

ABSTRACT

CONTRIBUTION TO THE STUDY OF A STRENGTHENED PROCESS OF DRYING FOR THYME (*Thymus vulgaris* L.): APPLICATION OF POWER ULTRASOUNDS AND INTERMITTENT DRYING

The effects of drying in food are frequently the result of different events that take place consecutively or simultaneously. Among them there are the removal of humidity and important changes of their properties such as flavor, color, degradation of vitamins, active components and texture.

From these considerations, the technological advances in the drying process have focused their efforts on the improvement of the final quality of the products and the reduction of the processing time considering how to diminish energy consumption that would reduce operating costs and environmental impact. One of the processes where such interests are pursued is drying by hot air that not only has an important place in food processing and postharvest handling systems, but it is also one of the industrial activities involving higher energy consumption and influence different quality parameters.

In this regard, it would be interesting to study the intensification of a common way of convective drying such as fixed beds and thyme (*Thymus Vulgaris* L), which is a product of great interest for the food-processing and pharmaceutical industries. Thyme belongs to the Labiatae family and is well-known as phenolic compounds source associated with antioxidant activity. The thyme antioxidant capacity (AC) is due to the contribution of phenolic monoterpenes and volatile aromatic compounds that help significantly to the antioxidant capacity. The principal compounds of the thyme's (thymol/carvacrol) essential oil can be affected by the magnitude of the operating conditions used during the drying process which makes it necessary to identify optimal conditions for processing that improve the drying kinetics and maximize the antioxidant capacity (AC).

The intensification of the effects of drying by hot air in thyme leaves beds can be addressed from the point of view of the drying kinetics improvement and the preservation of compounds with antioxidant activity sensible to the heat.

The introduction of new technologies such as additional sources of energy and the application of an intermittent drying allow intensifying the drying process. Within the additional sources of energy to be considered, the application of power ultrasounds can be highlighted, which may influence the drying rate without producing a significant temperature increase of the material. This favors its application in the drying of materials sensitive to heat. As an intermittent drying process it is important to point to the process that is controlled through solid's surface temperature carried out with different temperatures of the drying air.

Therefore, the objective of this work was to intensify convective drying with the purpose of reducing the processing time and preserve the final quality of the dried product.

To address this objective, the thyme leaves were dried following a methodology that consisted of applying a convective drying under constant conditions of process, a convective drying assisted by power ultrasounds, and an intermittent drying controlled by the temperature of the surface of the dried solid, and then analyze the effects each technique tested regarding the drying kinetics and the AC as it is presented in the following sections:

Convective Drying under constant conditions

For the study of the intensification of the drying process of thyme leaves in fixed beds, the effect of the convective drying under conditions of constant operation in regard the drying kinetics and the antioxidant capacity of the dried thyme leaves extracts were analyzed as a starting point.

For the study of the drying kinetics, drying experiences were performed at different temperature (40, 50, 60, 70 °C) per 1 m s^{-1} . In order to describe the evolution of the moisture as a function of

time and analyzing the effect of temperature and velocity, empirical models were used. A theoretical model of infinite sheet based upon the particular Fick law and an empirical model “black-box” of neural network.

The drying rate showed a direct relation with the magnitude of the applied drying temperature. From the proposed theoretical model, was determined that the effective diffusivity (DL^2) is between 3.68×10^{-5} and $2.12 \times 10^{-4} \text{ s}^{-1}$, and the dependency of the diffusivity and the drying temperature was represented by the Arrhenius equation with an activation energy equal to $49.42 \text{ kJ mol}^{-1}$. The goodness of fit of the theoretical model was not satisfactory, which is attributed to the hypothesis considered for the model development. Based on these results and for a later study it is necessary to develop a diffusional theoretical model that considers internal and external resistance to heat and mass transfer simultaneously.

The proposed empirical models were fitted to the experimental data; additionally, the dependency of each model's parameters to the drying temperature was determined from a polynomial relationship. This allowed estimating the evolution of the humidity contents at any temperature within the time interval established. Furthermore, a comparison of the goodness of fit from the models used was made using the percentage of relative errors (ER) and the explained variance (VAR). The neural network developed showed to be more accurate than the models tested to predict the evolution of humidity with $\text{VAR} > 99.3\%$ and an $\text{ER} < 8.7\%$. From these results it can be concluded that the models developed through neural network may be considered of special interest in the formulation and resolution of optimization problems on-line as well as the predictive process control.

