Universitat
de les Illes Balears

DOCTORAL THESIS
2019

DRYING PROCESS INTENSIFICATION BY USING FREEZING PRE-TREATMENTS AND ULTRASOUND APPLICATION AT HIGH AND LOW TEMPERATURE

Francisca Vallespir Torrens

Universitat
de les Illes Balears

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2019

Doctoral Programme of Chemical Science and Technology

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Doctor by the Universitat de les Illes Balears

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Illes Balears

Dr Carmen Rosselló Matas, of University of the Balearic Islands

I DECLARE:

That the thesis titles *Drying process intensification by using freezing pre-treatments and ultrasound application at high and low temperature,* presented by Francisca Vallespir Torrens to obtain a doctoral degree, has been completed under my supervision.

For all intents and purposes, I hereby sign this document.

Signature

Palma de Mallorca, 3rd June 2019

Universitat de les
Illes Balears

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PAPERS LIST

This doctoral thesis titled “Drying process intensification by using freezing pre-treatments and ultrasound application at high and low temperature” whose author is Francisca Vallespir Torrens, is presented as papers compendium, which are listed below:

- Vallespir, F., Rodríguez, Ó., Eim, V. S., Rosselló, C., & Simal, S. (2018). Freezing pre-treatments on the intensification of the drying process of vegetables with different structures. Journal of Food Engineering, 239, 83-91. doi: 10.1016/j.jfoodeng.2018.07.008
- Vallespir, F., Rodríguez, Ó., Eim, V. S., Rosselló, C., & Simal, S. (2019). Effects of freezing treatments before convective drying on quality parameters: Vegetables with different microstructures. Journal of Food Engineering, 249, 15-24. doi: 10.1016/j.jfoodeng.2019.01.006
- Vallespir, F., Cárcel, J. A., Marra, F., Eim, V. S., & Simal, S. (2018). Improvement of mass transfer by freezing pre-treatment and ultrasound application on the convective drying of beetroot (Beta vulgaris L.). Food and Bioprocess Technology, 11(1), 72-83. doi: 10.1007/s11947-017-1999-8
- Vallespir, F., Rodríguez, Ó., Cárcel, J. A., Rosselló, C., & Simal, S. (2019). Ultrasound assisted low-temperature drying of kiwifruit: Effects on drying kinetics, bioactive compounds and antioxidant activity. Journal of the Science of Food and Agriculture, 99(6), 2901-2909. doi: 10.1002/jsfa.9503
- Vallespir, F., Crescenzo, L., Rodríguez, Ó., Marra, F., & Simal, S. (2019). Intensification of low-temperature drying of mushroom by means of power ultrasound: effects on drying kinetics and quality parameters. Food and Bioprocess Technology, 12(5), 839-851. doi: 10.1007/s11947-019-02263-5

Co-authors agreement letters are presented in Annex I.

Furthermore, the contributions to national and international congresses from the studies presented in this doctoral thesis have been collected in Annex II.

To my parents, my sister

and my soulmate, Miquel.

ACKNOWLEDGEMENT

I would like to acknowledge my directors, Carmen and Susana for their dedication and support as well as my laboratory colleagues, especially Valeria, Óscar and Rafa which I also consider my mentors.

Moreover, the author and the directors would like to acknowledge the Spanish government for the MINECO fellowship (BES-2013-064131) and the financial support for the following projects:

- “Aplicación de los ultrasonidos de potencia (UdP) en la intensificación de los procesos de secado a baja temperatura (DPI 2012-37466-C03-02)” of the Spanish government (MINECO).
- “Revalorización integral de subproductos en función de sus usos potenciales: Extracción de compuestos de interés mediante aplicación de US de potencia y estudios de bioaccesibilidad in vitro (RTA 2015-00060-C04-03)” of the National Institute of Research and Agro-Food Technology (INIA) and co-financed with ERDF funds.

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ABSTRACT

Drying process is commonly used to reduce fruits and vegetables moisture content in order to enlarge their shelf life. However, convective drying can promote product quality parameters losses due to thermal and air exposure. Low-temperature drying at temperatures below 20 °C but above 0 °C usually produces high quality dried products but it may exhibit low mass transfer rates. In order to intensify convective drying, both freezing pre-treatment and ultrasound application have been used in this study with the aim of shortening drying time and preserving quality parameters. Freezing pre-treatments at different freezing rates as well as ultrasound application at different power densities and/or drying temperatures (hot-air and low-temperature drying) may have different effects on different products and few studies have been found about it.

Consequently, the two general objectives of this work were, on the one hand, to study the drying process intensification at drying temperature above 20 °C by using freezing pre-treatments and ultrasound application; and on the other hand, to study also the intensification of the low-temperature drying process (at temperatures between 0 and 20 °) when ultrasound was applied. In order to reach these aims, the effects on both the drying kinetics and the quality parameters of the products were evaluated.

In Chapter 1, the effects of different freezing pre-treatments (at –20 °C, at –80 °C and by liquid nitrogen immersion) on the hot-air drying kinetics (at 50 °C), microstructure and quality parameters of three vegetal products with different initial microstructure (beetroot, apple and eggplant), were studied.

The results presented in this chapter indicated that freezing pre-treatments significantly reduced the drying time (12-34%). Freezing pre-treatment affected differently depending on both the original microstructure of the vegetal and the freezing rate. The original beetroot microstructure seemed to be more compact as it has a low porosity figure. Meanwhile, apple and eggplant have medium-high porosity figures and more fragile original microstructures. Thus, the magnitude of the drying time reduction was higher in the most porous vegetable (eggplant), and lower in the less porous one (beetroot). Moreover, freezing by immersion in liquid nitrogen (freezing rate of –144±20 °C/min) had less impact in the drying time of beetroot and eggplant than freezing at –20 and –80 °C probably because the freezing velocity was lower in these cases than in freezing by immersion in liquid nitrogen (–0.8±0.2 ºC and –1.9±0.4 °C/min, respectively). Drying time of apple was similarly affected by the three studied freezing methods.

