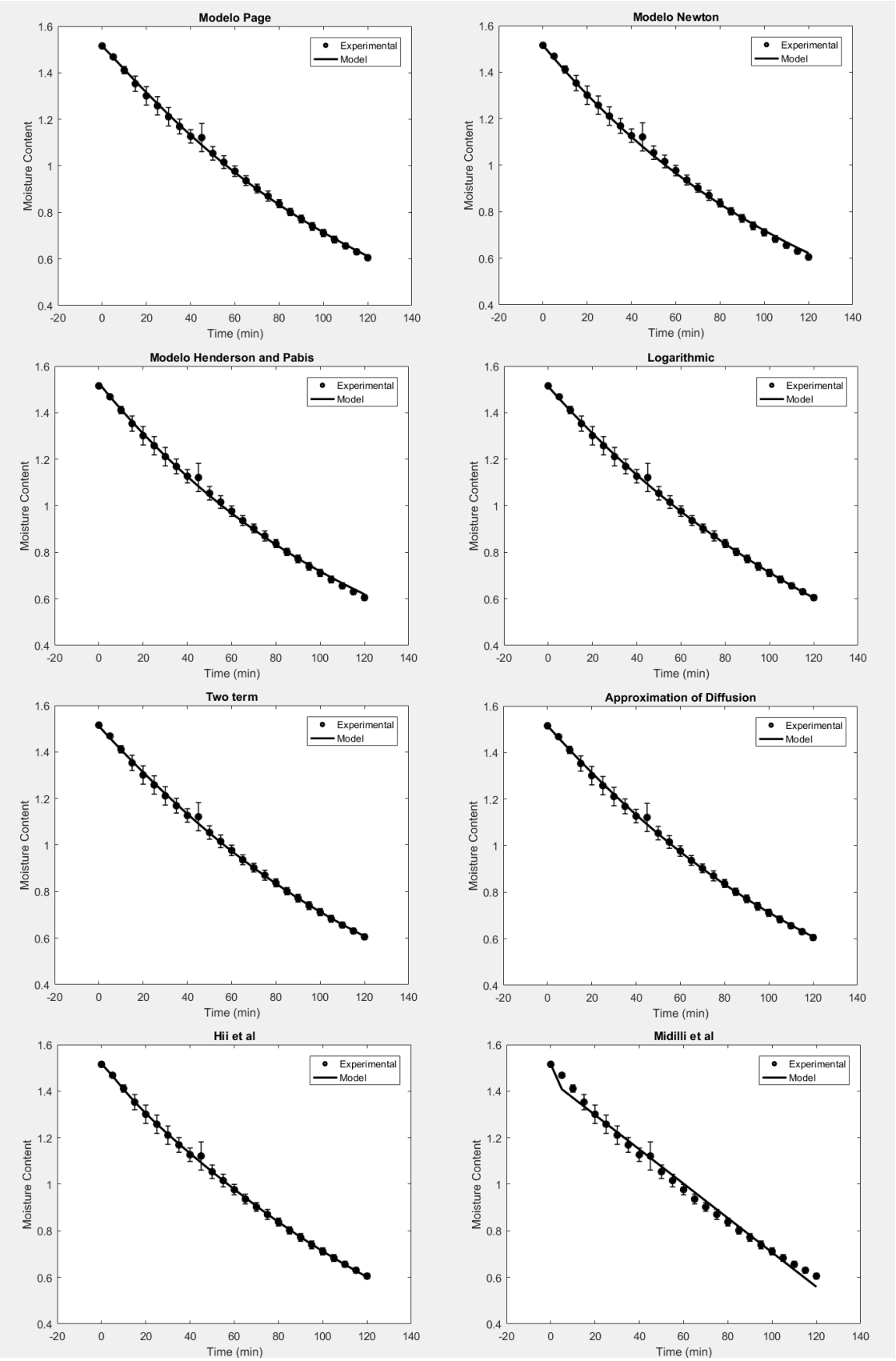
ANNEX B. Modeling of conventional drying of grape seeds at 55°C.



