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Temperature Effect of Cocoa (*Theobroma cacao* L.) Drying on Energy Consumption, Bioactive Composition and Vibrational Changes

David J. Jiménez-Rodríguez [1,2], Pedro García-Alamilla [3,*], Facundo J. Márquez-Rocha [4,*], Rubén Vázquez-Medina [1], Areli Carrera-Lanestosa [3], Fanny A. González-Alejo [3], Carlos A. Sánchez-Ramos [2] and Franco L. Ruiz-Santiago [5]

1 Instituto Politécnico Nacional, Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada Unidad Querétaro (CICATA Qro), Cerro Blanco 141, Colinas del Cimatario, Santiago de Querétaro 76090, Querétaro, Mexico; dajimenezr@ipn.mx (D.J.J.-R.); ruvazquez@ipn.mx (R.V.-M.)
2 Instituto Politécnico Nacional, Centro Mexicano Para la Producción más Limpia, Unidad Tabasco, Tabasco Business Center, Edificio FINTAB, Carr. Reforma-Dos Bocas, Km 17.920, Ra. Pechucalco, 2da. sección, Cunduacán 86691, Tabasco, Mexico; casanchezr@ipn.mx
3 División Académica de Ciencias Agropecuarias (DACA), Universidad Juárez Autónoma de Tabasco (UJAT), Carret. Villahermosa-Teapa Km 25, Ra. La Huasteca, Villahermosa 86280, Tabasco, Mexico; areli.carrera2000@gmail.com (A.C.-L.); adabel.0392@gmail.com (F.A.G.-A.)
4 Instituto Politécnico Nacional, Unidad Profesional Interdisciplinaria de Ingeniería Campus Hidalgo (UPIIH), Carretera Pachuca—Actopan Km. 1+500, San Agustín Tlaxiaca 42162, Hidalgo, Mexico
5 Instituto Politécnico Nacional, Centro de Investigación en Biotecnología Aplicada (CIBA), Ex-Hacienda San Juan Molino Carretera Estatal Tecuexcomac-Tepetitla Km 1.5, Tlaxcala 90700, Tlaxcala, Mexico; fruiz2000@alumno.ipn.mx
* Correspondence: pedro.garciaa@ujat.mx (P.G.-A.); fmarquez@ipn.mx (F.J.M.-R.)

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Abstract: Cocoa drying is the post-harvest thermal process used to condition the beans to a moisture content between 6.5 and 7% for storage and further processing. Convective drying is an energy-intensive process where time and temperature are considered critical factors for the degradation of bioactive compounds in edible products. In the present study, the energy parameters, vibrational spectroscopy, and changes in bioactive compounds of cocoa beans were studied during thin-layer hot air drying at 50 °C, 60 °C, and 70 °C. Moisture loss, specific energy consumption (SEC), energy efficiency, total phenolics (TPs), total flavonoids (TFs), and antioxidant activity (DPPH) were determined. Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflectance (ATR) was used to characterize the samples, and a multivariate analysis was applied to find interactions among the components. The obtained SEC was 18,947.30–24,469.51 kJ/kg, and the energy efficiency was 9.73–12.31%. When the temperature was 70 °C, the best values for SEC and energy efficiency were obtained. The results also showed that the convective drying generated changes in the TP levels for the three temperatures, mainly after 300 min, with maximum levels between 360 and 600 min, at 70 °C; however, it does not have a clear relationship with the TFs and the antioxidant activity. The FT-IR and the multivariate analysis revealed changes in several signals in the 1800 to 400 cm^{-1} range, confirming the variation in the associated signal with phenolic compounds.

Keywords: moisture loss; convective drying; energy efficiency; FT-IR; multivariate analysis; total phenolics; total flavonoids; antioxidant activity

1. Introduction

Cocoa tree beans (*Theobroma cacao* L.) are the main raw material for the manufacture of chocolate, cocoa powder, and other cocoa products [1]. Cocoa drying is one of the stages of the post-harvest process; it consists of reducing the water content of the beans from approximately 55% to a range of 6.5 to 7% moisture, which is the desired limit that the

beans must contain to avoid the growth of fungi and unpleasant aromas that deteriorate the quality and also to maintain adequate storage conditions, transport, handling, and marketing [2]. However, during this process, some structural or chemical changes may occur, which may affect the nutritional or organoleptic properties of the product.

Convective drying is the most commonly used process, and some studies have reported cell destruction that is proportional to the amount of moisture removed. There are other methods such as microwave and freeze-drying, among others, that have been studied, but these methods have presented several disadvantages, such as longer drying time and high energy consumption [3]. Some studies have been carried out on different food-type products involving convective drying and parameters such as specific energy consumption (SEC) and energy efficiency [4–6]. A few studies reported these parameters for cocoa but only using solar drying. Simo-Tagne et al. [7] reported an SEC value between 7 and 15 kWh/kg, while the efficiency was between 9 and 17%. Vásquez-Uribe et al. [8] reported an SEC value of 27,793.90 kJ/kg and an efficiency value of 12.94%.

Bioactive compounds in foods are often referred to as "phytochemicals" because they are naturally in products of plant origin, including carotenoids, phytosterols, polyphenols, and sulfur compounds such as glucosinolates, among others [9]. The beneficial effects of cocoa polyphenols depend on the amount consumed, their bioavailability, and the biological activity of the conjugates formed [9,10]. Cocoa beans and their co-products are a very rich source of beneficial health-promoting compounds, including polyphenols and methylxanthines [1]. The health benefits that have been attributed to their consumption have been found to be attributed to the presence of polyphenols, mainly flavonoids, in cocoa beans and their by-products.

Flavonoids are the most abundant class of phenolic compounds in cocoa beans and, according to the review by Oracz et al. [1], include mainly flavan-3-ols, anthocyanins, and flavonols. It was also reported that cocoa beans and cocoa products can also contain significant amounts of another group of polyphenols, such as phenolic acids, stilbenes, and N-phenylpropenoyl-L-amino acids (NPAs), which belong to the family of polyphenol/amino acid conjugates. These bioactive compounds are secondary metabolites of cocoa that also contribute significantly to the organoleptic properties of cocoa beans and cocoa products [1].

The antioxidant properties of cocoa can be influenced by factors such as genotype, agroclimatic conditions, fermentation, drying, and the industrialization process [11]. There are studies that include antioxidant effect assays such as DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging and oxygen radical absorbance capacity (ORAC) to evaluate the antioxidant capacity of cocoa and chocolate [12–14].