After the analyses of the drying kinetics through the diffusion model, the identified effective diffusion coefficient significantly increased when the freezing pre-treatments were applied between 18 and 31% (beetroot), between 42 and 64% (apple), and between 18 and 72% (eggplant), and, in all cases, the higher figure was observed when samples were frozen at –20 °C before drying.

Microstructure of frozen beetroot, apple and eggplant was studied by scanning electron microscopy (SEM) and light microscopy techniques. Each product was affected differently by the freezing pre-treatments depending on their fresh tissue structure, which was very different among them. Moreover, comparing among different freezing treatments, the lower the freezing velocity the more important damage observed, probably because of larger ice crystals grown. After drying, shrinkage and collapse was observed in all samples. After drying, frozen samples presented the sum of freezing and drying effects, thus, a more damaged structure than the corresponding of the untreated samples was observed.

Regarding the physical properties, total colour change and texture were evaluated after freezing and also after drying. Total colour change of all frozen samples with regard to untreated samples before drying was higher than 2.3 which is a noticeable colour change. After drying, total colour change of frozen samples was significantly higher than that of untreated samples and differences were smaller in the case of beetroot (2-4 units) than in the case of apple and eggplant (15-22 units). Texture profiles, obtained by the compression of frozen and defrozen samples before drying, were significantly lower than corresponding untreated samples. However, no significant differences were observed among the texture of all frozen apple and eggplant samples, respectively, and only minor differences were observed in beetroot between samples frozen by liquid nitrogen immersion and at –20 °C or at –80 °C.

Total polyphenol content and antioxidant activity of frozen samples were, in general, significantly lower than those of the corresponding untreated samples before and after drying. The freezing pre-treatment by liquid nitrogen immersion was the one which promoted the lowest losses, probably due to a lower degradation and oxidation of bioactive compounds since freezing rate was very fast and small crystals were grown. In fact, total polyphenol content and antioxidant activity of beetroot sample frozen by liquid nitrogen immersion were not significantly different to those of the untreated sample before (total polyphenol content and antioxidant activity) and after (antioxidant activity) drying.

To sum up, freezing pre-treatment promoted higher changes on high porosity products (eggplant and apple) than in low porosity products (beetroot). Thus, higher drying rate enhancement and quality parameters losses were observed in eggplant and apple than in beetroot. With regard to the different freezing pre-treatments studied, freezing by liquid nitrogen immersion seemed to promote minor structure damage, less drying rate enhancement and quality parameters losses probably due to its fast freezing rate and small crystals formation. Meanwhile, freezing pre-treatments at –20 and –80 °C could not be distinguished among themselves in analysed parameters due their slow and similar freezing rates.

In Chapter 2, the effects of both freezing (at –20 °C) prior to drying and the ultrasound assistance during drying (at acoustic power densities of 16.4 and 26.7 kW/m^3) on the drying kinetics (at 40 °C), microstructure and quality parameters of beetroot were evaluated.

From the obtained results, it has been observed that drying time of beetroot significantly decreased when ultrasound was applied during drying being higher the reduction when the highest acoustic density was applied (36 and 43% at 16.4 and 26.7 kW/m^3, respectively). Higher beetroot drying time decreases were observed when samples were frozen before drying without (46%) or with ultrasound application being also slightly higher when the highest acoustic density was applied (55 and 58% at 16.4 and 26.7 kW/m^3, respectively).

Analysing the drying curves by using a diffusion model, it was observed that freezing pre-treatment induced an increase in the effective diffusion coefficient by 158%. Moreover, ultrasound application during drying induced considerable increases in both the external mass transfer coefficient (28 and 49% at 16.4 and 26.7 kW/m^3 of acoustic density, respectively) and the effective diffusion coefficient (60 and 73% at 16.4 and 26.7 kW/m^3 of acoustic density, respectively). When freezing pre-treatment and ultrasound were both applied, higher increases of effective diffusion coefficient (204 and 211% at 16.4 and 26.7 kW/m^3 of acoustic density, respectively) were observed and, as it was expected, no effect of the freezing pre-treatment on the external mass transfer coefficient was observed. Therefore, both freezing pre-treatment and ultrasound application during beetroot drying were suitable to significantly reduce the drying time and enhance the mass transfer.

Microstructure observations pointed out that disruptions and fissures occurred in beetroot tissue after freezing pre-treatment and shrinkage took place when samples were dried. Moreover, when drying was carried out by applying ultrasound, larger pores and micro-channels were observed.

With regard to the effects of processing, freezing caused significant bioactive compounds contents and antioxidant activity increases (between 16 and 57%), probably due to the release of free forms of active compounds from the food matrix, meanwhile drying had the opposite effect (decreases between 10 and 54%). Moreover, in general, when samples were frozen before drying or ultrasound was applied during drying, decreases were higher (28-58% and 39-81%, respectively), especially when they were applied simultaneously (decreases between 50 and 79%). However, in the case of betalain contents, no significant differences were observed between raw and frozen samples after drying and between frozen samples after drying when different acoustic densities were applied, probably due to thermal exposure time shortening.

In conclusion, freezing pre-treatment and ultrasound application enhanced beetroot drying but important changes in microstructure, bioactive compounds contents and antioxidant activity were promoted although drying time shortening preserved betalain contents in some cases.

Finally, in Chapter 3, the effects of the ultrasound application (at acoustic power density of 20.5 kW/m^3) on the low-temperature drying kinetics (at 5, 10 and 15 °C), microstructure and quality parameters of kiwifruit and mushroom were evaluated.

In kiwifruit drying assisted by ultrasound, drying time shortening of 55-65% was observed. From the drying kinetics analyses through the diffusion model, it was concluded that the acoustic energy caused an increment in the effective diffusion coefficient by up to 120-175% and in the external mass transfer coefficient by up to 103-231%, which indicates an important improvement in the drying rate. The rise of the drying temperature, decreased the ultrasound application effects on kiwifruit drying rate within the rage of temperatures studied.

