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Management of Surface Drying Temperature to Increase Antioxidant Capacity of Thyme Leaf Extracts (Thymus Vulgaris L.)

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MANAGEMENT OF SURFACE DRYING TEMPERATURE TO INCREASE ANTIOXIDANT CAPACITY OF THYME LEAF EXTRACTS (*THYMUS VULGARIS* L.)

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Abstract

Thyme leaves are an important source of essential oils with antioxidant activity; these compounds are located in trichomes on the leaf surface. The drying conditions affect not only the drying time but also the antioxidant activity. In the literature, a drying temperature of 70 ºC appears to be the best for drying thyme leaves according to their antioxidant capacity. Considering drying periods at different temperature also could be quality beneficial. From these considerations, the goal of this work was to establish a drying strategy with which to manage a drying temperature on the leaf surface which will enable the drying time to be shortened and improve the antioxidant capacity (AC) of the extract of dried thyme leaves. The drying strategy consisted of two consecutive drying periods in order to manage the drying temperature on the leaf surface. The first drying period was carried out at 80°C (T_{a1}) until the sample surface reached a temperature of 70 ºC, which then immediately being set to 70, 60, 50 and 40 °C (second drying period (T_{a2})), at a different air velocity (v) (1 and 2 m s^{-1}). Compared with constant drying conditions, two consecutive drying periods were found to improve the drying kinetics, the AC increased from 10.5% to 27.4 % while reducing the drying time by 14.5% to 39.2 %.

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The use of this drying strategy was found to be an interesting means of intensifying the convective drying of thyme leaves and its application should be considered when drying similar materials with bioactive compounds on the surface.

KEYWORDS: Changing boundary drying model, two step drying, drying time reduction

INTRODUCTION

For many years, aromatic plants have been used for a large number of purposes (medicine, nutrition, flavorings, beverages, cosmetics, and industrial uses). It has been acknowledged that many of them have medicinal properties and possess a variety of antioxidant effects. The essential oil of lamiaceae herbs, like thyme, is a very rich source of phenolic compounds known for their antioxidant activity [1,2]. The essential oil is stored in peltate trichomes located on the epidermal surface on both sides of the leaves [3].

Thyme has a high water content (65–80%, in w.b.), requiring a preservation method in order to lengthen its useful life for further use. Hot air drying, one of the oldest food preservation processes, is by far the most widely used treatment and is considered the first step in many food processes. It is recognized that drying is an energy-intensive process as heat needs to be supplied for water evaporation. Both the effect that the heat treatment has on the product quality and also energy consumption issues are key factors.

Drying forestalls biochemical changes and, simultaneously, it can give rise to other alterations that affect herb quality, such as changes in appearance and alterations in aroma caused by losses in volatiles or the formation of new volatiles as a result of oxidation or esterification reactions [4–6].

Different research has reported the effect of drying methods on the essential oil compounds present in thyme and their antioxidant properties[7–10]. Considering two drying methods, freeze-drying and oven drying at two temperatures (30 °C and 60 °C), Venskutonis[8] noticed an increase in antioxidant capacity while drying at 60 ºC examining the effect of the drying method on the essential oil composition of *Thymus vulgaris* [8]. In others works[9] it was found that the best drying temperature for increasing the antioxidant capacity of *Thymus vulgaris* L was 70ºC. It has been reported[10] the effect of six different drying treatments on the essential oil components and found that a temperature of 70 ºC led to an increase in the content of the major constituents of *Thymus daenensis* subsp. *Daenensis,* thymol/carvacrol.

Drying not only led to the disappearance of some compounds but also to the appearance of others which were absent in fresh leaves. Air temperatures of over 70 ºC could improve the drying kinetics, thereby reducing the drying time; nevertheless, long-time application results in the loss of volatile compounds and a decrease in the antioxidant capacity [9]. Therefore, it can be considered that drying time and temperature are crucial parameters for the preservation of the main compounds of the essential oil.

When addressing product quality it should also be considered energy consumption in order not to increase costs. A significant effort has been made to search for and develop ways to reduce the energy consumption of drying technologies for three reasons: the need to improve product quality, reduce operating costs and lessen the environmental impact [11]. To that end, new or improved technologies can be introduced[12] or the process can be carried out considering a different approach [13]. Therefore, the selection of a suitable drying method and a good management process, are all essential in order to achieve high quality products, of lower cost and higher yield.

As a management procedure, the application of a drying strategy time-varying temperature profile can be considered during the drying process[14]; this approach could lead to the reduction of the effective drying time [13,14,15], and the preservation of the final quality. For that purpose a mathematical model would be necessary to establish the operating conditions in the drying strategy for a particular case [13]. Because there is an influence of drying temperature on essential oil antioxidant properties and the essential oil is located at the surface of the leaves, it could be interesting to consider surface temperature on the management procedure.