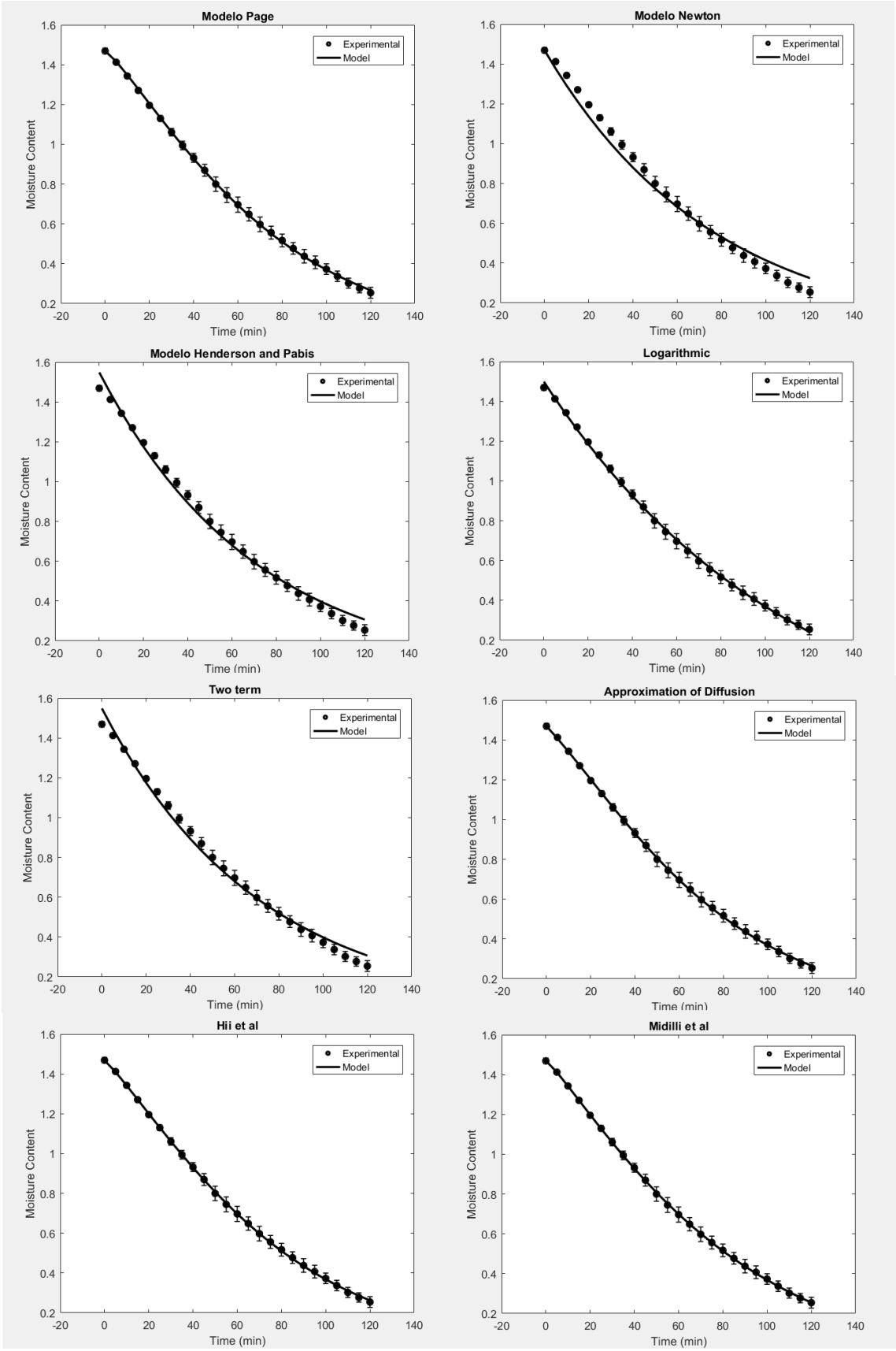
ANNEX C. Modeling of conventional drying of grape seeds at 70°C.