Regarding mushroom drying, when ultrasound was applied, also significantly shorter drying times were observed (41-66% decrease) and significantly higher effective diffusion coefficient (76-184% increase) and external mass transfer coefficient (61-157% increase) were identified with the proposed diffusion model, compared with the drying without ultrasound application, within the studied temperature range (5-15 ºC). Thus, ultrasound enhanced also mushroom moisture removal during drying. Moreover, effects of ultrasound application in mushroom drying enhancement were higher at higher drying temperatures.

Comparing between the ultrasound effects on low-temperature drying process of kiwifruit and mushroom, similar drying rate enhancement was observed because similar drying time reductions and mass transfer coefficients increments were obtained. However, the drying temperature influence was higher in kiwifruit drying than in mushroom drying. Moreover, as the temperature rose, higher ultrasound application effects were observed in mushroom drying than in kiwifruit drying. Therefore, different products showed again, different behaviours under ultrasound application within the range of conditions considered.

After drying, significantly lower bioactive compounds contents (14-54% of loss) and antioxidant activity (23-69% of loss) were observed in all dried kiwifruit samples, compared with the fresh sample, being the sample dried at 15 ºC the one that exhibited higher losses. Ultrasound applied during drying at 5 and 10 °C promoted higher losses of both bioactive compounds contents (vitamin E and total polyphenol content) and antioxidant activity (35-65% and 43-62%, respectively) in comparison with samples dried without ultrasound application (14-43% and 23-50%, respectively). However, when drying was carried out at 15 °C, ultrasound contributed to the preservation of these bioactive compounds contents and antioxidant activity (30-47% and 47-58%, respectively) better than in samples obtained without using ultrasound (39-54% and 57-69%, respectively).

Mushroom microstructure presented tissue shrinkage and the formation of hollows after drying at 5, 10 and 15 °C being more pronounced as the temperature rose. Ultrasound application during drying promoted micro-channels formation due to sponge effect, which were wider when increasing the temperature.

When drying temperature increased up to 15 °C, significantly higher losses of ergosterol content and antioxidant activity (according to FRAP and CUPRAC methods), browning index and water retention capacity were observed. However, when ultrasound was applied, compared with experiments without ultrasound application, significantly higher bioactive compounds contents and antioxidant activity figures were observed although antioxidant activity at 5 °C was not significantly different. Moreover, when ultrasound was applied, significantly lower losses of browning index (at 10 and 15 °C) and hydration properties and fat adsorption capacity values (at 15 °C) were obtained, compared with experiments without ultrasound application.

Therefore, although the rise of the drying temperature from 5 to 15 ºC promoted higher kiwifruit and mushroom quality parameters losses, the use of ultrasound at 15 ºC allowed to obtain a shorter drying kinetic and better maintained the final bioactive compounds contents and antioxidant activity.

In overall, freezing pre-treatments enhanced hot-air drying of beetroot, apple and eggplant and freezing pre-treatment and ultrasound application enhanced also beetroot hot-air drying, but significant quality parameters losses were observed in both cases. Moreover, ultrasound application intensified the low-temperature drying of kiwifruit and mushroom promoting significant drying time reductions together with quality parameters retention, especially at 15 °C.

RESUMEN

El proceso de secado se aplica en frutas y verduras para reducir el contenido en humedad, fundamentalmente con el objetivo de alargar su vida útil. Sin embargo, el secado convectivo provoca pérdidas en la calidad del producto debido a la degradación térmica y la exposición al aire. El secado a baja temperatura, por debajo de 20 °C pero por encima de 0 °C, permite la obtención de productos deshidratados de alta calidad, aunque velocidad de transferencia de materia suele ser baja. Para intensificar el proceso de secado convectivo, es este trabajo se han utilizado el pretratamiento por congelación y los ultrasonidos de potencia durante el secado, con el objetivo de reducir el tiempo de secado, y preservar la calidad del producto. La congelación previa al secado a diferentes velocidades, así como la aplicación de ultrasonidos a diferentes densidades de potencia acústica durante el secado a alta o baja temperatura (secado con aire caliente o frío) pueden tener efectos diferentes sobre las distintas matrices alimentarias, habiendo sido dichos efectos, poco estudiados en la bibliografía.

Por tanto, los dos objetivos generales de este trabajo fueron, por una parte, el estudio de la intensificación del proceso de secado a temperaturas superiores a 20 °C mediante pretratamientos de congelación y aplicación de ultrasonidos durante el secado y, por otra parte, el estudio también de la intensificación del secado a baja temperatura (a temperaturas entre 0 y 20 °C) mediante la aplicación de ultrasonidos durante el secado. Para alcanzar dichos objetivos, se evaluaron los efectos sobre las cinéticas de secado y sobre los parámetros de calidad de los productos.

En el Capítulo 1, se presenta el efecto de diferentes pretratamientos de congelación (a –20 °C, a –80 °C y por inmersión en nitrógeno líquido) sobre las cinéticas de secado convectivo a 50 °C, la microestructura y los parámetros de calidad de tres matrices vegetales con diferente microestructura inicial (remolacha, manzana y berenjena).

Los resultados presentados en este capítulo indicaron que los pretratamientos de congelación redujeron significativamente el tiempo de secado (12-34%). Además, el pretratamiento de congelación afectó de forma diferente según la microestructura de la matriz vegetal y la velocidad de congelación. La microestructura original de la remolacha es compacta y presenta una baja porosidad. En cambio, la manzana y la berenjena presentan valores de porosidad medios-altos y tienen una microestructura original más frágil. Así, la mayor o menor reducción del tiempo de secado observada fue en función de su porosidad, superior en el producto más poroso (berenjena) e inferior en el producto menos poroso (remolacha). En cuanto a la velocidad de congelación, la congelación por inmersión en nitrógeno líquido (velocidad de congelación de –144±20 °C/min) tuvo menor impacto en el tiempo de secado de la remolacha y la berenjena que la congelación a –20 °C o a –80 °C, probablemente debido a que en estas últimas condiciones la velocidad de congelación fue menor (–0.8±0.2 ºC y –1.9±0.4 °C/min, respectivamente). Los diferentes

pretratamientos de congelación afectaron de forma similar al tiempo de secado de la manzana.