To permit real time management, the model must allow for rapid calculations, providing an accurate enough description of the process. The complexity of the drying process arises from the simultaneous heat and mass transfer between the air and the product. In order to address this complexity, it is necessary to model the process adequately. A number of drying models have been proposed, which can be classified into empirical [16,17] and mechanistic models [18,19]. It is important to consider a time-varying boundary conditions model if a particular surface temperature is to be considered. This kind of model is of interest as the antioxidant capacity of dried thyme is linked to the process; a high drying air temperature allows the process to proceed quicker, but a high product temperature diminishing the antioxidant capacity.

The surface temperature of thyme leaves is important because compounds of interest are located there. Because in the initial drying steps product temperature is lower due to water evaporation, it seems of interest to attain a surface temperature of around 70 ºC quickly[9,10] by increasing drying air temperature. Since it is difficult to measure thyme leaf surface temperature inside a bed, modeling would be an interesting means of approaching the thyme-varying temperature on the product surface inside the bed.

The aim of this work was to address a two-step drying strategy, for the purpose of increasing the antioxidant capacity linked to drying kinetics. To that end, the influence that the temperature, air velocity and proposed drying strategy had on the drying kinetics and antioxidant capacity was analyzed.

MATERIALS AND METHODS

Sample Preparation

This study was carried out with fresh thyme leaves (*Thymus vulgaris* L.), which were obtained locally (Vivarium Albogarden in Valencia, Spain). The leaves of the plant were plucked manually. In order to preserve their original quality, fresh plant material was placed in a closed container and stored under refrigeration at 4 °C until the drying experiments. The initial moisture content (62–74 %, w.b) was determined according to

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the AOAC standards (1997) [20]. The toluene displacement method [21] was used to determine the density of the dry solid (128.6-178.2 kg m^{-3}).

Drying Experiments

An automatic laboratory scale convective drier was used, as already described in previous works [22]. The ambient air temperature (between 24 and 26 ºC) and relative humidity (between 50 and 60%) were measured using a sensor of environmental parameters (TG 80, Galltec + mela, Germany), the hot air temperature was measured with a Pt100 thermoresistance, the air velocity with a vane anemometer (Wilh, Lambrecht GmbH, Göttingen, Alemania), and the sample weight was periodically weighted (PM4000, Mettler Toledo, Greifensee, Suiza). Such experimental data were automatically registered periodically. From the ambient temperature and humidity, and from hot air temperature, the hot air relative humidity and moisture content were estimated considering the air behaves as ideal gas.

Thyme samples of approximately 20 g were subjected to different drying processes, and were run in triplicate. The thyme leaves were distributed uniformly inside the drying chamber, forming a bed of 159 cm^2 with a thickness of 3 ± 0.3 cm, through flow air was supplied perpendicular to the bed.

In order to fit and test the model, drying experiments were carried out under constant conditions of air temperature (80 (maximum drier temperature), 70, 60, 50 and 40 ºC) and air velocities (1 and 2 m s^{-1}), until the final moisture content was under 10% (w.b.). For further testing, drying experiments were carried out in two consecutive drying steps at different air temperatures.

Modeling

Due to the difficulty involved in measuring the evolution of the temperature on the leaf surface during the drying process inside the bed and the effect of heat transfer by radiation, performing thermographic measurements could be misleading. For that reason, a mathematical model reported in a previous work [22] was considered for such a purpose, taking into account the simultaneous heat and mass transfer phenomena both in the bed and in the thyme leaves.

The governing equations (Table 1) were obtained from the mass and energy balances in the bed and leaves, considering the following assumptions: mass transport diffusivity and thermal conductivity in the leaves were considered as temperature and moisture dependent respectively; initially uniform temperature and moisture in the bed; uniform air conditions in the bed, due primarily to its relatively small thickness; the balances of heat and mass transfer in the leaves were performed considering the behavior as an infinite slab because its elongated shape (between 0.004 and 0.006 m of length, and 0.003 mm as average width) and its average thickness ($3.5\ 10^{-4} \pm 1.1\ 10^{-5}$ m), and the shrinkage effect was neglected. These assumptions were considered to simplify the mathematical model formulation and therefore its resolution, in order to facility its application in a real time control of the drying process.

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A dimensionless distance was considered (Eq. 1) for the leaves in the respective governing equations.

$$z = \frac{x}{L} \wedge z \in [0,1] \qquad (1)$$

The governing equations obtained (Table 1) represent the unsteady-state heat and mass balances describing the evolution of the air temperature (T_a) and air moisture content (X_a) in the bed, and the evolution of the local moisture content (τ) and temperature (T) in the leaves.