There are studies focused on food-type products that report the monitoring of the degradation of bioactive compounds such as total phenolics (TPs) and total flavonoids (TFs) as well as antioxidant activity during the drying process of products other than cocoa [3,15]. The studies on cocoa drying were focused on moisture kinetics and the evaluation of TPs in short periods of time; however, they did not evaluate antioxidant activity through any method [16–19].

The kinetics of the oxidation reaction of polyphenols during cocoa drying have been studied using kinetic equations, working with temperatures between 40 °C and 60 °C and relative humidity between 50% and 80% [16]. It has been observed that higher temperature and relative humidity of the drying air can lead to changes in the polyphenol residues of cocoa beans due to enzymatic oxidation of polyphenols [16], but more studies are necessary to understand these changes since cacao bean properties are influenced by the variety and edaphic and geographic conditions.

Fourier transform infrared (FT-IR) spectroscopy is one of the most widely used methods for analyzing and detecting components of interest during food processing. FT-IR spectroscopy has been successfully applied for characterizing a variety of agricultural products [15,20,21]. Furthermore, the use of FT-IR combined with attenuated total reflectance (ATR) is a spectroscopic technique that has been widely used as a tool for the study of

products such as red pepper, coffee cherry pulp, and sugar cane [15,22,23]; it is also a well-established analytical technique for rapid, high-throughput, non-destructive analysis of a wide range of products such as edible oil types [24]. FT-IR has been used to quantify other quality parameters of interest in cocoa, such as fat, nitrogen, and moisture content, but for final drying times and for very diverse samples [25]; likewise, near- and mid-IR has been used to characterize dried cocoa beans according to their geographical origin [26]; however, the behavior during the process has not been monitored as proposed in this study.

Previous studies have not addressed in detail whether temperature can affect the vibrational changes of the bioactive compounds present in Mexican cocoa beans during drying or if these changes can also be evaluated through FT-IR, along with their relationship with energy consumption during thin-layer cocoa drying. Therefore, the aim of this work was to characterize dried cocoa samples by FT-IR spectroscopy and study their energy parameters, bioactive compounds (TPs and TFs), and antioxidant activity. In this study, the effect of time and temperature was considered during the drying process at different temperatures (50, 60, and 70 °C). The data were also analyzed using MetaboAnalyst 6.0 software. To the best of our knowledge, this is the first study developed in Mexico on the determination of energy consumption, TPs, TFs, and antioxidant activity, complemented with FT-IR-ATR vibrational analysis and multivariate analysis, for the cocoa bean drying process.

2. Materials and Methods

2.1. Cocoa Material

The analyses and experiments for this study were conducted on samples of fermented cocoa beans (*Theobroma cacao* L.) obtained from the "Finca Las Delias" farm located in Rancheria Sur, Primera Seccion, Comalcalco, Tabasco, Mexico, with the following coordinates: 18°13′07″ N 93°14′35″ W, at an altitude of 16.81 m above mean sea level. The plantation farm was mostly planted with the Criollo cocoa variety called "Almendra Blanca". The cocoa pods were hand-harvested from the trees 24 h before they were split open for the extraction of 600 kg of the wet beans, and the wet beans were then selected by eliminating any type of diseased-like and/or undesired state of physiological maturity. The bean size was not selected under any criteria. The wet beans were placed in three wood fermentation boxes (*Cedrela odorata* L.) covered with henequen sacks at the farm.

Fermentation was carried out for seven days with mixing starting after 48 h and then every 24 h until the last day of the fermentation process. The temperature in the central part of the fermentation boxes was recorded and reached an average temperature of 48 °C. The drop in temperature levels and a cutting test were considered as final fermentation criteria. The cocoa materials used for drying were randomly collected from the wooden boxes on the last day of the fermentation stage, and two kilograms was used for each test of the drying process.

2.2. Drying Experiments and Sample Conditioning

Fermented cocoa beans were convectively dried in a forced air flow oven (Felisa, FE-292ADU, Guadalajara, Mexico) with temperature and air flow control, with the tempered material placed in a thin layer on a metal mesh. Since the morphology of cocoa beans is very irregular, only broken or very small grains were discarded. Drying experiments were performed at temperatures of 50 °C, 60 °C, and 70 °C at an air flow velocity of 2.3 m/s for 24 h. Temperatures between 50 and 70 °C were selected according to other studies [16,17,19,27,28] where these conditions were established as adequate to eliminate volatile compounds, mainly acetic acid, and thus avoid the production of acidic cocoa beans with undesired sensory quality properties. In the present study, the independent variable was the drying temperature; this condition is similar in commercial dryers where only temperature is available as a control parameter. Air flow velocity and ambient air temperature were also controlled in order to remain constant. The relative humidity was not controlled as in most drying studies. Samples were taken at time intervals (0–1400 min) for a total of 15 samples per temperature and were heated to 103 °C for 24 h to a constant weight,

and their moisture content was determined by the gravimetric method [29]. Samples were taken starting with the "zero" time, and successive samples were taken at fixed time intervals (30 min, 1 h and 2 h) to cover up to 24 h of drying. Once the drying process reached the final time, the beans were immediately cooled to approximately 20 °C for 10 min. The dried cocoa bean samples were stored in hermetically sealed plastic containers (500 g) at −20 °C for subsequent analyses. Samples were analyzed within 6 to 12 h of storage, and all experiments were performed in duplicate for each drying temperature. Due to the variation in the initial moisture content of the different samples, the drying curves were also expressed in terms of dimensionless moisture (X) for comparison, which was obtained by dividing each value of the dry base moisture by the initial dry base moisture.

The drying rate was estimated from experimental data by fitting an exponential equation represented as Equation (1). These types of models are frequently used to describe drying in fruits and vegetables and have proven to be efficient at the level of dryer engineering and design [30] but have limitations in application under the experimental conditions of studies.

$$X = X_0 + Ae^{-Rot} \tag{1}$$

where *Xo*, *A*, and *R* are the model constants and *t* is time.

2.3. Energy Parameters

The oven used for the drying was started before the experiments until it reached stable conditions, and the energy consumption was continuously recorded using a power quality analyzer (AEMC instruments, Powerpad 8335, Dover, NH, USA). The velocity and temperature of the air flow were recorded using a thermo-anemometer (CEM, DT618, Shenzhen, China), and the ambient temperature was measured with a thermo-hygrometer (CEM, DT321S, Shenzhen, China).