Analizando las cinéticas de secado mediante el modelo difusivo propuesto, el coeficiente de difusión efectiva identificado aumentó significativamente al aplicar los diferentes pretratamientos, entre un 18 y un 31% (remolacha), un 42 y un 64% (manzana), y un 18 y un 72% (berenjena), y en todos los casos el valor más elevado se observó cuando las muestras se congelaron antes del secado a –20 °C.

La microestructura de las muestras congeladas de remolacha, manzana y berenjena se analizó mediante microscopía electrónica de barrido (SEM) y microscopia óptica. Cada materia prima se vio afectada de forma diferente por los pretratamientos de congelación en función de su microestructura original. Además, comparando entre los diferentes métodos de congelación utilizados, cuanto más baja fue la velocidad de congelación más importante fue el daño observado en la microestructura, probablemente a causa del crecimiento de cristales de mayor tamaño. Después del secado, se observó contracción y colapso en la microestructura de todas las muestras; y todas las muestras congeladas previamente presentaron la suma de los efectos de la congelación y del secado, observándose una estructura más dañada que en las muestras sin congelar.

En relación a las propiedades físicas, se evaluaron el cambio total de color y de textura después de la congelación y también después del secado. Antes de secar, el cambio total de color de las muestras congeladas, respecto a la correspondiente muestra sin tratar, fue superior a 2.3 unidades, lo que supone un cambio de color perceptible. Después del secado, el cambio total de color de las muestras congeladas previamente fue significativamente mayor que en la correspondiente muestra sin tratar; las diferencias observadas fueron menores en remolacha (2-4 unidades) que en manzana y berenjena (15-22 unidades). Los perfiles de textura, obtenidos por compresión de las muestras congeladas antes del secado, fueron significativamente inferiores que los correspondientes a las muestras sin tratar. Sin embargo, no se observaron diferencias significativas en la textura de las muestras sometidas a los diferentes pretratamientos de congelación tanto de manzana como de berenjena, aunque se observaron pequeñas diferencias entre las muestras de remolacha congeladas por inmersión en nitrógeno líquido y a –20 °C o a –80 °C.

El contenido total en polifenoles y la actividad antioxidante de las muestras sometidas a los diferentes pretratamientos de congelación fueron, en general, significativamente menores que las correspondientes muestras sin tratar, antes y después del secado. Las menores pérdidas en estos parámetros se observaron en las muestras sometidas al pretratamiento de congelación por inmersión en nitrógeno líquido, probablemente debido a la menor degradación y oxidación de los compuestos bioactivos a consecuencia de una velocidad de congelación rápida y el crecimiento de cristales de pequeño tamaño. De hecho, el contenido total en polifenoles y la actividad antioxidante de la muestra de remolacha congelada por inmersión en nitrógeno líquido no fueron significativamente diferentes a los correspondientes de la muestra sin tratar, antes (contenido total en polifenoles y actividad antioxidante) y después (actividad antioxidante) del secado.

En resumen, el pretratamiento de congelación provocó mayores cambios en productos de alta porosidad (berenjena y manzana) que en productos de baja porosidad (remolacha). Por tanto, se observó un mayor incremento en la velocidad de secado y mayores pérdidas en los parámetros de calidad en berenjena y manzana que en remolacha. En cuanto a los diferentes pretratamientos de congelación estudiados, la congelación por inmersión en nitrógeno líquido provocó menor daño en la estructura, menor incremento de la velocidad de secado y menores pérdidas en los parámetros de calidad probablemente debido a su rápida velocidad de congelación y a la formación de cristales de pequeño tamaño. Asimismo, los pretratamientos a –20 °C y a –80 °C no pudieron ser diferenciados entre sí en los parámetros analizados debido a sus lentas y similares velocidades de congelación.

En el Capítulo 2, se evaluaron los efectos de la congelación (a –20 °C) previa al secado y de la asistencia acústica durante el secado (a densidades de potencia acústica de 16.4 y 26.7 kW/m^3) sobre las cinéticas de secado (a 40 °C), la microestructura y los parámetros de calidad de la remolacha.

En los resultados obtenidos se observó que el tiempo de secado disminuyó significativamente cuando se aplicaron ultrasonidos durante el secado siendo mayor la reducción cuando se aplicó la mayor densidad acústica (36 y 43% a 16.4 y 26.7 kW/m^3, respectivamente). Además, se observaron mayores reducciones del tiempo de secado cuando las muestras fueron congeladas previamente al secado sin (46%) o con la aplicación de ultrasonidos, siendo también la reducción ligeramente superior cuando se aplicó la mayor densidad acústica (55 y 58% a 16.4 y 26.7 kW/m^3, respectivamente).

Analizando las curvas de secado mediante un modelo difusivo, se observó que el pretratamiento de congelación indujo un incremento en el coeficiente de difusión efectiva del 158%. Así mismo, la aplicación de ultrasonidos durante el secado indujo incrementos considerables en el coeficiente de transferencia externa de materia (28 y 49% a 16.4 y 26.7 kW/m^3, respectivamente) y en el coeficiente de difusión efectiva (60 y 73% a 16.4 y 26.7 kW/m^3, respectivamente). En los experimentos en que se aplicó el pretratamiento de congelación y ultrasonidos durante el secado, se observaron incrementos mayores del coeficiente de difusión efectiva (204 y 211% a 16.4 y 26.7 kW/m^3, respectivamente), no viéndose afectado por la congelación, como era de esperar, el coeficiente de transferencia externa de materia. Es decir, tanto el pretratamiento de congelación como la aplicación de ultrasonidos durante el secado de remolacha permitieron reducir considerablemente el tiempo de secado y mejorar la transferencia de materia.

De acuerdo con las observaciones de la microestructura, se produjeron disrupciones y fisuras en la estructura celular de la remolacha después del pretratamiento de congelación y contracción de la misma durante del secado. Además, cuando el secado se llevó a cabo con la aplicación de ultrasonidos, se observó la aparición de poros y micro-canales de mayor tamaño.

