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Introduction

The wine industry is a worldwide consolidated business. However, for every 100 liters of wine produced, 31.7 kilograms of waste are generated, which includes skins, stems and seeds [1]. 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 [2]. But this material is a rich source of bioactive compounds, thus its use by the food, cosmetics and pharmaceutical industries has been growing over the last years [3].

To stabilize this raw material, drying is frequently used because it decreases the available water and, consequently, the proliferation of fungi and bacteria, as well as internal reactions that degrade the quality of grape pomace [4].

It is estimated that drying accounts for about 60% or more of the energy costs involved in the entire agro-food production process [5]. An alternative for reducing the energy costs of the drying process and less damage the material is the use of intermittent operation, which operates with transient inputs of air conditions, such as the supply temperature, which may affect the levels of phenolic compounds as well as the antioxidant activity of grape pomace [3]. 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.

This study aims to assess and compare the drying of grape pomace components by conventional operation versus to the intermittent drying method, and evaluate the obtained material in terms of bioactive compounds and antioxidant activity.

Materials and Methods

Samples. The pomace sample (mixture of seeds, skins and stems) was provided by the company Adega Cooperativa de Silgueiros. Grape skins were manually separated and used to prepare hydroethanolic (80% v/v) extracts.



Conventional and Intermittent drying. After separation, the skin was dried in duplicate at temperatures of 40, 55 and 70 °C for a total period of 2 hours. During drying process, periodic measurements were made every 5 minutes using a semi-analytical balance. 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.

Mathematical modeling:

Conventional drying.

Table 1. Mathematical models adjusted to the conventional drying method.

Model n°.	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	$MR = a \exp(-k_0t) + b \exp(-k_1t)$
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.	$MR = a \exp(-kt^n) + bt$

The parameters were adjusted by minimizing the objective function (sum of least squares) represented by the Equation 1:

$$\phi = \sum (Y_{s_{exp}} - Y_{s_{cal}})^2, \quad (1)$$

Intermittent drying. The modeling for the intermittent drying was conducted considering both mass and energy balance equations (Equations 2 and 3).

$$\frac{dY_s}{dt} = -K(Y_s - Y_{s_e}), \quad (2)$$

$$\frac{dE}{dt} = \dot{Q} - \dot{W} + \dot{m}_i \left(u_i + \frac{v_i^2}{2} + g z_i \right) - \dot{m}_o \left(u_o + \frac{v_o^2}{2} + g z_o \right), \quad (3)$$

Chemical Analysis. Total Phenolic Compounds (TPC) and Total Flavonoids content (TFC) were determined by spectrophotometry at 765 nm and 510 nm as previously reported [6].

Antioxidant activity. Reducing power and DPPH radical scavenging were determined by spectrophotometry at 690 nm and 517 nm, respectively, using a microplate reader as previously described [6].



Statistical analysis. Sisvar (version 5.7) was used for data analysing. All results were expressed as a mean value. The data was submitted to Tukey Test with a significant level of 0,05.

Results

Conventional Drying

The statistical parameters presented in Table 2, showed that the model that best fit the experimental data for the conventional drying was the **Approximation of diffusion model**.

Table 2. Average of the statistical parameters for conventional drying of grape skins.

Model name	χ^2	NRM	MSE	EF	RMSE
Approximation of diffusion	1,2514.10 ⁻⁰⁴	8,433.10 ⁻⁰⁴	1,10.10 ⁻⁰⁴	0,9991	9,567.10 ⁻⁰³

Intermittent Drying

For the intermittent drying operation, equations were deduced based on mass and energy balance that led to a fit with a maximum global deviation of 10% in comparison to experimental data. In both experiments (tempering periods of 5 min and of 10 min) the adjustment was satisfactory, but the 5-minute intermittence better suited the model.

Table 3. Average of the statistical parameters for intermittent drying of grape skins.

Parameter	5 min	10 min
EF	0,987514	0,987191
χ^2	7,22.10 ⁻⁰⁴	8,21.10 ⁻⁰⁴
RMSE	2,25.10 ⁻⁰²	2,47.10 ⁻⁰²
ϕ	0,023262	0,023167