Specific energy consumption (SEC) expresses the ratio of total energy consumption (Ec_{total}) per kilogram of water evaporated from the product. The SEC of cocoa beans processed in a convective dryer can be determined by Equation (2) [31]:

$$\text{SEC} = \frac{E_{c\ total}}{M_w} \tag{2}$$

M_w represents the weight loss (kg), which can be obtained from Equation (3):

$$M_w = m_i - m_f \tag{3}$$

where m_i expresses the initial mass and m_f the final mass of the product.

The energy efficiency can be determined by Equation (4) [32]:

$$\eta_e = \left(\frac{Q_w}{E_{C\ total}}\right) \tag{4}$$

The energy required to evaporate moisture (Q_w) can be calculated by Equation (5)

$$Q_w = h_{f \cdot g} \cdot M_w \tag{5}$$

where η_e is the energy efficiency (%), Q_w is the energy (consumed energy) required to evaporate moisture (kJ), $h_{f \cdot g}$ is the latent heat of vaporization (kJ/kg), and M_w represents the weight loss (kg). $h_{f \cdot g}$ is calculated as a function of absolute temperature (K) and was obtained from thermodynamic tables of saturated water [33].

2.4. Preparation of Extracts

For this purpose, dried cocoa beans were manually deshelled before the grinding, sifting, and defatting of the cotyledons; then, 100 mg of defatted cotyledon powder with a particle size of 420 microns was extracted with 10 mL of a hydroalcoholic mixture of 70% ethanol at room temperature for 2 h using an orbital shaker at 200 rpm (Thermo Fisher

Scientific, 2346, Waltham, MA, USA). The mixture was centrifuged at 7280× g for 15 min (HERMLE, Z236K, Wehingen, Germany) and filtered. The extracts were kept refrigerated at 4 °C until further use.

2.5. Determination of Total Phenolics

The TPs were determined by the Folin–Ciocalteu colorimetric method for hydroalcoholic extracts [12] with slight modifications. An aliquot of 0.20 mL of the extract was mixed with 1.5 mL of Folin–Ciocalteu's, the solution was allowed to settle for 5 min at room temperature, and then 1.5 mL of 0.55 M sodium bicarbonate was added. After 90 min in the dark, the absorbance of the samples was measured at 725 nm using a spectrophotometer (Thermo Fisher Scientific, UV-Vis Genesys 10S, Waltham, MA, USA). The calibration curve was plotted in the range of 0–0.3 mg GAE mL^{-1} (gallic acid equivalents).

2.6. Determination of Total Flavonoids

The TFs were determined according to the method described by Zhishen, Mengcheng, and Jianming [34] with slight modifications. In a test tube, a 0.20 mL aliquot of the extract was mixed with 0.80 mL of distilled water and 0.15 mL of 5% sodium nitrite solution. After 5 min, 0.15 mL of aluminum chloride solution (10%) was added. At 6 min, 2.0 mL of sodium hydroxide (4%) was added. The solution was supplemented up to 5 mL with distilled water. The absorbance of the final mixture was measured at 410 nm against a target on a spectrophotometer (Thermo Fisher Scientific, UV-Vis Genesys 10S, Waltham, MA, USA). A calibration curve was generated with quercetin from a working solution of 100 μg mL^{-1} in a range of 0.2–1.0 mg mL^{-1}. The TFs of the extracts were expressed as quercetin-equivalent mg/g sample (mg EQ g^{-1}).

2.7. Determination of Antioxidant Activity

The method proposed by Shimada et al. [35] based on the 1,1-diphenyl-2-picrylhydrazil (DPPH) radical was used to determine the free radical scavenging ability of the extracts. The samples were measured at 517 nm against a blank. Then, 150 μL of the extract was mixed with 1350 μL of DPPH (0.1 mM) in 95% ethanol. An equal amount of ethanol and DPPH were used as a blank (control). The mixture was kept in the dark at room temperature for 30 min. The absorbance of the samples was measured at 517 nm against a blank using a spectrophotometer (Thermo Fisher Scientific, UV-Vis Genesys 10S, Waltham, MA, USA). The DPPH radical scavenging activity was calculated using Equation (6).

$$\%DPPH\ radical\ scavenging\ activity = \frac{Abs\ control - Abs\ extract}{Abs\ control} \times 100, \quad (6)$$

2.8. Characterization by Vibrational Analysis

Samples of 10 grains per time were used, and they were dried under vacuum (lyophilization) using a Sentry 2.0 freeze dryer (−52 °C for 48 h); subsequently, they were deshelled, ground, and sifted with 20 and 40 meshes to obtain 420-micron powdered cotyledon samples. Vibrational analysis was performed using an FT-IR spectrometer (Perkin Elmer, Frontier, Waltham, MA, USA), coupled with a diamond-tipped attenuated total reflection (ATR) unit, using a 32-scan configuration with a resolution of 4 cm^{-1} in the spectral region of the range between 4000 and 400 cm^{-1}. Background spectra were obtained from the air after every sample measurement according to the modified method of Meza-Márquez et al. [36]. A powdered sample was placed on the glass of the ATR for each sampling time, and a background was executed after each sample measurement. A baseline correction and smoothing pretreatment was performed on all the spectra obtained, using the Spectrum 10.6.2 software of the FT-IR spectrometer (Perkin Elmer, Frontier, Waltham, MA, USA). The generated data were then processed in the Origin 8.5.1 software to assign the main signals. From the kinetics spectral data obtained in triplicate, a matrix was constructed, and a multivariate analysis was performed using the MetaboAnalyst 6.0 software.

3. Results and Discussion

3.1. Drying Curves and Rates

Moisture curves during the drying process were obtained for the three temperatures (50, 60, and 70 °C) and expressed as dimensionless moisture, and the increase in the rate of moisture loss with temperature can be observed in Figure 1a, since the fastest drying occurs at 70 °C.