Equation 2 was applied to calculate the average moisture content in the leaves.

$$\bar{\tau} = \int_0^1 \tau(z,t)\,dz \qquad (2)$$

The initial and boundary conditions were considered to complete the drying model (Table 1). As boundary conditions, the distribution of the moisture content and the temperature in the leaves are assumed to be symmetrical. For the specific case of two-step drying, the final conditions in the first drying step are the initial conditions of the second drying step. For the mass transfer boundary condition on the leaf surface, it is assumed that the liquid water that diffuses into the surface per unit area is evaporated at the same rate (dynamic equilibrium) and is transported by convection to air. Summarized in table 2 are the thyme and air physical properties needed in the model.

The energy boundary conditions assume that the heat transmitted by convection from the air to the leaf surface increases the temperature of the leaf and evaporates the water reaching the surface.

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The effect of temperature on the diffusivity was described by an Arrhenius type equation.

In order to analyze the results, a dimensionless average moisture content was considered for the leaves in the bed (Eq. 3).

$$\omega = \frac{\bar{\tau} - \tau_{eq}}{\tau_0 - \tau_{eq}} \qquad (3)$$

Heat And Mass Transfer Coefficient

The values of the heat and mass transfer coefficients (h and h_{mv}) can be calculated from empirical equations involving dimensionless numbers [28].

$$h_{mv} = \frac{Sh\, D_{AB}}{L_c},\ h = \frac{Nu\, k_a}{L_c} \qquad (4)$$

In early works [28], a mathematical expression was established as being one of the best for calculating those dimensionless numbers for a porous bed of particles.

$$Nu = \frac{a}{\varepsilon} Re^b\, Pr^{1/3},\quad Sh = \frac{a}{\varepsilon} Re^b\, Sc^{1/3} \qquad (5)$$

$$\varepsilon = \frac{V_a}{V} \qquad (6)$$

To establish the effect that the air velocity and air temperature during the drying process have on transport phenomena, an optimization problem was formulated to identify D/L^2 and the parameters a and b (Eq. 5). In the optimization problem, the parameters were considered as the decision variables, and the objective function was the mean relative error calculated through the comparison of experimental and calculated average moisture contents.

Computational Tools

The COMSOL Multiphysics ® 3.4[29] tool was used to solve the mathematical model (Table 1) applying the finite element method. This tool has been used by various authors for the numerical solution of mathematical models describing food dehydration [30,31]. The mathematical model was constituted by 4 governing equations, specifically 2 ordinary differential equations, with time as independent variable, and 2 partial differential equations, with time and a spatial variable as independents variables, and its respective initial and boundary conditions. To define the model in the working environment of COMSOL, the appropriate physics, the one-dimensional space dimension and the unsteady-state study type were selected. A line of length equal to the half thickness of a leaf was considered as geometric entity that forms a complete geometric description of the model.

Preliminary tests were performed to adjust the resolution settings of the tool and establish a suitable discretization of the geometry. A mesh of 10 domain elements with fixed sizes was selected as the best option in terms of computation time, convergence and accuracy.

The MUMPS (multifrontal massively parallel sparse direct solver) linear system solver and the BDF (backward differentiation formula) method of time stepping were used by COMSOL to solve the mathematical model.

The results obtained in COMSOL were exported to a Matlab® R2011a® [32] type file.

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From this file it was extracted the code functions that Matlab needs to implement to solve the model through interconnection with COMSOL. Applying these functions, the process simulation was carried out to calculate the objective function for the optimization problem developed with Matlab to identify model parameters (D/L^2, a and b).

Drying Strategy

From the results of the drying kinetics, the model parameters (D/L^2, a and b) would be identified under different constant conditions. The identified parameters, a and b*,* allow the heat (h) and mass transfer (h_{mv}) coefficients to be established. Subsequently, in order to further test their robustness, the identified parameters were used to predict the drying kinetics of the process that consisted of applying two consecutive drying steps at different air temperatures. During the first drying step, the product was subjected to a high air temperature (80 ºC) (T_{a1}) for 300 s, and in the second drying step the product was subjected to a lower air temperature (40, 50, 60, 70 ºC) until the desired final moisture content was reached.