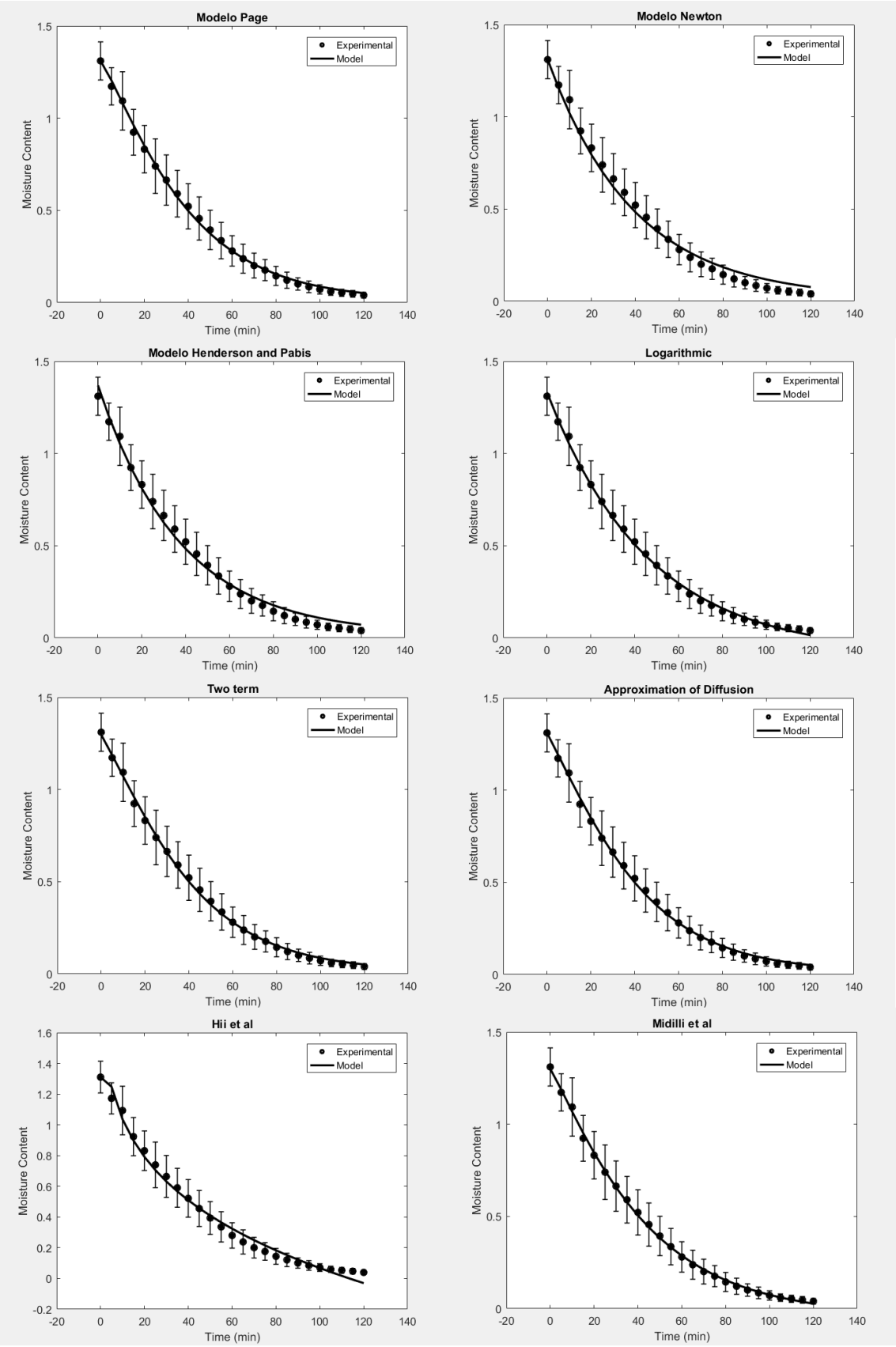
ANNEX D. Modeling of conventional drying of grape skins at 40°C.