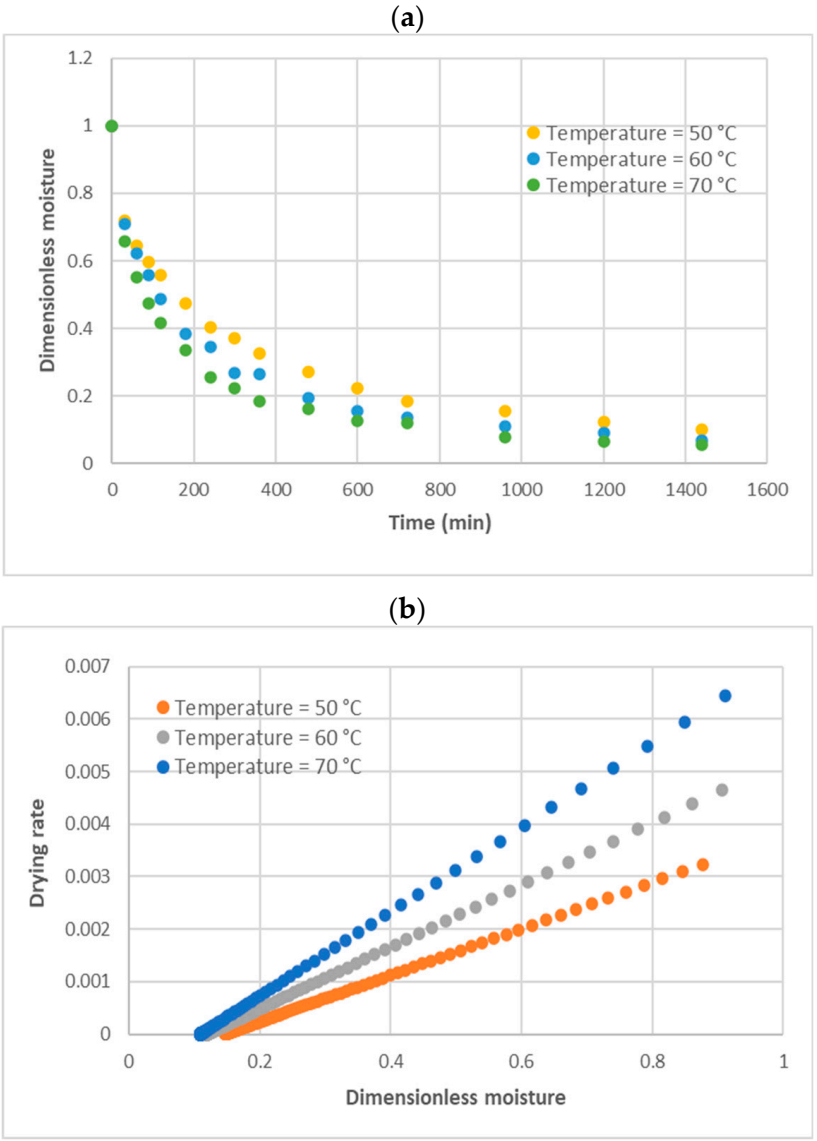

Figure 1. Moisture curves (**a**) and drying rates (**b**) during thin-layer drying of cocoa beans at different temperatures (50 °C, 60 °C, and 70 °C).

Drying rates were also obtained for the three temperatures (50, 60, and 70 °C). Equations (7)–(9) present the exponential models obtained for each temperature, as well as the coefficients of determination (R^2) with adjustment results above 0.96.

$$X(50\ ^\circ\mathrm{C}) = 0.14584 + 0.73184exp(-0.00442t)\ R^2 = 0.964 \quad (7)$$

$$X(60\ ^\circ\mathrm{C}) = 0.11875 + 0.7874exp(-0.00591t)\ R^2 = 0.974 \quad (8)$$

$$X(70\ ^\circ\mathrm{C}) = 0.10923 + 0.80252exp(-0.00803t)\ R^2 = 0.969 \quad (9)$$

The derivatives were estimated from Equations (7)–(9) with which the drying rate was generated for each temperature, as shown in Figure 1b.

As shown in Figure 1, as the temperature of the drying air increased, it produced an increase in the moisture loss rate, obtaining a faster drying at the 70 °C temperature. The equilibrium moisture was not reached until 1400 min.

Figure 1 also shows the dynamics of the drying rate as a function of moisture. A dependence as a function of the drying temperature can be observed. These results establish that the drying rate increases as a function of the temperature and moisture of the sample. The behavior is typical of drying kinetics and defines diffusion as the single dominant mechanism for mass transfer.

3.2. Energy Consumption and Energy Efficiency

Table 1 lists the SEC values of convective drying for cocoa beans; the lowest SEC (18,947.30 kJ/kg) was obtained at 70 °C drying temperature, and the highest SEC (24,469.51 kJ/kg) was obtained at 50 °C.

Table 1. Results of moisture, SEC, and energy efficiency (η_e) of cocoa beans at different drying temperatures.

Temperature (°C)	Moisture (%)	Energy Consumption (Wh)	SEC (kJ/kg)	η_e (%)
50	8.90	3471.50	24,469.51	9.73
60	6.54	3388.30	23,218.35	10.15
70	5.02	2791.00	18,947.30	12.31

As the drying temperature of the dryer increased, the SEC decreased; the reason can be related to the fact that at higher temperatures, the thermal gradient and mass transfer increase, resulting in faster moisture loss, which decreased the SEC [5]. The operational performance of the dryer at each temperature can also have an effect on energy consumption. SEC was found to be between 7000.79 and 16,000.20 kJ/kg using microwave power for drying kiwi slices [37]. In another study conducted on sweet potatoes with a convective dryer, the amount of SEC was in the range of 56,304.00–310,932.00 kJ/kg) [5]. Studies on the drying of cocoa beans reported a specific energy consumption (SEC) value of 27,793.9 kJ/kg using a greenhouse-type dryer [8] and 13,290.00–35,430.00 kJ/kg using a solar dryer integrated with thermal energy storage [38].

In terms of energy efficiency, the highest energy efficiency was achieved at 70 °C (12.31%), while the lowest energy efficiency was observed at 50 °C (9.73%), but not much difference was observed for 60 °C (10.15%). According to other studies, increasing the drying temperature increased the moisture loss and shortened the drying time due to the thermal gradient between the product and the drying temperature, resulting in higher process efficiencies [5]. In other studies using hot air convective drying, the energy efficiency for chamomile was in the range of 1.91–6.76%, for *Pistacia atlantica* was 5.65%, for kiwi was 4.11–12.15%, and for apple slices was 3.42–12.29% [6,39]. These results also showed that the efficiency increased as the temperature increased, which was explained by the reduction in the drying process. Another study for solar drying of cocoa by forced convection reported an energy efficiency between 9 and 17% [7].

As shown, the results of this work are consistent with other previously published results. The differences between SEC and energy efficiency are a function of the drying method, the product, and the use of a pretreatment. To our knowledge, no recent studies have reported these parameters for convective cocoa drying.