Once the model has been tested, the drying strategy was established. The optimum leaf surface temperature was assumed to be 70 ºC; this hypothesis is supported by several authors[8,9]. At this temperature it is increased the content ophenolic monoterpenes, such as thymol and carvacrol, which contribute significantly to the total antioxidant capacity [10,33], and, on the other hand, the effect of the high temperature on enzymatic reaction (monooxygenases) favors the conversion of *p*-cymene to thymol, which is negligible at low temperatures[33].Thus in order to prevent any damage or degradation of compounds of interest caused by excessive exposure to air temperatures of 80 ºC, the length of time the sample has to be exposed to air at this temperature for its surface to reach 70 ºC must be estimated from modeling (T_{a1}). This would be linked to product and bed characteristics in each particular case.

The drying strategy consisted of two consecutive drying steps. The first drying step was carried out at an air temperature of 80 ºC and for the length of time computed for that particular case (T_{a1}), and immediately set to 40, 50, 60 and 70 ºC (second drying step (T_{a2})) until the final moisture content dropped to under 10% (d.b.) at 1 and 2 m s^{-1}. The results of this drying strategy were compared with drying experiments carried out at a constant air temperature (40, 50, 60, and 70 ºC) in order to check the degree of improvement.

Compared with processes during which the heat is continuously supplied at lower air temperatures, the application of an air temperature of 80 ºC during the first step could reduce the total drying time (t), therefore improving energy efficiency [15]. To asses this assumption the energy necessary to heat the drying air was estimated; table 3 shows the equations used for that purpose.

Extraction Of The Essential Oils

The Supercritical Fluids Extraction method (SFE) was used to extract the essential oil of the dried thyme in order to analyze the influence of the proposed drying conditions on the AC[34]. Its low operating temperature allows the essential oil characteristics to be preserved compared with other extraction methods whose high operating temperatures can affect essential oil components.

From each dried batch, a sample of 3.5 g was taken, mixed with 7 mL of ethanol as co-solvent and placed in the extraction cartridge (capacity of 200 mL). The extraction process was carried out under constant conditions of pressure and temperature: 350 bar and 35 ºC for 1 h (previously established). The extract (3 -5 mL) was collected from the bottom of the vessel and was kept refrigerated at 4 ºC in opaque flasks until the analyses were carried out.

Determination Of The Antioxidant Capacity

The FRAP (ferric reducing activity power) method was used to estimate the antioxidant capacity (AC) of the extracts. The FRAP is a method commonly used to measure the antioxidant activity of plant extracts [35,36]

Statistical Analysis

The data were reported as the mean and standard deviation of at least three replicates. The average value of the relative errors (ER) and the explained variance (VAR) statistics were used to evaluate the accuracy of fit. To test the goodness of the fit, the t-test and Lilliefors test were carried out by applying the “ttest” and the “lillietest” functions of Matlab® R2011a.

RESULTS AND DISCUSSION

Modeling

The model was fitted to the experimental kinetics obtained under constant conditions (Table 4, VAR ≥ 99.7 %; ER ≤ 3.9 %). In every case, the t-test showed that it was highly probable that the residual vectors were to be found within the confidence interval with mean 0, and the Lilliefors test failed to reject the corresponding null hypothesis at the default 0.05 significance level. As a consequence, the normality of the residuals was established. The developed mathematical model was able to describe the evolution of the moisture content taking into account the surface temperature of the leaves, under constant drying conditions.

Table 4 reports the average values of the identified parameters, D/L^2, h_{mv} and h, for drying experiments carried out at a constant air temperature (40, 50, 60, 70 and 80 ºC). It can be observed that the identified parameters were linked to air temperature and air velocity. The influence of air velocity on the drying kinetics is mainly related to external resistance; no statistically significant D/L^2 differences were found at 1 or 2 m s^{-1}. D/L^2 increased as the air temperature rose, which means that the internal resistance to mass transfer decreased as the air temperature went up.

As the velocity increases, there is a reduction in the thickness of the boundary layer around the body [37]. Therefore, the mass transfer coefficient grew as air velocity increased. The external resistance was also affected by air temperature (Table 4); the mass transfer coefficient increased as the air temperature rose, which implies a reduction in the external resistance to mass transfer. Therefore, the mass transfer mechanisms

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involved in the drying of thyme leaves were significantly affected by both air velocity and air temperature. It could be deduced that the heat transfer coefficient behaves similarly to the mass transfer coefficient. Therefore, under these operating conditions (80 ºC) it is important to manage the evolution of the sample surface temperature to avoid antioxidant capacity losses. In addition to the velocity and the temperature, the geometric ratio (height of the bed/particle size) has an effect on the heat and mass transfer coefficients [38]. This is an added difficult to compare the values obtained with values found in the literature. Nevertheless, the average values of the mass and heat transfer coefficient showed in table 4 are of the order of magnitude of the values reported in several works[38–41].