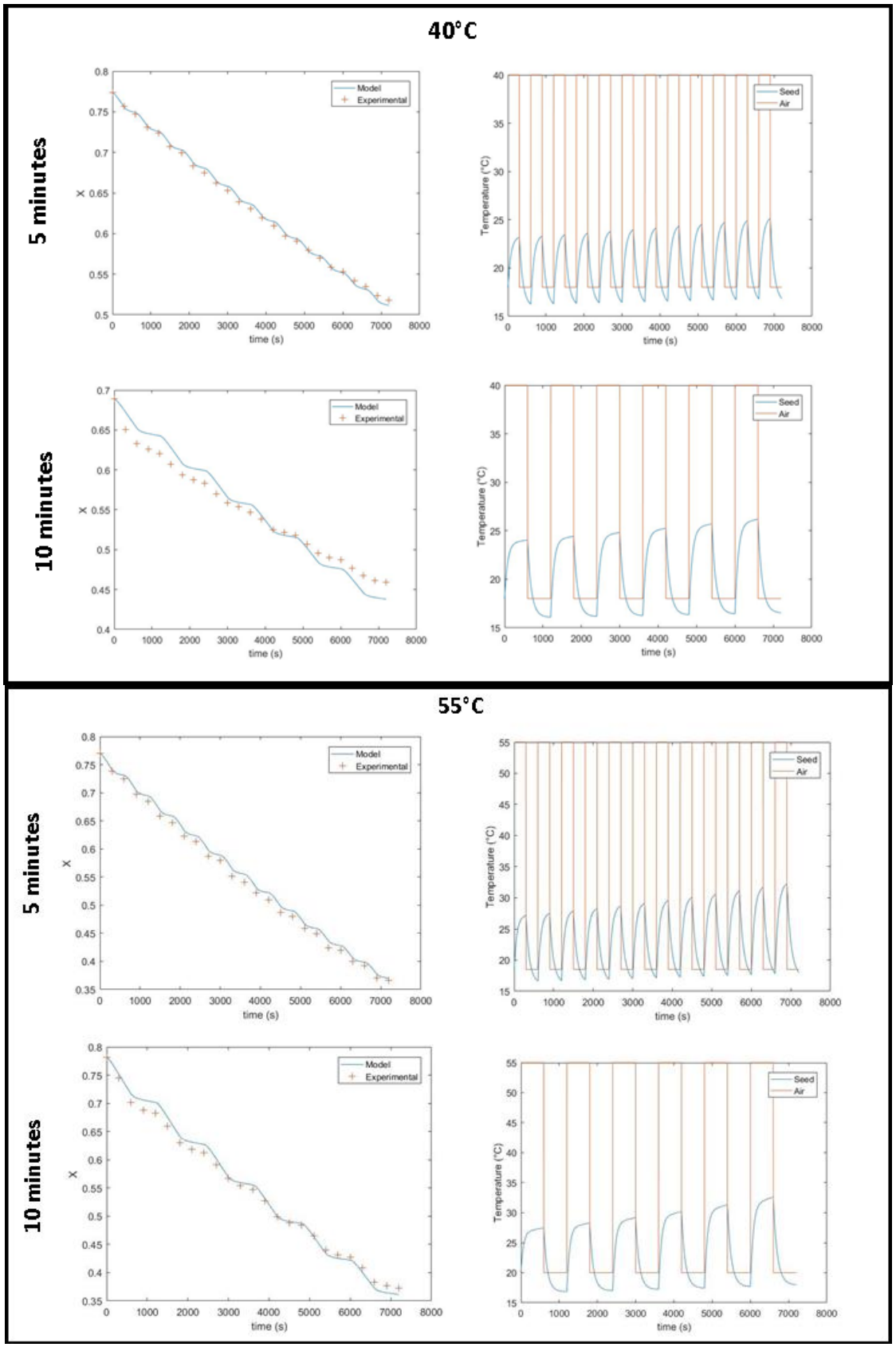
ANNEX E. Modeling of conventional drying of grape skins at 55°C.