3.3. Bioactive Compounds and Antioxidant Activity

The following figures present the results obtained from the analysis of the bioactive compounds considered in this study (TPs and TFs) and the antioxidant activity by DPPH, showing the behavior through the drying time at the different temperatures used for the

process. The quantification of these compounds was conducted considering the sampling at fixed time periods and the lyophilization of the samples to avoid oxidation, in order to facilitate the detection of significant evidence on the effects of drying temperature.

Studies on bioactive compounds focus primarily on the evaluation of TPs and TFs in order to detect any changes caused by the process. In the case of cocoa drying, evidence has been reported [40] that these compounds decrease during the fermentation and drying processes through the enzymatic activity of polyphenol oxidase. This condition makes it possible to reduce the bitterness and astringency of the product, as well as the appearance of a brown color. These changes are desirable and can be associated with the development of aroma precursors [41].

The results of the present study explored the behavior of TPs, TFs, and DPPH as a function of time and temperature during the drying process of Criollo cocoa grains. Regarding the results of TPs, small evident changes were found before 300 min, under the evaluation conditions, as shown in Figure 2. However, after this time, there was an increase in the TP levels. This increase may be related to the degradation of the cellular structure of the cocoa beans during drying, which would release the bound phenolic compounds and lead to increased TP levels. The changes that occur after 300 min imply a moisture loss in the grain between 60 and 80% from the initial moisture, a condition where the effects of temperature are more significant at the structural and cellular level. Previous studies [16,17] on the modeling of the kinetics of TPs reported a linear decrease in the initial stages of drying (<300 min) but showed no evidence of changes after these times. On the other hand, in the case of TFs, no changes were observed in the results at the three temperature conditions that led to a decrease or increase in their levels. The presence of flavonoids in other studies [18] was associated with antioxidant activity and implies that changes in TPs during drying may be associated with compounds from other families. Furthermore, TPs and TFs can vary according to the variety of cocoa in question (Forastero, Trinitario, or Criollo) since the composition of origin and the types of phenolic compounds are influenced by each variety. Criollo-type cocoa in particular lacks anthocyanidins, which visually give a violet color to the Forastero and Trinitario [42]. As mentioned, the present study was focused on the Mexican Criollo cocoa variety, being the first work that reports TPs and TFs during convective drying in thin layers. Likewise, the changes in these compounds are also influenced by the performance of the previous fermentation process that involves enzymatic and microbial activity. The enzymatic activity reported by [28,43] indicates that the changes may be associated with the variety, geographical area, fermentation process, drying, climatic conditions, sample preparation, extraction method, and purification strategy.

Figure 3 shows the results of the DPPH radical assay at the three temperature conditions. Statistical analysis was performed using the Pearson correlation coefficient; the results for DPPH showed low correlation at 50 °C and 60 °C and no correlation at 70 °C during the drying process of cocoa beans. The matrix of results can be consulted in the Supplementary Materials (Table S1). At the drying temperature of 70 °C, a phenomenon was observed where the antioxidant activity remained practically constant at an approximate value of 90%. This implies that the amount of bioactive compounds throughout the drying process of Mexican Criollo-type cocoa was sufficient to inhibit approximately 90% of the DPPH radicals at the studied concentration. A study on the antioxidant capacity and phenolic compounds in cocoa showed a dependence of the results on the type of extraction medium (aqueous or hydroalcoholic) [12].

For the TPs and TFs, the results showed no correlation with temperature or time. The results between TFs and DPPH at 50 °C showed moderate correlation; no correlations were found in the other conditions of the present study (Table S1). Antioxidant activity not only depends on TPs and TFs, but there are also recent studies that showed its relation with bioactive peptides, lipids, and methylxanthines [44]; however, the drying process has not yet been addressed to evaluate the effect of these substances.