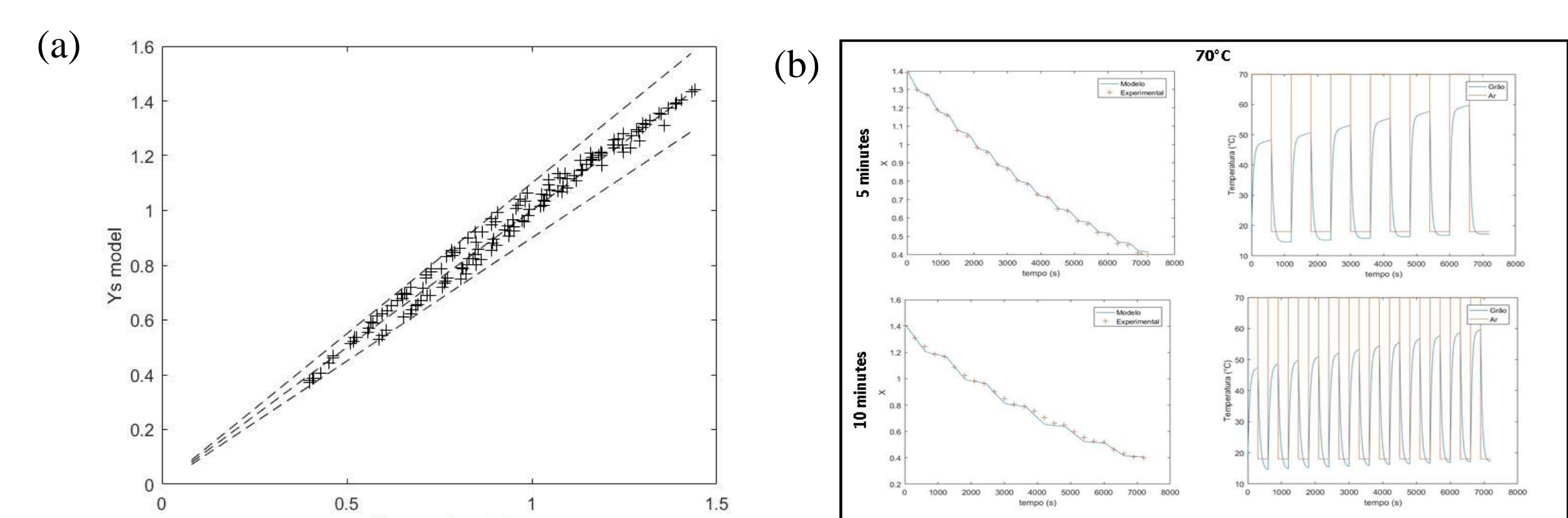


Figure 1. (a) moisture of grape skin as proposed by the model versus Experimental results; (b) Moisture content for intermittent drying of grape skins at 70°C with 5 and 10 minutes intermittence.

Determination of bioactive compounds and Antioxidant Activity

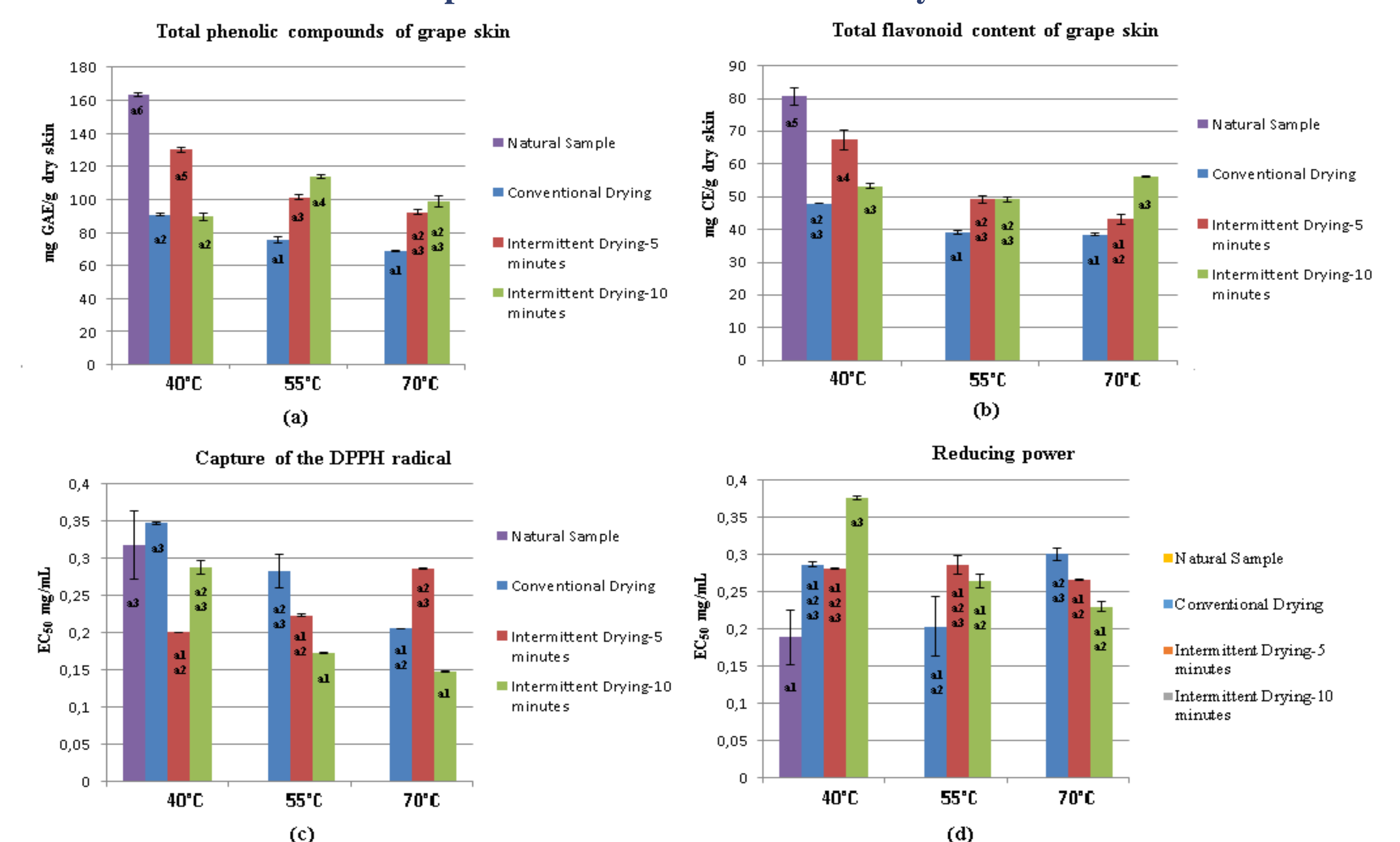


Figure 2. (a) total phenolic compounds (TPC), (b) total flavonoids (TF) (c) DPPH assay of grape pomace and (d) line reducing power (RP) in comparison with extracts of wet grape pomace (statistically significant difference is marked with different letters and numbers, $p < 0.05$)

Conclusion

- Conventional drying had the highest impact on lowering the content of bioactive compounds and antioxidant activity.
- Among the drying conditions assayed, the one that allowed maintaining the highest amounts of bioactive compounds was the 5 min of tempering period performed at 40°C.
- The present work 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.

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