La congelación causó un aumento significativo de los contenidos de compuestos bioactivos y de la actividad antioxidante (entre 16 y 57%), probablemente debido a la liberación de compuestos activos desde la matriz del alimento, a partir de moléculas más complejas sin actividad. El secado, en cambio, tuvo el efecto contrario, provocando reducciones de dichos parámetros (entre 10 y 54%). Además, al aplicar la congelación previa al secado o los ultrasonidos durante el secado, se observaron, en general, mayores pérdidas (28-58% y 39-81%, respectivamente), especialmente cuando se aplicaron ambos (reducciones entre 50 y 79%). Sin embargo, en el caso de los contenidos en betalainas, no se observaron diferencias significativas entre la muestra fresca y la congelada después de secar ni entre las muestras congeladas después de secar con asistencia acústica a diferentes densidades acústicas, probablemente debido a la reducción del tiempo de exposición térmica.

En conclusión, el pretratamiento de congelación y la aplicación de ultrasonidos aceleraron el secado de remolacha, pero se produjeron importantes cambios en la microestructura, los contenidos en compuestos bioactivos y la actividad antioxidante, si bien la reducción del tiempo de secado preservó los contenidos en betalainas en algunos casos.

Finalmente, en el Capítulo 3, se evaluaron los efectos de la aplicación de ultrasonidos (a una densidad de potencia acústica de 20.5 kW/m^3) sobre el secado a baja temperatura (a 5, 10 y 15 °C), la microestructura y los parámetros de calidad de kiwi y champiñón.

En el secado acústico de kiwi, se observó una reducción del tiempo de secado de 55-65%. Tras el análisis de las cinéticas de secado mediante el modelo difusivo se concluyó que la energía acústica causó un incremento en el coeficiente de difusión efectiva de 120-175% y en el coeficiente de transferencia externa de materia de 103-231%, lo que indica importantes aumentos de la velocidad de secado. El efecto de los ultrasonidos sobre la velocidad de secado de kiwi fue menor al aumentar la temperatura de secado, dentro del rango de temperaturas estudiado.

En relación al secado de champiñón, cuando se aplicaron ultrasonidos, también se observaron reducciones significativas del tiempo de secado (41-66% de reducción) y se identificaron, mediante un modelo difusivo, valores significativamente superiores del coeficiente de difusión efectiva (76-184% de incremento) y del coeficiente de transferencia externa de materia (61-157% de incremento), comparado con el secado sin aplicación de ultrasonidos, en el rango de temperaturas estudiado (5-15 °C). Por tanto, la aplicación de ultrasonidos aceleró la eliminación del contenido en humedad del champiñón durante el secado. Además, en este caso, los efectos de los ultrasonidos en la velocidad de secado de champiñón fueron mayores a temperaturas de secado superiores.

Comparando el secado acústico a baja temperatura de kiwi y de champiñón, se observaron comportamientos similares en cuanto a la reducción del tiempo de secado y el incremento de los coeficientes de transferencia de materia. Sin embargo, la influencia de la temperatura de secado fue mayor en el secado de kiwi que en el de champiñón. Además, con el aumento de temperatura, se observaron mayores efectos de la aplicación de ultrasonidos en el secado de champiñón que en el de kiwi. Por consiguiente, matrices vegetales diferentes mostraron de nuevo diferentes comportamientos durante la aplicación de ultrasonidos en el secado, dentro del rango de condiciones considerado.

Después del secado, se observaron valores significativamente inferiores de contenidos en compuestos bioactivos (14-54% de pérdida) y de actividad antioxidante (23-69% de pérdida) en todas las muestras de kiwi secas, comparadas con la muestra fresca, siendo la muestra deshidratada a 15 °C la que presentó mayores pérdidas. Cuando se aplicaron ultrasonidos en el secado a 5 y 10 °C se provocaron mayores pérdidas en los contenidos en compuestos bioactivos (vitamina E y contenido total en polifenoles) y de actividad antioxidante (35-65% y 43-62%, respectivamente) en comparación con las muestras secas sin aplicación de ultrasonidos (14-43% y 23-50%, respectivamente). Sin embargo, cuando el secado se llevó a cabo a 15 °C, los ultrasonidos contribuyeron preservar dichos contenidos en compuestos bioactivos y actividad antioxidante (30-47% y 47-58%, respectivamente) mejor que en el secado sin aplicación de ultrasonidos (39-54% y 57-69%, respectivamente).

La microestructura de champiñón presentó contracción del tejido y aparición de oquedades después del secado a 5, 10 y 15 °C siendo éstas de mayor tamaño en las muestras deshidratadas a temperaturas superiores. La aplicación de ultrasonidos durante el secado provocó la formación de micro-canales en el tejido de champiñón, los cuales fueron más profundos con el aumento de la temperatura.

Cuando se incrementó la temperatura de 5 a 15 °C en el secado de champiñón, se observaron pérdidas significativas en el contenido en ergosterol y la actividad antioxidante (métodos FRAP y CUPRAC), en el índice de pardeamiento y en la capacidad de retención de agua. Sin embargo, cuando se aplicaron los ultrasonidos en el secado de champiñón, en comparación con los experimentos sin aplicación de ultrasonidos, se obtuvieron valores significativamente mayores de contenidos en compuestos bioactivos y de actividad antioxidante, aunque a 5 °C la actividad antioxidante no fue significativamente diferente entre los experimentos con y sin aplicación de ultrasonidos. Además, cuando se aplicaron ultrasonidos, se observaron pérdidas significativamente menores en el índice de pardeamiento (a 10 y 15 °C) y en las propiedades de hidratación y en la capacidad de adsorción de grasa (a 15 °C), en comparación con los experimentos sin aplicación de ultrasonidos.

Por consiguiente, aunque el aumento de la temperatura de secado de 5 a 15 °C provocó mayores pérdidas de los parámetros de calidad de kiwi y champiñón, la aplicación de ultrasonidos a 15 °C permitió obtener una cinética de secado más corta, y se conservaron mejor los contenidos en compuestos bioactivos y la actividad antioxidante.