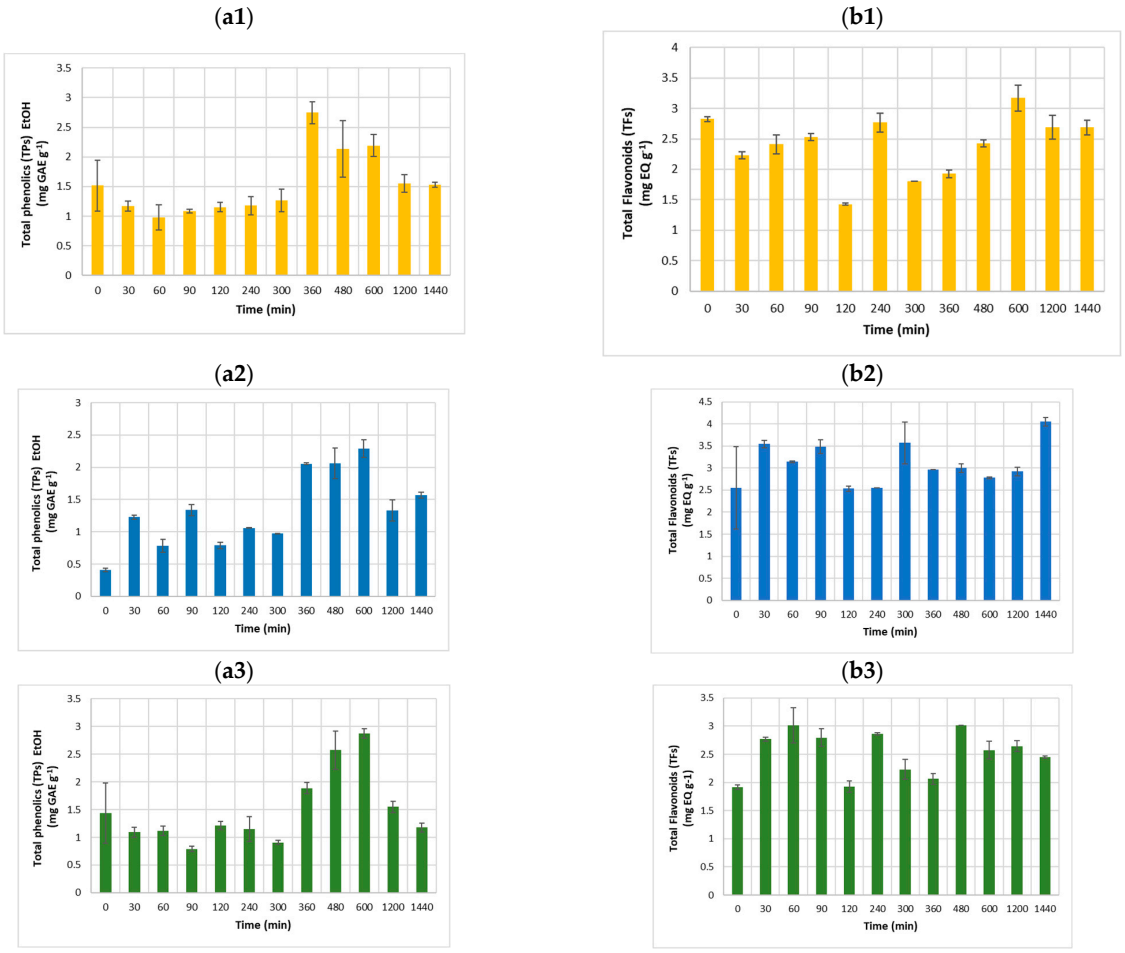

Figure 2. Bioactive compound behavior as a function of time in cocoa beans convectively dried for (**a1**–**a3**) TPs at temperatures of 50 °C, 60 °C, and 70 °C and (**b1**–**b3**) TFs at temperatures of 50 °C, 60 °C, and 70 °C.

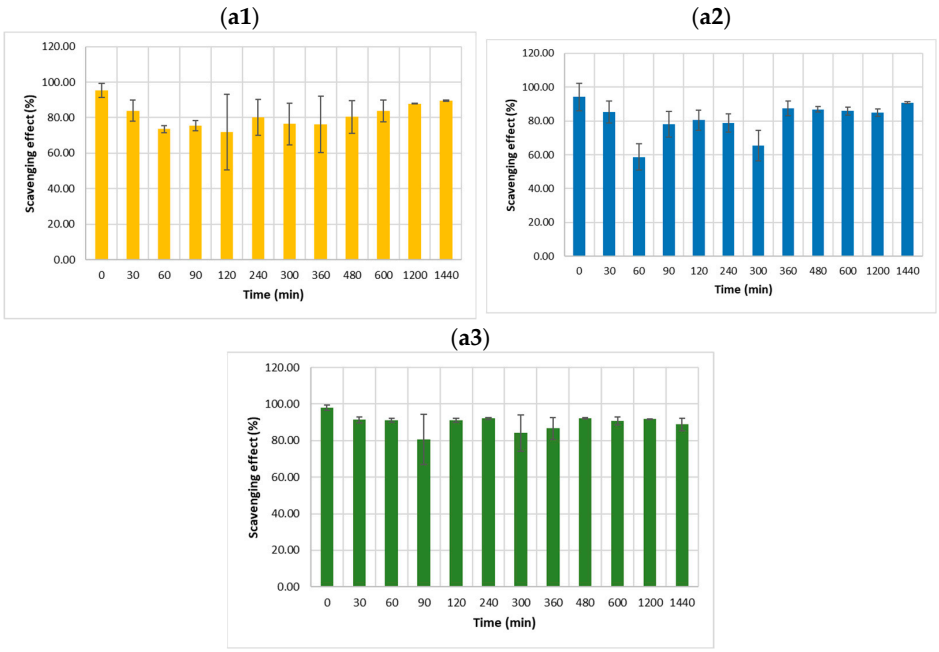

Figure 3. DPPH behavior as a function of time in cocoa beans convectively dried at (**a1**–**a3**) temperatures of 50 °C, 60 °C, and 70 °C.

3.4. FT-IR Spectra

The bands of the FT-IR-ATR spectrum of dried cocoa represent all the functional groups present in the molecules that constitute this product. Figure 4 shows the FT-IR spectra; a variation in the different bands can be seen as the drying time increases. These figures show the absorbance in the different spectral bands and their signal allocation assignment. The vibrational signals of the FT-IR spectra changed during the drying process, which may indicate changes in the composition of some compounds. The decrease in the signals of these groups was reported by other authors for materials other than cocoa [36,45].