The effect of operating conditions regarding the antioxidant capacity (AC) were studied at temperatures (40, 50, 60, 70, 80 °C) and a velocity of drying air (1 and 2 m s^{-1}). The essential oil was extracted from the dried samples by means of the technique of extraction by CO_2 supercritical to $35 \times 10^3 \text{ kPa}$, 35 °C. From the obtained samples, AC was determined by the Ferric Reducing Activity Power (FRAP) method. From the AC and the experimental values of the drying kinetics measures, an optimization problem was formulated to determine the operating conditions that would maximize the AC of the dried thyme extracts. In order to formulate the optimization problem, the drying temperature (T), drying air velocity (V) and the drying time (t) were considered as decision variables, and the antioxidant capacity of the dried thyme extracts were defined as the objective function. Due to the complexity involved in the development of theoretical models, and since there are no references of models to predict the evolution of the product AC in terms of the operating conditions, a neural network model (ANN) was developed for this purpose. The restrictions that limit the search region of the decision variables were determined from the experimental values of the drying conditions and the results from the process. The V and T limits can be established directly, and the restriction of drying time (t) is fixed indirectly by the values of the remaining operating conditions and the desired final moisture (W_f). To estimate the final moisture content of the dry product in terms of the operating conditions, an ANN was developed. The ANNs were developed considering multiple architecture, forward feeding and a retro-propagation learning process.

The AC values from the dried product extracts varied between 21.0 and 107.2 [Trolox] (mmol/L). The AC was significantly increased when the temperature and the velocity of the air increased; however, the AC decreased for air temperatures above 70 °C at 2 m s^{-1} , which may be due to the degradation of some compounds with antioxidant capacity.

The developed ANNs showed good accuracy between the experimental values and the ones calculated with a correlation coefficient greater than 0.993 and a relative error less than 3.06%.

The optimization problem was solved for different experimental cases, and the AC result calculated at the optimal conditions obtained by the developed tool increased between 4.9% and 360.4% according to different cases considered. Additionally, the developed tool was validated obtaining differences between the calculated values and the experimental values of the AC between 2 and 7%. From these results, it should be noted that to maximize dried thyme AC, an optimal management of the process should be performed.

Convective Drying assisted by power ultrasounds

Intensifying the effect of convective drying by application of high intensity ultrasound may be a way of improving traditional convective drying. Therefore, the main objective of this study was to evaluate the influence of high intensity ultrasound in transfer phenomena during convective drying on a high porosity bed of non-porous materials, such as leaves of thyme, and assessing the antioxidant capacity of the extracts of the dried leaves.

To study the effect of ultrasound on transfer phenomena, drying experiments were conducted at 1, 2, and 3 m s⁻¹ and different temperatures of the air (40, 50, 60, 70, and 80 ± 1.2 °C), and to different acoustical density level (0, 6.2, 12.3, 18.5 kW m⁻³). In order to establish the effect of ultrasounds over the drying kinetics, a theoretical diffusional model was developed, considering mass and heat transfer phenomena simultaneously, in both the bed and thyme leaves, internal and external resistance to the transport processes with boundary conditions variable with time. The model consisting of a system of partial differential equations is solved using the finite element numerical method.

From the results of the drying kinetics, it was observed that the drying rate increased with the velocity and temperature of the air and the ultrasound power applied increased. The effect of ultrasound was observed at air temperatures below 70 °C. The effect of ultrasound on intensified drying kinetics was also influenced by the velocity of air: the higher the air velocity, the effect of ultrasound was lower.

The diffusional model with boundary conditions variable with time allowed us understand better the transport mechanisms that occur during the drying process. The developed model showed a good adjustment between the experimental values and the calculated ones (VAR ≥ 99.4%; ER ≤ 4.9%); this allowed us identify the effective diffusivity (D/L^2), the transfer coefficient of mass (h_{mv}), and the transfer coefficient of heat (h). From the analysis of the identified parameters, it was observed that these were affected by the temperature of the air, velocity of the air and the ultrasounds.

From the analysis of the parameter variation D/L^2 as a function of the operating conditions, the effects of these conditions over the internal resistance to the mass transfer were determined. The effect of the velocity of the air affects the external resistance. The effect of the temperature was observed on D/L^2 that increased when the temperature increased which means that the internal resistance to the mass transfer decreased as the temperature increased. The effect of the ultrasounds on D/L^2 was only observed for temperatures lower or equal to 60 °C.