En conclusión, los pretratamientos de congelación aceleraron el secado con aire caliente de remolacha, manzana y berenjena; el pretratamiento de congelación y la aplicación de ultrasonidos aceleraron también el secado con aire caliente de remolacha; se observaron pérdidas significativas de parámetros de calidad en ambos casos. Además, la aplicación de ultrasonidos intensificó el secado a baja temperatura de kiwi y champiñón provocando reducciones significativas del tiempo de secado junto con la retención de los parámetros de calidad, especialmente cuando el secado se llevó a cabo a 15 °C.

RESUM

El procés d’assecat s’utilitza en fruites i verdures per a reduir el contingut en humitat, fonamentalment per allargar d’aquesta manera la seva vida útil. Però l’assecat convectiu provoca pèrdues en la qualitat del producte a causa de la degradació tèrmica i de l’exposició a l’aire. L’assecat a baixa temperatura, per sota de 20 °C però per sobre de 0 °C, permet l’obtenció de productes deshidratats d’alta qualitat tot i que presenta la velocitat de transferència de matèria sol ésser baixa. Per a intensificar el procés d’assecat convectiu, en aquest treball, s’han utilitzat el pretractament de congelació i l’aplicació d’ultrasons de potència durant l’assecat amb l’objectiu de reduir el temps d’assecat i preservar la qualitat del producte. La congelació prèvia a l’assecat a diferents velocitats, així com l’aplicació d’ultrasons a diferents densitats de potència acústica durant l’assecat a alta i baixa temperatura (assecat amb aire calent i fred) poden tenir efectes diferents en les diverses matrius alimentàries, havent estat aquests efectes, poc estudiats en la bibliografia.

Conseqüentment, els dos objectius generals d’aquest treball foren, d’una banda, l’estudi de la intensificació del procés d’assecat a temperatures superiors a 20 ° mitjançant pretractaments de congelació i aplicació d’ultrasons durant l’assecat i, per l’altra, l’estudi també de la intensificació de l’assecat a baixa temperatura (a temperatures entre 0 i 20 °) mitjançant l’aplicació d’ultrasons durant l’assecat. Per a assolir aquests objectius, s’avaluaren els efectes en les cinètiques d’assecat i en el paràmetres de qualitat dels productes.

En el Capítol 1, es presenten els efectes de diferents pretractaments de congelació (a –20 °C, a –80 °C i per immersió en nitrogen líquid) en les cinètiques d’assecat convectiu a 50 °C, la microestructura i els paràmetres de qualitat de tres matrius vegetals amb diferent microestructura inicial (remolatxa, poma i albergínia).

Els resultats presentats en aquest capítol indiquen que els pretractaments de congelació reduïren significativament el temps d’assecat (12-34%). A més, el pretractament de congelació va afectar de forma diferent segons la microestructura de la matriu vegetal i la velocitat de congelació. La microestructura original de la remolatxa és compacta ja que té una porositat baixa. En canvi, la poma i l’albergínia presenten valors de porositat mitjans-alts i una microestructura original més fràgil. Així, la major o menor reducció del temps d’assecat observada fou en funció de la porositat, superior en el producte més porós (albergínia) i menor en el producte menys porós (remolatxa). Quant a la velocitat de congelació, la congelació per immersió en nitrogen líquid (velocitat de congelació de –144±20 °C/min) va tenir menor impacte en el temps d’assecat de la remolatxa i l’albergínia que la congelació a –20 °C o a –80 °C, probablement a causa de que en aquests últims casos la velocitat de congelació fou menor (–0.8±0.2 ºC i –1.9±0.4 °C/min, respectivament). Els diferents pretractaments de congelació afectaren de forma similar el temps d’assecat de la poma.

Analitzant les cinètiques d’assecat mitjançant el model difusiu proposat, el coeficient de difusió efectiva identificat augmentà significativament en aplicar els pretractaments de congelació entre un 18 i un 31% (remolatxa), un 42 i un 64% (poma), i un 18 i un 72% (albergínia), i en tots els casos el valor més elevat es va obtenir quan les mostres es congelaren abans de l’assecat a –20 °C.

La microestructura de les mostres congelades de remolatxa, poma i albergínia, fou estudiada mitjançant microscòpia electrònica de escombrat (SEM) i microscòpia òptica. Cada matèria prima fou afectada de forma diferent per els pretractaments de congelació en funció de la seva microestructura. A més, comparant entre els diferents mètodes de congelació utilitzats, quan més baixa fou la velocitat de congelació més important fou el dany observat en la microestructura, probablement a causa del creixement de cristalls de major mida. Després de l’assecat, es va observar contracció i col·lapse en la microestructura de totes les mostres i totes les mostres congelades prèviament presentaren la suma del efectes de la congelació i de l’assecat, observant-se una estructura més danyada que en les mostres sense congelar.

En relació a les propietats físiques, s’avaluaren el canvi total de color i de textura després de la congelació i també després de l’assecat. Abans d’assecar, el canvi total de color de les mostres congelades, respecte a la corresponent mostra sense tractar, fou major a 2.3 unitats, la qual cosa suposa un canvi de color perceptible. Després de l’assecat, el canvi total de color de les mostres prèviament congelades fou significativament major que en la corresponent mostra sense tractar; les diferències observades foren menors en remolatxa (2-4 unitats) que en poma i albergínia (15-22 unitats). Els perfils de textura, obtinguts per la compressió de les mostres congelades (prèvia descongelació) abans de l’assecat, foren significativament inferiors que els corresponents a les mostres sense tractar. Tot i així, no s’observaren diferències significatives en la textura de les mostres sotmeses als diferents pretractaments de congelació de poma i albergínia, respectivament, però si s’observaren petites diferències entre les mostres de remolatxa congelades per immersió en nitrogen líquid i a –20 °C o a –80 °C.

El contingut total en polifenols i l’activitat antioxidant de les mostres sotmeses als pretractaments de congelació foren, en general, significativament menors que les corresponents mostres sense tractar, abans i després de l’assecat. Les menors pèrdues s’observaren en les mostres sotmeses al pretractament de congelació per immersió en nitrogen líquid, probablement a causa de la menor degradació i oxidació dels composts bioactius conseqüència d’una velocitat de congelació molt ràpida i el creixement de cristalls petits. De fet, el contingut total en polifenols i l’activitat antioxidant de la mostra de remolatxa congelada per immersió en nitrogen líquid no foren significativament diferents als de la corresponent de mostra sense tractar abans (contingut total en polifenols i activitat antioxidant) i després (activitat antioxidant) de l’assecat.