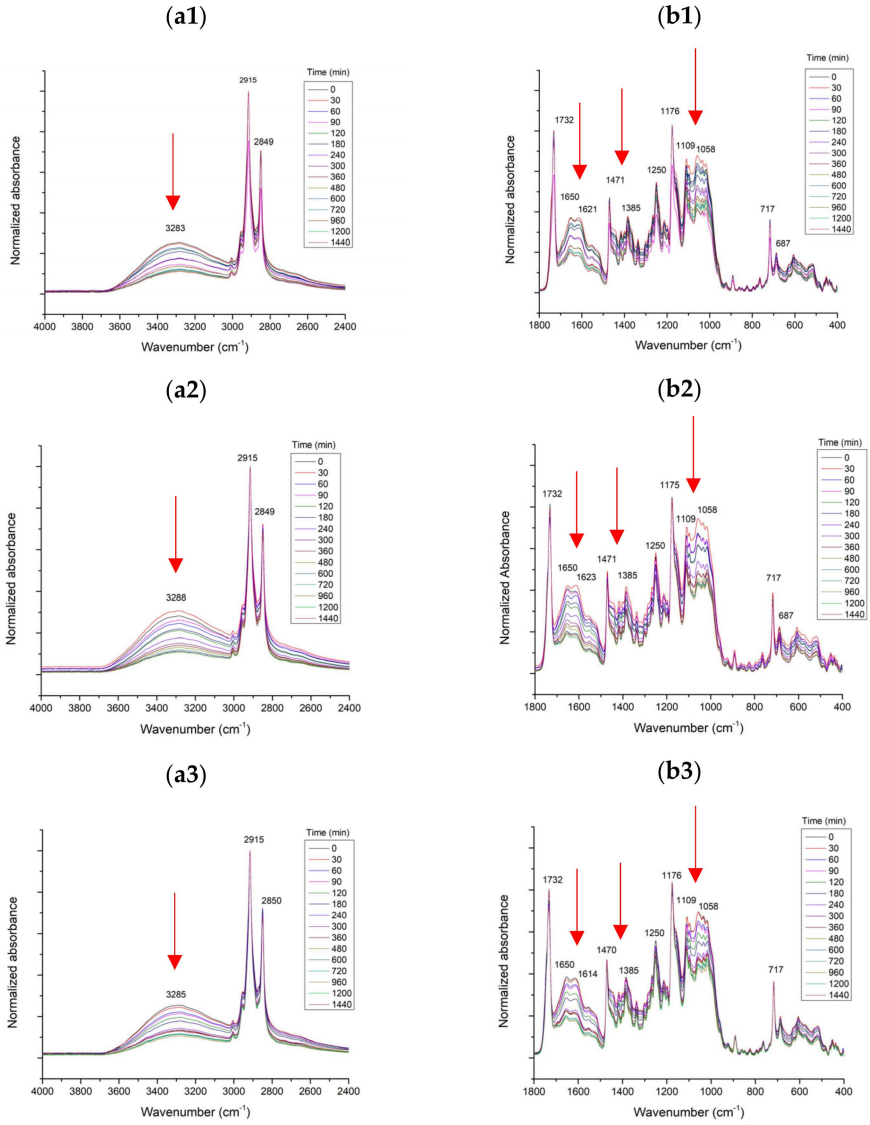

Figure 4. FT-IR vibrational spectra of cocoa powdered samples during the drying process in the region of 4000–2600 cm^{-1} at (**a1**–**a3**) temperatures of 50 °C, 60 °C, and 70 °C and in the region of 1800–400 cm^{-1} at (**b1**–**b3**) temperatures of 50 °C, 60 °C, and 70 °C.

The cocoa cotyledon contains many chemical compounds that can be grouped into different chemical classes, including volatiles such as acids, alcohols, aldehydes, ketones, esters, fatty acids, and pyrazines, mainly, as well as non-volatile compounds like alkaloids, amino acids, flavonoids, phenolic acids, sugars, carboxylic acids [11]. This implies certain difficulties in their correct interpretation by superimposing the signals of the functional groups. In terms of proximal analysis, cocoa contains fat (40–50%), protein (14–18%), digestible carbohydrates (12–14%), and crude fiber [46]. A change in the concentration of these compounds can be observed as a function of drying time and temperature. At

least four regions of changes were located in the signals of 3263 cm^{-1}, 1650–1621 cm^{-1}, 1471–1385 cm^{-1}, and 1109–1058 cm^{-1} (Figure 4). Therefore, signals in the range of 2957 to 2849 cm^{-1} (Figure 4a1–a3) can be found, which were assigned to symmetrical and asymmetric extension vibration modes of methyl and methylene groups, present in groups of lipids, fatty acids, alcohols, amines, phenolic compounds, and aromatic compounds [13,47]. Figure 4b1–b3 show the signals found in the region of 1800 to 400 cm^{-1} from highest to medium intensity; the differences with respect to Figure 4a1–a3 can be clearly observed. The signals at 1744 cm^{-1} and 1162 cm^{-1} were identified for fats and associated with esters [48]. In the present study, these signals were displaced to 1732 cm^{-1} and 1176 cm^{-1}.

The signal at 1650 cm^{-1} corresponded to Amide I, predominantly to the C = O extension vibration, and the signal at 1614 cm^{-1} was associated with the extension vibration of the phenyl group ring. It can be clearly seen that this region undergoes changes as a function of time and temperature during cocoa drying (Figure 4b1–b3).

The signal at 1470 cm^{-1} was associated with methylene flexion, while the signal at 1385 cm^{-1} was assigned as a symmetrical scissor-swinging flexion of the methyl group of proteins [49]. A signal at 1250 cm^{-1} can also be observed; it was attributed to vibrations of C-O extension and CH_2 flexion [49]. The signal at 1158 cm^{-1} showed evident changes during the drying process, which were attributed to C-O extension vibrations of proteins and carbohydrates. Another signal related to fat was found at 1100 cm^{-1} [50], but in this study, it was present at 1109 cm^{-1}. The signal at 717 cm^{-1} related to CH_2 linear chain signals (>4) was considered to be linked to lipids present in cocoa. The changes observed in the aforementioned regions confirm the variation in phenolic compounds as a function of temperature and drying time, in addition to the presence of other types of reactions that can modify amides, proteins, and carbohydrates.

3.5. Multivariate Analysis

The complex FT-IR spectra were successively analyzed by using MetaboAnalyst 6.0 software. MetaboAnalyst algorithms were used on the matrix M, and PCA (scores and loadings) was performed (see Figure 5). A heatmap was integrated using the correlation matrices between variables and between samples (data not included); the heatmap was useful to represent the correlations between the samples and variables graphically, as shown in Figure 6.

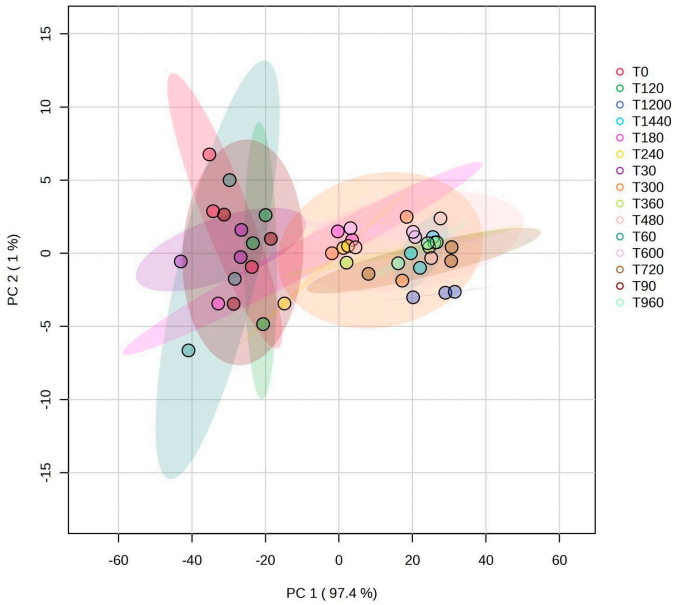

Figure 5. Principal component analysis (PCA) score chart.