In regard the value of the parameters h_{mv} and h , a more marked effect in the application of ultrasounds was observed compared to the D/L^2 values. This behavior may be related to the effects of the acoustical energy incurred on the bed. The bed, which is very porous, allows the ultrasounds to penetrate and affects the external resistance on the leaves. The thyme leave, being a slightly porous material with small intercellular spaces characteristic of this product, makes it less prone to the influence of ultrasounds, so that the effect on the internal resistance was lower.

The effect of the air velocity is linked to the external resistance, the mass transfer coefficient increased as the air velocity increased. The external resistance to mass transfer was significantly affected by the application of ultrasonic energy, but US have a greater effect at low air velocity and remained negligible at a velocity of 3 m s⁻¹. This suggests that the external resistance is more influenced by ultrasounds at low air velocity, not only due to the larger thickness of the boundary layer at low air velocity but also due to the disturbance of the ultrasonic field presented at high air velocities.

The parameters h_{mv} , and h related to the external resistances increased as the temperature increased, thus the resistances to mass and heat transfer decreased as the temperature increased. The mass and heat transfer coefficients increased in function of the intensity of the ultrasounds applied, but this effect was only observed when the air temperature was less than 70 °C. Therefore, the influence of ultrasounds decreased as the temperature increased.

The effect of the ultrasounds application on the antioxidant capacity of the dried leaves extracts was analyzed. For that purpose the essential oil was extracted by a supercritical fluid extraction method, and the antioxidant capacity of the extracts was measured by means of the Ferric Reducing Activity Power (FRAP).

From the experimental conditions and the results obtained, an optimization problem to determine the operating conditions that maximized the AC of dried thyme extracts (objective function) was formulated. As decision variables the controllable operating conditions were considered: temperature of the drying air (T), the velocity of the drying air (V_H), ultrasonic power and drying time (t). The restrictions of the decision variables were established from the experimental values of the operating conditions and results of drying experiments. To quantify the objective function in terms of the operating conditions considered as decision variables, a mathematical model was developed. Due to the complexity involved in the development of theoretical models to predict the evolution of antioxidant capacity during drying thyme process and to avoid long calculations for management applications in real time, a neural network (ANN) was developed for this purpose.

In addition, it was analyzed the influence of the ultrasound (US) on the drying rate (r_d), this was calculated from the experimental values of the evolution of the moisture content. The drying rate increased with temperature and velocity of the air; therefore, the drying time is reduced to achieve the desired final moisture content. The effect of power ultrasounds on the r_d was observed at drying temperatures between 40 and 60 °C and an air velocity between 1 and 2 m s⁻¹. For air temperatures above 60 °C, at a drying air velocity of 3 m s⁻¹ and the application of US did not increase the r_d ; therefore, the influence of the US under these operating conditions was negligible. The fact that US does not influence drying rate at an air velocity of 3 m s⁻¹ is attributed to the perturbation of the acoustic field.

From the AC measurements, it was observed that, in general, it increased significantly in terms of the magnitude of the operating conditions applied in the drying process. The AC values are greater for drying samples at 2 m s⁻¹ than at 1 m s⁻¹, which decreases in samples dried at 3 m s⁻¹. This may be due to a greater surface heating. The effect of temperature on the AC shows a direct relationship; however, at 2 m s⁻¹ and with drying temperatures above 70 °C, the AC decreased. This may be caused by the degradation of the essential oil. The US effect on the drying kinetics was observed at air velocities between 1 and 2 m s⁻¹ at temperatures lower or equal to 60 °C; for temperatures over 60 °C and drying air velocities 3 m s⁻¹ the US effect was negligible, impacting indirectly on the variation of AC.

The AC variation in this study may be attributed mainly to the effect of temperature, air velocity and ultrasound on the drying kinetics, and therefore, the degradation and formation of the phenolic compounds with antioxidant capacity.

The management tool developed to determine optimal operating conditions based on the initial conditions of the sample and environmental conditions, proved to be very useful. It allowed establishing the values of the operating conditions in order to maximize the AC. To test the reliability of the management tool developed three validation experiments were carried out with different moisture content of the samples. The AC of dried thyme extracts was measured and compared with the calculated results showed a difference between 3.3 and 4.5%.

Intermittent drying controlled by the temperature of the sample surface

Selecting an appropriate drying method, good management of the process and development of a suitable mathematical model for determining the optimum operating conditions are essential to obtain products of high quality at a low cost, with a maximum yield.