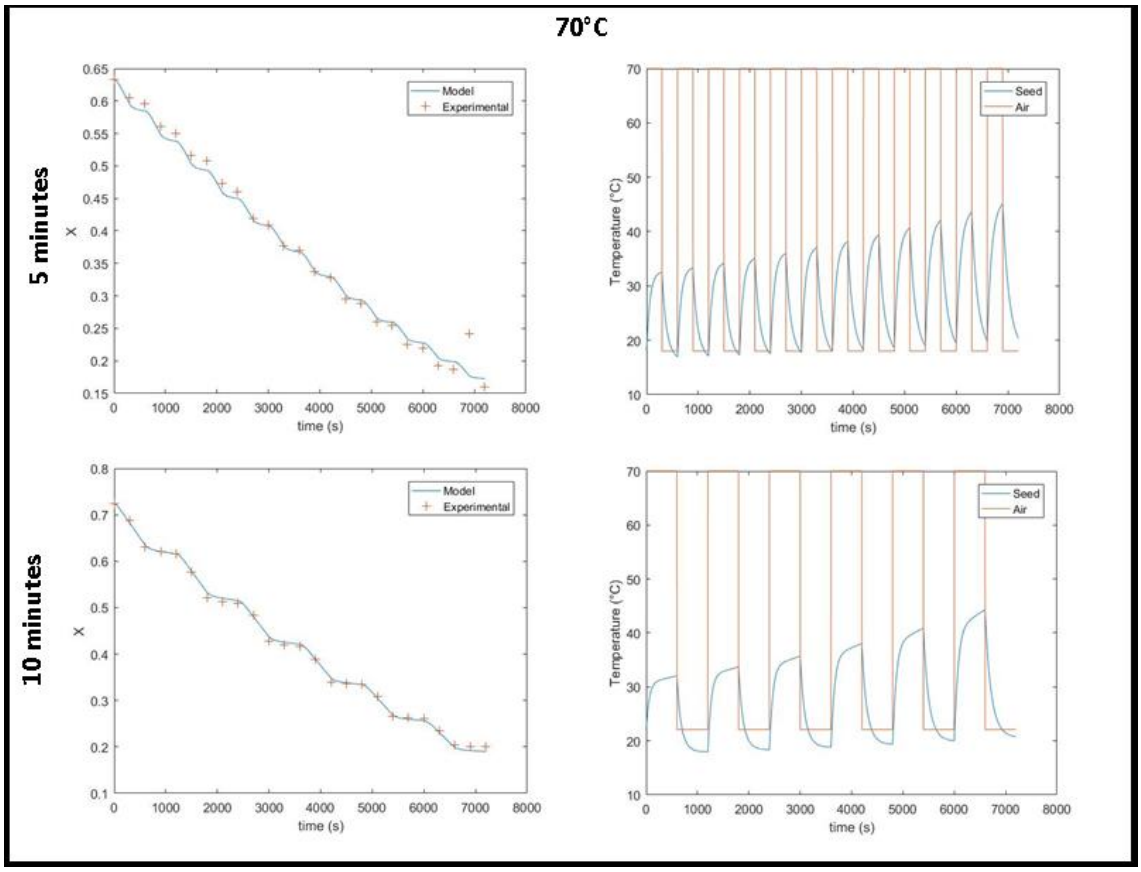


ANNEX F. Modeling of conventional drying of grape skins at 70°C.