En resum, el pretractament de congelació va provocar majors canvis en productes d’alta porositat (albergínia i poma) que en productes de baixa porositat (remolatxa). Per tant, es va observar un major increment en la velocitat d’assecat i majors pèrdues en el paràmetres de qualitat en albergínia i poma que en remolatxa. Quant als diferents pretractaments de congelació estudiats, la congelació per immersió en nitrogen líquid va provocar menor dany en l'estructura, menor increment de la velocitat d'assecat i menors pèrdues en el paràmetres de qualitat probablement degut a la seva ràpida velocitat de congelació i a la formació de cristalls de mida petita. Així mateix, els pretractaments a –20 °C i a –80 °C no es pogueren distingir entre sí en els paràmetres analitzats a causa de les seves lentes i similars velocitats de congelació.

En el Capítol 2, s'avaluaren els efectes de la congelació (a –20 ºC) prèvia a l'assecat i l'assistència per ultrasons durant l'assecat (a densitats de potència acústica de 16.4 i 26.7 kW/m^3) en les cinètiques d'assecat (a 40 °C), la microestructura i els paràmetres de qualitat de la remolatxa.

En els resultats obtinguts s'observa que el temps d'assecat va disminuir significativament quan s'aplicaren ultrasons durant l'assecat essent major la reducció quan es va aplicar la major densitat acústica (36 i 43% a 16.4 i 26.7 kW/m^3, respectivament). S'observaren majors reduccions del temps d'assecat quan les mostres foren congelades abans de l'assecat sense (46%) o amb l'aplicació d'ultrasons essent també la reducció lleugerament superior quan es va aplicar la major densitat acústica (55 i 58% a 16.4 i 26.7 kW/m^3, respectivament).

Analitzant les corbes d'assecat mitjançant un model difusiu, es va observar que el pretractament de congelació va induir un increment en el coeficient de difusió efectiva del 158%. Així mateix, l'aplicació d'ultrasons durant l'assecat va induir increments considerables en el coeficient de transferència externa de matèria (28 i 49% a 16.4 i 26.7 kW/m^3, respectivament) i en el coeficient de difusió efectiva (60 i 73% a 16.4 i 26.7 kW/m^3, respectivament). En els experiments en què es va aplicar el pretractament de congelació i els ultrasons, es varen observar increments majors del coeficient de difusió efectiva (204 i 211% a 16.4 i 26.7 kW/m^3, respectivament), sense veure's afectat per la congelació, com era d'esperar, el coeficient de transferència externa de matèria. És a dir, tant el pretractament de congelació com l'aplicació d'ultrasons durant l'assecat de remolatxa permeteren reduir el temps d'assecat considerablement i millorar la transferència de matèria.

D'acord amb les observacions de la microestructura indiquen, es produïren disrupcions i fissures en l'estructura cel·lular de la remolatxa després del pretractament de congelació i contracció de la mateixa durant l'assecat. A més, quan l'assecat es va dur a terme amb l'aplicació d'ultrasons, es va observar l'aparició de porus i micro-canals de major mida.

La congelació va causar un augment significatiu dels continguts de composts bioactius i de l'activitat antioxidant (entre 16 i 57%), probablement a causa de l'alliberació de composts actius de la matriu de l'aliment, a partir de molècules més complexes sense activitat. L'assecat, en canvi, va tenir l'efecte contrari, provocant reduccions d'aquests paràmetres (entre 10 i 54%). A més, en aplicar la congelació prèvia a l'assecat o els ultrasons durant l'assecat s'observaren, en general, majors pèrdues (28-58% i 39-81%, respectivament), especialment quan s'aplicaren ambdós (reduccions entre 50 i 79%). Tot i així, en el cas dels continguts en batalaines, no s'observaren diferències significatives entre la mostra fresca i la congelada després d'assecar ni entre les mostres congelades després d'assecar amb assistència acústica a diferents densitats acústiques, probablement a causa de la reducció del temps d'exposició tèrmica.

En conclusió, el pretractament de congelació i l'aplicació d'ultrasons acceleraren l'assecat de remolatxa, però es produïren importants canvis en la microestructura, els continguts en composts bioactius i l'activitat antioxidant, tot i que la reducció del temps d'assecat va preservar els continguts en betalaines en alguns casos.

Finalment, en el Capítol 3, s'avaluaren els efectes de l'aplicació d'ultrasons (a una densitat de potència acústica de 20.5 kW/m^3) en l'assecat a baixa temperatura (a 5, 10 i 15 °C), la microestructura i els paràmetres de qualitat de kiwi i xampinyó.

En l'assecat acústic de kiwi, es va observar un reducció del temps d'assecat de 55-65%. Després de l'anàlisi de les cinètiques d'assecat mitjançant el model difusiu es va concloure que l'energia acústica va causar un increment en el coeficient de difusió efectiva de 120-175% i en el coeficient de transferència externa de matèria de 103-231%, la qual cosa indica importants augments de la velocitat d'assecat. L'efecte dels ultrasons sobre la velocitat d'assecat de kiwi fou menor en augmentar la temperatura d'assecat, en el rang de temperatures estudiat.

En relació a l'assecat de xampinyó, quan s'aplicaren ultrasons, també s'observaren reduccions significatives del temps d'assecat (41-66% de reducció) i s'identificaren, mitjançant un model difusiu, valors significativament superiors del coeficient de difusió efectiva (76-184% d'increment) i del coeficient de transferència externa de matèria (61-157% d'increment), comparat amb l'assecat sense aplicació d'ultrasons, en el rang de temperatures estudiat (5-15 °C). Per tant, l'aplicació d'ultrasons va accelerar l'eliminació del contingut en humitat del xampinyó durant l'assecat. A més, en aquest cas, els efectes dels ultrasons en la velocitat d'assecat de xampinyó foren majors a temperatures d'assecat superiors.