As a management procedure, the application of a drying strategy with variable temperature profile during the process may be considered. This approach can result in reduced drying time and preservation of compounds with antioxidant capacity. The purpose of this particular study was to implement a drying strategy based on two consecutive drying periods that would allow to manage the process in order to reduce drying time and increase the antioxidant capacity of the extracts of dried leaves (AC). To do this, the influence of the air velocity, air temperature and drying strategy proposed on drying kinetics and on the AC were examined.

From the literature, it was found that 70 °C was the best drying temperature which favors the appearance of compounds with antioxidant capacity, and temperatures above this cause excessive damage to the structure of the material and loss of essential oil. Based on these considerations, a drying strategy was established consisting of applying two consecutive periods of drying. During the first drying period the product is subjected to a temperature of 80 °C for a given time, preventing that the leaf surface exceeds 70 °C. In the second drying period, the product is subjected to a lower air temperature (40, 50, 60, 70 °C) until a desired final moisture content is reached. Applying the first drying period of high temperature may reduce the total drying time (t) compared to processes in which the heat supply is continuous, and therefore, it can improve energy efficiency.

To prevent damage or degradation of the compounds of interest from exposure to excessive temperatures of 80 °C, it was necessary to set the exposure time at 80 °C for the time in which the surface of the sample reaches a temperature of $68 \text{ °C} \pm 2 \text{ °C}$. Given the difficulty of experimental measurement of the surface temperature of the leaves during the drying process, the evolution of this temperature was determined using a diffusion model considering internal and external resistances. The model developed considered heat and matter transfer phenomena in the bed and thyme leaves simultaneously.

From the drying process model it is established an exposure time at 80 °C so that the surface of the sample may reach a temperature of 68 °C. For the drying process at 80 °C and air velocities 1 and 2 m s⁻¹ no significant differences in the evolution of the surface temperature were found. Therefore, the exposure time to the surface of the sample to reach a temperature of about 68 °C was 600 s.

To extend the application to other temperatures, corroborate the results for other drying temperatures, and test the accuracy of the model developed, the drying strategy considered was performed in two consecutive drying periods: the first drying period was 80 °C for 300 s (T_{a11}) or 600 s (T_{a12}), and the second drying period (40, 50, 60 and 70 °C (T_{a2})) was immediately developed until the final moisture content was lower than 10% (d.b.) at 1 and 2 m s⁻¹. These strategy results of drying experiment were compared with the air drying at a constant temperature (40, 50, 60, and 70 °C).

As expected, increasing the time of the first drying period increased drying kinetics. Therefore, the total drying time was reduced between 7.9 and 39.2%, compared to experiences of drying at a constant air temperature. The model developed was fitted to the experimental results, showing good accuracy (VAR \geq 99.7%; ER \leq 5.9%). The mathematical model allowed identifying parameters related to the processes of internal and external transport. From the analysis of the identified parameters, it was concluded that the mechanisms of heat and mass transfer involved in drying thyme leaves were significantly affected by the velocity and air temperature. These results allowed explaining the behavior of the drying kinetics obtained by applying two consecutive drying periods.

AC values showed a variation between 39.9 ± 0.6 and 114.1 ± 1.6 mmol / LTrolox. The implementation of the first drying period allowed AC increase between 4.7 to 27.4% compared to the values obtained under constant drying conditions. However, at a constant air temperature of 80 °C, there was a decrease in the AC, which may be due to degradation of the compound with antioxidant capacity and changes in their structure. Based on these results, it appears that the increased antioxidant activity observed when applying two consecutive drying periods is probably due to the particular composition of these essential oils, and the effect of time/temperature of the first period drying over its main components, allowing the rapid formation of compounds with antioxidant properties.

Therefore, through this drying strategy time could be shortened so that the leaf surface temperature reaches 70 °C, allowing to increase the amount of compounds with antioxidant capacity and to reduce the total drying time, which is related to energy consumption and productivity.

It can be concluded that the use of power ultrasound and the intermittent drying strategy considered allowed intensifying the drying process reducing the drying time and increasing the

antioxidant capacity of the extracts of dried thyme. These contribute to increase efficiency, productivity and to reduce energy consumption compared to constant temperature processes.

From the results obtained through each drying methodology it is worth to notice that to maximize the AC of dried thyme it is necessary to carry out an adequate process management, establishing the optimal operating conditions for each particular case.