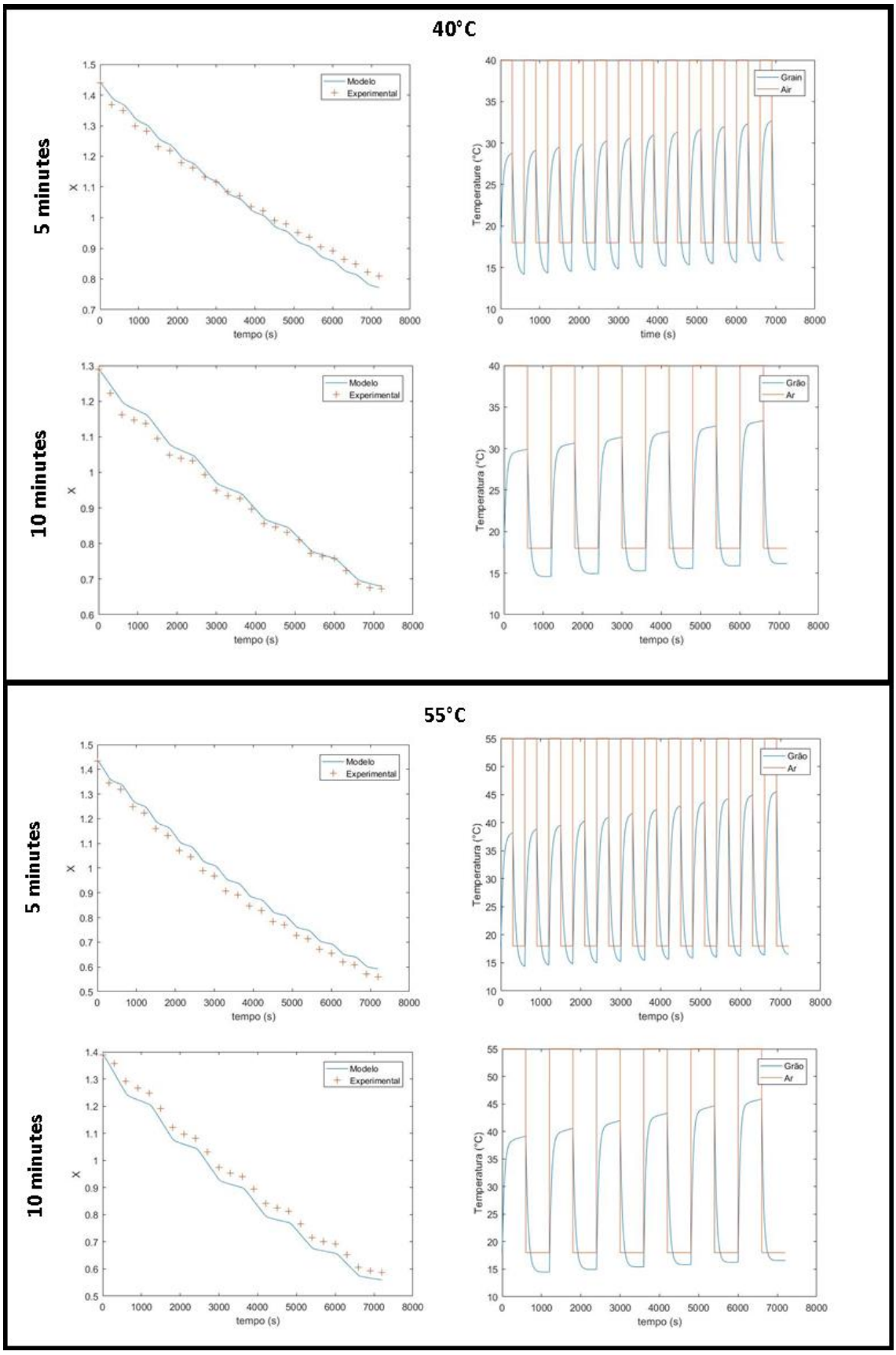


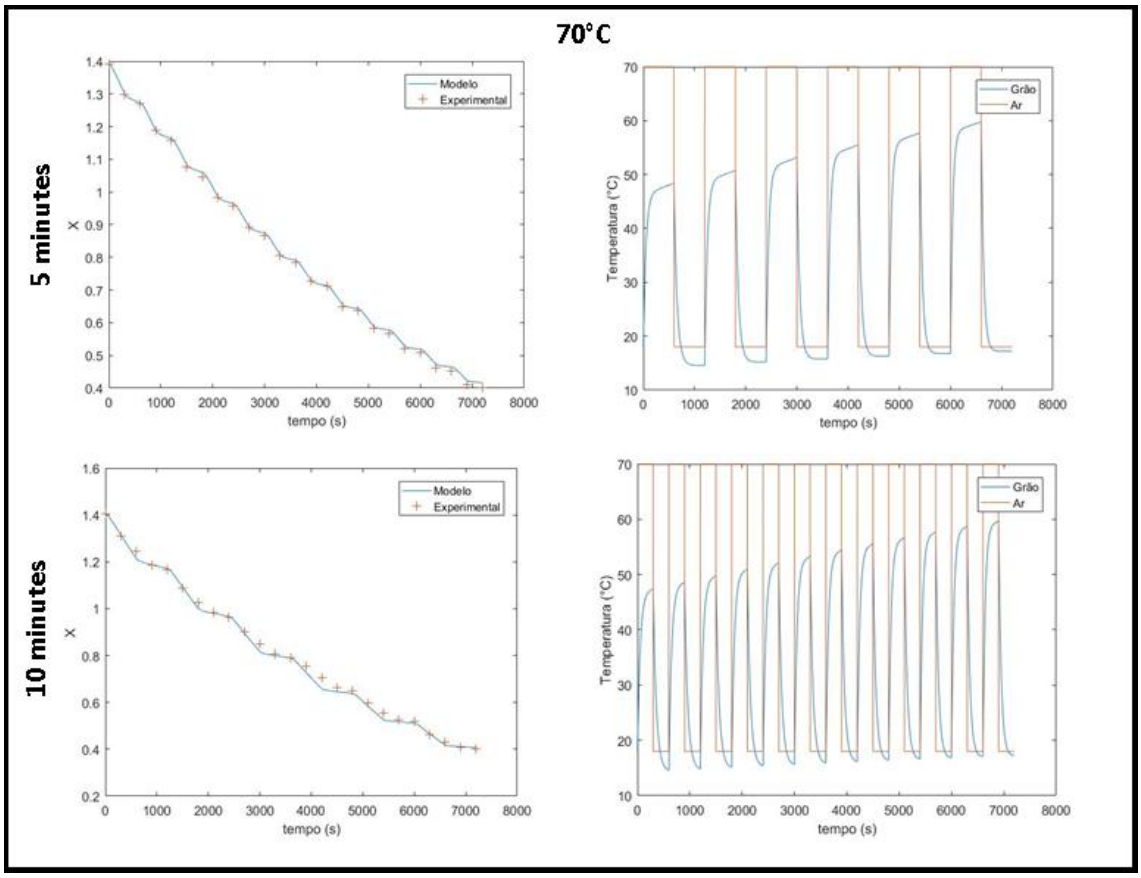
ANNEX G. Modeling of intermittent drying of grape seeds




70°C
5 minutes
10 minutes
Model
Experimental
Seed
Air
X
Temperature (°C)
time (s)

ANNEX H. Modeling of intermittent drying of grape skins




70°C
5 minutes
10 minutes
Modelo
Experimental
Grão
Ar
X
Temperatura (°C)
tempo (s)