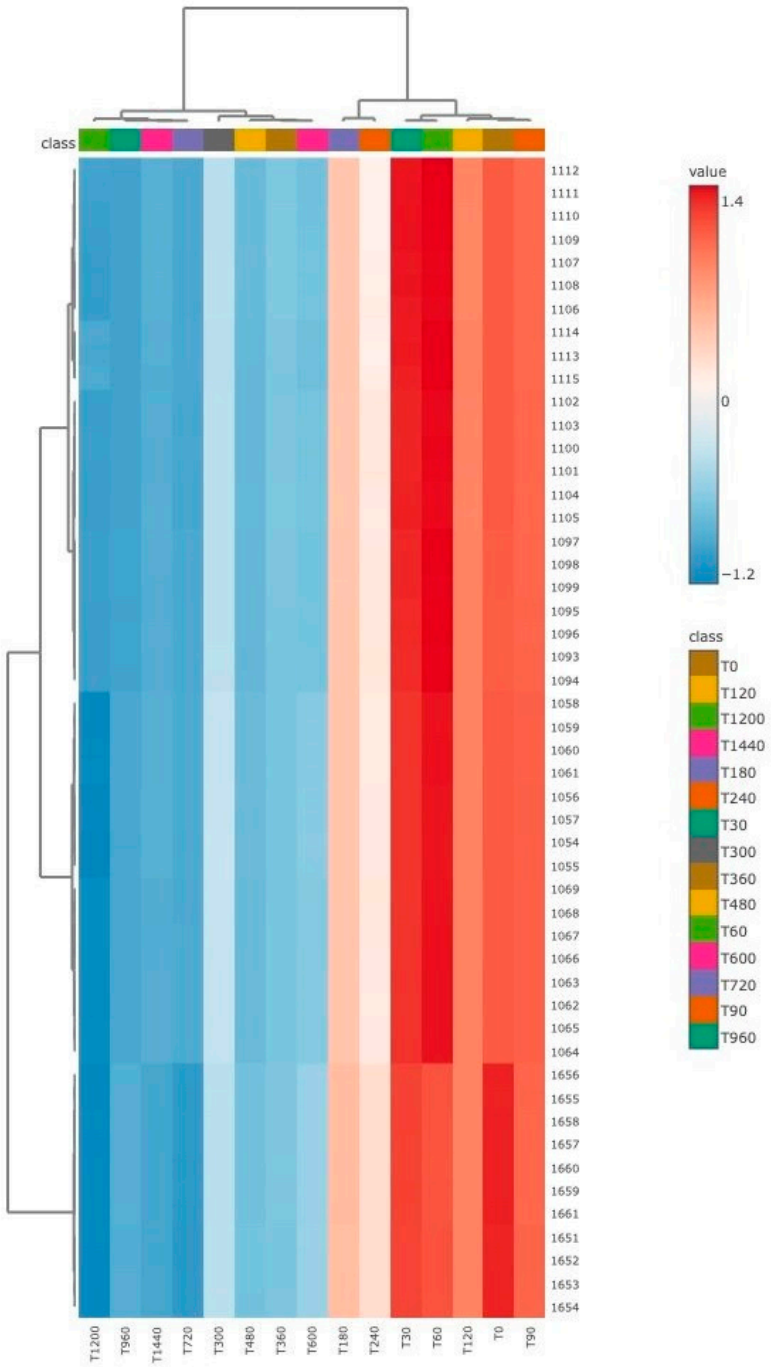

Figure 6. Heatmap showing wavenumber changes of the spectral analysis and the drying times.

In the range of 4000 to 400 cm^{-1}, medium- to high-intensity signals were identified in the X-H region and the fingerprint region. A data matrix was formed from the infrared signals, and PCA was performed using MetaboAnalyst 6.0 software. The results showed that the first main component (PC1) described 97.4% of the explained total variance, while the second component (PC2) described only 1.1% (Figure 6). It was also found that the main changes associated with the clustering were between times 0 and 120 min and between times 180 and 1440 min. This methodology has been similarly used to verify the authenticity and quality of commercial oils [24].

The analysis of PC1 was described by three wavenumbers from the infrared region with a positive contribution to 1732, 1731, and 1730 cm^{-1}. PC2 showed positive contributions to 1730 cm^{-1} and in the regions 715–558 cm^{-1} and 615–675 cm^{-1}, as described

by the loading plot (Figure S1, Supplementary Materials) and eigenvectors of the signals (Table S2, Supplementary Materials).

The separation results of the two regions of the PCA indicate that there are significant changes that cannot be appreciated by the conventional analysis techniques presented in this study.

The data matrix that was used for the analysis considered the signals of the infrared spectrum obtained for each time in the drying kinetics; therefore, the observed separation is a function of signals that are maintained or appear or disappear, so the result of the PCA suggests the presence of new components or transformation of the existing ones. It is worth mentioning that in the framework of this PCA, the main signals were not analyzed according to the intensity or area under the curve, so complementary work could generate new information or evidence on the changes and represents an opportunity for the continuation of the present study.

Figure 6 shows a heatmap over an interval of 50 infrared signals that were significant over drying time. The heatmap shows the correlations established between the variables and the samples that are plotted. As Socaciu et al. [24] explained, the heatmap shows the positive correlations (intense red) between the samples (in our case the times) and the specific wavenumbers, while negative relationships are shown in blue. The grouping is displayed at the top. Therefore, it can be established, without a doubt, that there were changes in the signals of the vibrational groups at each time evaluated during the drying process and also in the concentration of the different compounds where the study signals are involved. In addition, most of the signals shown in the heatmap are associated with the fingerprint region (1800–400 cm^{-1}) and only three signals (3283, 2915, and 2849 cm^{-1}) have been assigned to -OH and symmetrical stretch groups of CH_3 and CH_2, respectively.

It is possible that interferences may occur in the powdered samples of whole cotyledons that were used for FT-IR analysis due to the complexity of the matrix and the presence of many compounds. Therefore, it is suggested that this study can be complemented with a subsequent analysis that includes the separation of phases (lipids and cocoa) of the powdered samples since phenolic compounds can be found in greater proportion in the cocoa phase.

4. Conclusions

The present study showed that vibrational changes of bioactive compounds attributed to changes in −OH can be identified as a function of temperature and time through FT-IR; moreover, the separation of the two main components of the PCA indicates the presence of significant changes in some compounds. Therefore, the use of FT-IR spectroscopy combined with multivariate analysis was useful in detecting the effects of the drying conditions on the in vitro compound levels of Criollo cocoa beans, which are not easily detected by conventional analytical techniques.

The results showed that the energy consumption assessed through the SEC during cocoa drying is a function of the temperature imposed on the system. The highest temperature led to better SEC and energy efficiency. Also, some effects of temperature were found on the TP levels, but no changes were observed in TFs and DPPH, which may indicate that the changes in TPs during the drying process are related to compounds from other families. Noteworthily, further research studies are recommended, including wider drying temperature values and CG-MS and HPLC-MS analysis, to identify the specific compounds related to the changes detected in the TPs during the drying process.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr12112523/s1. Table S1: Pearson correlation coefficient matrix of variables measured during thin-layer cocoa drying; Figure S1: Loading plot of infrared signals; Table S2: Eigenvectors of the infrared signals.

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