To test how suitable the model is to predict drying processes with changing boundary conditions, experiments including two drying steps were considered, as already pointed out. The results are shown in table 5 and could be considered satisfactory. Additionally, figures 1 and 2 show the fit between the experimental data and calculated results for several drying experiments carried out. Therefore, the model using the parameters identified will be used to characterize the process.

From the modeling and the identified parameters, the necessary length of time that the sample must be exposed to air at 80 ºC for its surface to reach a temperature of 70 ºC was calculated for samples of 4.71 kg water (kgds)$^{-1}$ of moisture content and bed heights of 3 cm. For drying conditions of 80 ºC and air velocities of 1 and 2 m s^{-1}, the differences between the time needed by the surface of the leaves to reach 70ºC were found to be within the experimental errors. Therefore, the time of exposure needed by the thyme leaves to reach a surface temperature of approximately 70 ºC was 600 s.

Drying Kinetics

Table 6 reports the average values of the total drying time for drying processes carried out under constant conditions as well as for the drying strategy proposal. As expected, the application of the first drying step leads to an improvement in the drying kinetics, reducing the total drying time (between 14.5% and 39.2 %) when compared with a drying experiment performed at a constant air temperature of lower than 80 ºC. The reduction of drying time, on the experimental set-up considered, applying the drying strategies proposed resulted in considerable reductions (between 6 and 30 %) of the necessary energy to heating air; the figures are shown in table 6.

It is difficult to compare with drying strategies proposed by other authors because the experimental set-up efficiency plays an important role. Nevertheless, comparing with a two-step intermittent drying[13] it is expected that this drying strategy consume less energy although the productivity will decrease because longer total drying times are involved. Other drying strategies like the use of ultrasound could not be compared because the effect of ultrasound at temperatures around 70ºC is negligible[22] and a drying step at higher temperatures is required for antioxidant capacity improvement as shown in the literature[9].

Antioxidant Capacity

The drying process affects the AC values in function of how intense the operating conditions are. Table 7 shows the average AC values of the dried product extracts. There was a marked variation between the values from different experiments, ranging from 39.9 ± 0.6 to 114.1 ± 1.6 mmol/LTrolox equivalents under constant conditions (40 ºC) and with two consecutive drying steps ($T_{a1(600s)}$-70 ºC), respectively. Two consecutive drying steps allowed the AC extracts to increase between 10.5% and 27.4 % with respect to AC values obtained from dried products under constant drying conditions. It can be observed in Table 7 that AC values showed a direct relationship with both the first drying step and the air temperature of the second drying step. Nevertheless, compared to the values at 70 ºC, the AC decreases at a constant air temperature of 80ºC, which could be due to the degradation of compounds with antioxidant capacity and changes in their structure, as already pointed out by other authors [42].

Air temperatures of over 70 ºC could improve the drying kinetic, thereby reducing drying time; nevertheless, a long-time application leads to losses of volatile compounds and a decrease in the antioxidant capacity [9].

The increase in drying rate, linked to an increase in heat transfer thus surface temperature, influences the formation or degradation of certain compounds, which could explain why the AC values at 2 m s^{-1} were higher than those at 1 m s^{-1}. The drying rate being higher at 2 m s^{-1}.

Based on these results, it seems that the greater antioxidant activity observed when two consecutive drying steps are considered is probably due both to the particular composition of these essential oils and to time/temperature effects on their main constituents. The effect of the first drying step would allow the rapid formation of compounds with antioxidant properties.

Therefore, by employing a drying strategy to manage the process, the time needed by the leaf surface to reach 70 ºC, which the literature suggests is the most suitable temperature, can be shortened [9,10]. The compounds with antioxidant capacity increase and there is also an improvement in the drying kinetics, thus reducing the total drying time which is linked to energy consumption and productivity. More research needs to be carried out for a better understanding of the relationship between AC and temperature in the drying of thyme.

CONCLUSION

Managing the drying process by applying two consecutive drying steps**,** which were established according to the surface temperature of the leaf, appears to be an important means of intensifying the convective drying of a bed of thyme leaves increasing its antioxidant capacity.

The design of the drying strategy allowed for a case ($T_{a1\ (600)}$ - 60 ° C, 2 m s^{-1}) an increasing AC by 12.3 %, whilst that the drying time is shortened by 39.2% compared to the process of continuous drying (60 ° C). This time reduction represents 30% reduction of the necessary energy to air heating. Therefore, product quality and productivity may be increased. The best results for AC were obtained at $T_{a1(600s)}$ – 70ºC, showing an increase of almost 200 % compared to low temperature drying (40 ºC). For a better understanding of the drying process, a time-varying boundary conditions model was found to be necessary. This model will permit the estimation of the length of the first drying step to be established according to product characteristics, like initial moisture content, and bed characteristics, like bed volume. In that way, the drying operation may be managed successfully and optimal operating management can even be undertaken. For that purpose, the objective function must consider both AC and energy consumption.

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NOMENCLATURE

a	Parameter equation 4
a_w	Water activity
b	Parameter equation 4
Cp_{da}	Specific heat of dry air J kg^{-1} K^{-1}
Cp_v	Specific heat of water vapor J kg^{-1} K^{-1}
Cp_w	Specific heat of liquid water J kg^{-1} K^{-1}
Cp_{ds}	Specific heat of the dry solid J kg^{-1} K^{-1}

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D	Effective water diffusivity in the leaves $m^2 s^{-1}$
D_{AB}	Diffusivity of water in air $m^2 s^{-1}$
ER	Relative error %
h	Heat transfer coefficient $kW m^{-2} K^{-1}$
h_{mv}	Mass transfer coefficient $m s^{-1}$
k	Thermal conductivity of thyme $kWm^{-1}K^{-1}$
k_a	Thermal conductivity of air $kWm^{-1}K^{-1}$
L	Half thickness of the leaves m
L_c	Thickness of the bed m
M_{ds}	Mass of the dry solid kg
m_a	Dry air mass flow $kg s^{-1}$
PM_v	Molecular weight of water vapor $kg mol^{-1}$
Q	Energy for drying air heating W or kW
R	Ideal gas constant $kJ kmol^{-1}K^{-1}$
T	Temperature of the solid ºC
T(1,t)	Temperature on the leaf surface ºC
T_0	Initial temperature of the solid ºC
T_a	Air temperature ºC
T_{ae}	Air temperature bed exit ºC
T_{ai}	Air temperature bed inlet ºC
T_{pp}	Temperature on the gas-solid interface $(T(1,t) + T_a)/2$ ºC
$T_{a1(300s)}$	Air temperature of the first drying step (80 ºC for 300 s) ºC
$T_{a1(600s)}$	Air temperature of the first drying step (80 ºC for 600 s) ºC

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T_{a2} Air temperature of the second drying step ºC

T_{∞} Ambient air temperature ºC

t Time s

t_1 First step drying time s

t_2 Second step drying time s

v Air velocity m s^{-1}

V Volume of the bed m^{-3}

V_a Air volume in the bed m^{-3}

VAR Explained variance %

x Coordinate m

X_{a0} Initial air moisture content kg water $(kgdB)^{-1}$

X_a Air moisture content kg water $(kgdB)^{-1}$

X_e Moisture content of hot air kg water $(kgdB)^{-1}$

X_{eq} Equilibrium moisture content of hot air kg water $(kgdB)^{-1}$

z Dimensionless coordinate

Greek symbols

ε Bed porosity

λ Latent heat of water vaporization kJ kg^{-1}

ρ_{da} Density of the dry air kg m^{-3}

ρ_{dai} Density of the dry air at surface temperature kg m^{-3}

ρ_{ds} Density of the dry solid kg m^{-3}

$\bar{\tau}$ Average moisture content of the product kg water $(kgds)^{-1}$

τ Moisture content of the product kg water $(kgds)^{-1}$

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τ_{eq} Equilibrium moisture content kg water $(kgds)^{-1}$

τ_0 Dimensionless moisture content kg water $(kgds)^{-1}$

ω Dimensionless moisture content

Dimensionless numbers

Nu Nusselt number

Pr Prandtl number

Re Reynolds number

Sc Schmidt number

Sh Sherwood number

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Table 1. Governing equations and initial and boundary conditions considered for modeling the drying kinetics of fixed bed of thyme leaves.

Governing equations	Initial conditions	Boundaryconditions
Air temperature (T_a) evolution in the bed. $m_a \int_{T_{ae}}^{T_{ai}} \left(Cp_{da}(T_a) + X_e Cp_v(T_a)\right) dT_a + \left[(X_e - X_a) m_a - \right.$ $= -(1-\varepsilon) V \frac{h}{L}\left[T(1,t) - T_a\right] + \varepsilon \rho_{da} V \left[Cp_{da}(T_a) + X_a C\right.$	$T_a(t=0) =$	
Air moisture content evolution (X_a) in the bed $m_a (X_e - X_a) = \rho_{da}(T_{ai}, X_a)\varepsilon V \frac{dX_a}{dt} + M_{ds}\frac{d}{d}$	$X_a(t=0) =$	
Local moisture content (τ) evolution in the leaves. $\frac{\partial}{\partial z}\left(\frac{D}{L^2}\rho_{ds}\frac{\partial \tau}{\partial z}\right) = \rho_{ds}\frac{\partial \tau}{\partial t}$	$\tau(z,0) = \tau$	$\frac{\partial \tau}{\partial z}(0,t) = 0$ $-\frac{D}{L^2}\rho_{ds}\frac{\partial \tau}{\partial z}(1,t) = \frac{h_{mv}}{L}\left[\rho_{dai}\right.$
Temperature (T) evolution in the leaves. $\frac{D}{L^2}\rho_{ds}\frac{\partial \tau}{\partial z} Cp_w(T)\frac{\partial T}{\partial z} = \frac{\partial}{\partial z}\left(\frac{k(\tau)}{L^2}\frac{\partial T}{\partial z}\right) + \rho_{ds}\left[Cp_{ds}\right.$	$T(z,0) = T_($	$\frac{\partial T}{\partial z}(0,t) = 0$ $-\frac{h}{L}\left[T(1,t) - T_a\right] = \frac{k(\tau)}{L^2}\frac{\partial T}{\partial z}$ $-\frac{D}{L^2}\rho_{ds}\frac{\partial \tau}{\partial z}(1,$

Table 2. Properties of thyme and air considered in the model

Thyme properties
Water activity[23]: $a_w = \exp[-\exp(2.97977 - 0.00258492(T_a + 273.16)^{1.37743})\tau_{eq}^{-1.44139}]$
Thermal conductivity (kJ m^{-1} s^{-1} K^{-1})for fruits and vegetables [24]: $k = 1.418\ 10^{-1} + \frac{4.93\ 10^{-1}\tau}{(1+\tau)}-$
Air/vapor properties
Specific heat of dry air (kJ kg^{-1} K^{-1})[25]: $Cp_{da} = 2.9275\ 10^{-7}(T_a + 273.16)^3 + 4.704710^{-4}(T_a + 273.16)^2 + 1.782\ 10^{-2}(T_a + 273.16) + 1005.3$
Diffusivity of water in the air phase (m^2 s^{-1})[26]: $D_{AB} = 1.4738\ 10^{-4}\exp\left(\frac{-523.78}{T_{pp} + 273.16}\right)$
Dry air density [27]: $\rho_{da} = \frac{P}{R(T_a + 273.16)(0.035 + 0.056X_a)}$
Specific heat of water vapor (kJ kg^{-1} K^{-1})[25] : $Cp_v = 10384.59 - 50.37(T_a + 273.16) + 7.4\ 10^{-2}(T_a + 273.16)^2$

Table 3.Equations applied to estimate the energy to heat the drying air.

Drying at constant temperature $Q=m_a\,t\int_{T_\infty}^{T_{ai}}\left(Cp_{da}+X_aCp_v\right)dT_a$
Drying with two consecutive drying steps at different air temperatures
$Q=m_a\left[t_1\int_{T_\infty}^{T_{a1}}\left(Cp_{da}+XCp_v\right)dT_a+t_2\int_{T_\infty}^{T_{a2}}\left(Cp_{da}+XCp_v\right)dT_a\right]$

Table 4.Identified parametersfrom model fitting at constant condition of drying, relative error and explained variance.

v (m/s)	T (ºC)	D/L^2 [10^4] (s^{-1})	h_{mv}[10^4] (ms^{-1})	h [10^1] ($kWm^{-2}K^{-1}$)	ER (%)	VAR(%)
1	***40***	0.46 ± 0.06	1.42 ± 0.11	1.38 ± 0.09	3.1	99.8
	50	0.90 ± 0.09	1.79 ± 0.21	1.67 ± 0.16	1.4	99.9
	60	2.08 ± 0.38	2.13 ± 0.08	2.16 ± 0.05	2.1	99.9
	70	4.88 ± 0.63	2.45 ± 0.12	2.58 ± 0.10	2.7	99.9
	80	7.39 ± 0.18	3.01 ± 0.11	2.79 ± 0.09	2.8	99.7
2	***40***	0.54 ± 0.02	2.82 ± 0.06	1.91 ± 0.08	1.9	99.9
	50	0.89 ± 0.01	3.12 ± 0.05	2.09 ± 0.08	3.6	99.7
	60	2.12 ± 0.08	3.49 ± 0.07	3.11 ± 0.13	3.9	99.8
	70	5.10 ± 0.08	4.01 ± 0.11	3.98 ± 0.09	2.8	99.8
	80	7.52 ± 0.19	4.57± 0.12	4.37 ± 0.11	3.1	99.7

Table 5. Model testing considering to two consecutive drying steps, relative error and explained variance.

v (m/s)	T (ºC)	ER (%)	VAR(%)	v (m/s)	T (ºC)	ER (%)	VAR(%)
1	**$T_{a1(300s)}$ - 40**	7.1	97.9	**2**	**$T_{a1(300s)}$ - 40**	6.4	97.6
	$T_{a1(300s)}$ - 50	7.8	98.4		**$T_{a1(300s)}$ - 50**	7.6	98.7
	$T_{a1(300s)}$ - 60	7.3	98.4		**$T_{a1(300s)}$ - 60**	6.4	98.1
	$T_{a1(300s)}$ - 70	6.2	98.9		**$T_{a1(300s)}$ - 70**	5.5	98.9

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Table 6. Total drying time at constant temperature and applying the strategy proposed. Estimated reduction of energy forheating dryingair.

v (m/s)	T (ºC)	t (s)	Q (kJ)	ΔQ (%)	v (m/s)	T (ºC)	t (s)	Q (kJ)	ΔQ (%)
1	**40**	22200	3284		**2**	**40**	20800	6153	
	$T_{a1(600s)}$ - 40	16364	2657	-19		**$T_{a1(600s)}$ -**	13283	4403	-28
	50	11241	2765			**50**	10100	4968	
	$T_{a1(600s)}$ - 50	8206 ±	2196	-21		**$T_{a1(600s)}$ -**	7420 ±	4006	-19
	60	5733 ±	1974			**60**	3780 ±	2604	
	$T_{a1(600s)}$ - 60	4387 ±	1630	-17		**$T_{a1(600s)}$ -**	2300 ±	1822	-30
	70	2720 ±	1206			**70**	1400 ±	1241	
	$T_{a1(600s)}$ - 70	2120 ± 42	999	-17		**$T_{a1(600s)}$ - 70**	1180 ± 46	1165	-6
	80	1200 ± 60	651			**80**	1060 ± 32	940	

Q was calculated considering the average value of the corresponding drying times, and the average values of environmentalconditions (Temperature = 25 ºC; relative humidity= 0.55).

To calculate ΔQ the estimated Q of the correspondingdrying at constant temperature was considered as reference value.

Table 7. Average values of the antioxidant capacity of dried product extracts (AC)under different experimental conditions.

v (m/s)	T (ºC)	AC [Trolox] (mmol/L)	v (m/s)	T (ºC)	AC [Trolox] (mmol/L)
1	**40**	39.9 ± 0.6	**2**	**40**	44.1 ± 2.5
	$T_{a1(600s)}$- 40	44.1 ± 0.7		**$T_{a1(600s)}$- 40**	56.2 ± 1.6
	50	49.4 ± 0.5		**50**	63.6 ± 0.4
	$T_{a1(600s)}$ - 50	62.9 ± 4.3		**$T_{a1(600s)}$ - 50**	76.1 ± 1.5
	60	72.9 ± 0.8		**60**	79.7 ± 0.8
	$T_{a1(600s)}$ - 60	81.4 ± 1.3		**$T_{a1(600s)}$ - 60**	89.5 ± 1.3
	70	87.1 ± 2.4		**70**	99.7 ± 1.8
	$T_{a1(600s)}$ - 70	94.2 ± 0.6		**$T_{a1(600s)}$ - 70**	114.1 ± 1.6
	80	82.4 ± 1.2		**80**	92.9 ± 2.2

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Figure 1. Experimental and calculated values of moisture content evolution at 1 ms^{-1}

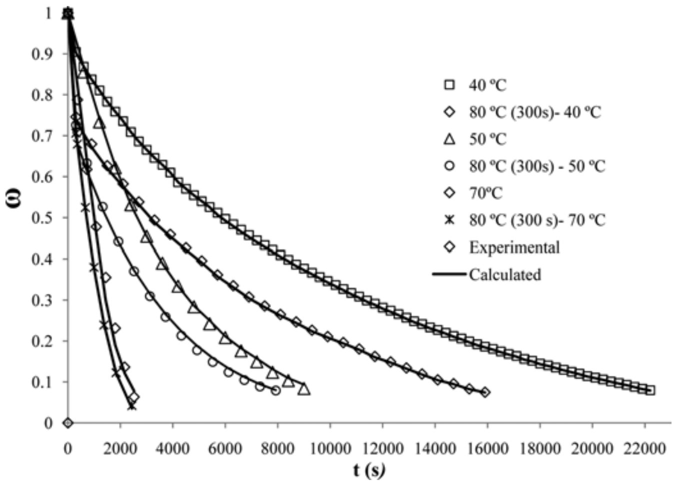

Figure 2. Experimental and calculated values of dimensionless moisture content. A) T_{a1} (300s) – 40 ºC, 1 m s^{-1}; B) T_{a1} (300s) – 50 ºC, 2 m s^{-1}