Comparant l'assecat acústic a baixa temperatura de kiwi i xampinyó, s'observaren comportaments similars quant a la reduccion del temps d'assecat i l'increment dels coeficients de transferència de matèria. Tot i així, la influència de la temperatura d'assecat fou major en l'assecat de kiwi que en el de xampinyó. És més, amb l'augment de temperatura, s'observaren majors efectes de l'aplicació d'ultrasons en l'assecat de xampinyó que en el de kiwi. Per tant, diferents productes mostraren de nou diferents comportaments durant l'aplicació d'ultrasons durant l'assecat en el rang de condicions considerat.

Després de l'assecat, s'observaren valors significativament inferiors de continguts en composts bioactius (14-54% de pèrdua) i d'activitat antioxidant (23-69% de pèrdua) en totes les mostres de kiwi assecades, comparades amb la mostra fresca, essent la mostra assecada a 15 °C la que va presentar majors pèrdues. Quan s'aplicaren ultrasons en l'assecat a 5 i 10 °C es provocaren majors pèrdues de continguts en composts bioactius (vitamina E i contingut total en polifenols) i d'activitat antioxidant (35-65% i 43-62%, respectivament) en comparació a les mostres assecades sense aplicació d'ultrasons (14-43% i 23-

50%, respectivament). Tot i així, quan l'assecat es va dur a terme a 15 °C, els ultrasons contribuïren a la preservació d'aquests continguts en composts bioactius i activitat antioxidant (30-47% i 47-58%, respectivament) millor que en l'assecat sense aplicació d'ultrasons (39-54% i 57-69%, respectivament).

La microestructura del xampinyó va presentar contracció del teixit i l'aparició de buits després de l'assecat a 5, 10 i 15 °C essent d'una major mida en les mostres assecades a temperatures superiors, mentrestant. L'aplicació d'ultrasons durant l'assecat va provocar la formació de micro-canals en el teixit de xampinyó, els quals foren més profunds amb l'augment de temperatura.

Quan es va incrementar la temperatura a 15 °C en l'assecat de xampinyó, s'observaren pèrdues significatives en el contingut en ergosterol i en l'activitat antioxidant (mètodes FRAP i CUPRAC), en l'índex de pardejament i en la capacitat de retenció d'aigua. Tot i així, quan s'aplicaren els ultrasons en l'assecat del xampinyó, en comparació amb els experiments sense aplicació d'ultrasons, s'obtingueren valors significativament majors de continguts en composts bioactius i d'activitat antioxidant , tot i que a 5 °C l'activitat antioxidant no fou significativament diferent. A més, quan s'aplicaren ultrasons, s'observaren pèrdues significativament menors en l'índex de pardejament (a 10 i 15 °C) i en les propietats d'hidratació i en la capacitat d'adsorció de grassa (a 15 °C), en comparació amb els experiments sense aplicació d'ultrasons.

Per tant, tot i que l'augment de la temperatura d'assecat de 5 a 15 °C va provocar majors pèrdues en els paràmetres de qualitat de kiwi i xampinyó, l'aplicació d'ultrasons a 15 °C va permetre obtenir una cinètica d'assecat més curta i es mantingueren millor els continguts en composts bioactius i l'activitat antioxidant.

En conclusió, els pretractaments de congelació acceleraren l'assecat amb aire calent de remolatxa, poma i albergínia; el pretractament de congelació i l'aplicació d'ultrasons acceleraren també l'assecat amb aire calent de remolatxa; s'observaren pèrdues significatives dels paràmetres de qualitat en ambdós casos. A més, l'aplicació d'ultrasons va intensificar l'assecat a baixa temperatura de kiwi i xampinyó provocant reduccions significatives del temps d'assecat juntament amb la retenció dels paràmetres de qualitat, especialment quan aquest es va dur a terme a 15 °C.

NOMENCLATURE

Parameters

a*	redness/greenness CIElab colour coordinate
A	face area (m^2)
AD	acoustic density (kW/m^3)
b*	yellowness/blueness CIElab colour coordinate
BI	browning index
D_e	effective water diffusion coefficient (m^2/s)
D_o	parameter in the diffusion model (m^2/s)
Def(t)	deformation along the time (m)
dm	dry matter (g or kg)
E	elastic modulus (kPa)
E_a	activation energy (kJ/mol)
F(t)	force along the time (N)
H_0	initial height of the sample (m)
h_m	external mass transfer coefficient (kg/m^2 s)
L	length (m)
L*	whiteness or brightness/darkness CIElab colour coordinate
n	number of experimental data
MRE	mean relative error (%)
p	probability value
R	universal gas constant (J/mol·K)
R^2	correlation coefficient of a linear regression
S_x	moisture content standard deviation (sample) (kg water/kg dm)
S_{yx}	moisture content standard deviation (calculated) (kg water/kg dm)
T	temperature (°C)
Th	thickness (m)
t	time (s or h)

V	sample volume (m^3)
var	percentage of explained variance (%)
W	moisture content (kg water/kg dm)
W	Toughness (mJ/m^3)
x,y,z	spatial coordinates (m)

Greek letters

α	significance level
ΔE	total colour change
ε	Henky strain
ρ_{dm}	dry matter density (kg dm/m^3)
σ	true stress (kPa)
φ	relative humidity

Subscripts

0	initial
∞	drying air
cal	calculated
e	equilibrium
exp	experimental
l	local
R	rupture point

Analyses abbreviations

AA	antioxidant activity (mg TE/g dm)
AAC	ascorbic acid content (mg L-ascorbic acid equivalent /g dm)
BCC	betacyanin content (mg BE/g dm)
BXC	betaxanthin content (mg IE/g dm)
EC	ergosterol content (mg ergosterol/g dm)
FAC	fat adsorption capacity (g/g dm)
SW	swelling (mL/g dm)
TPC	total polyphenol content (mg GAE/g dm)

VEC	vitamin E content (mg α-tocopherol equivalent/g dm)
WRC	water retention capacity (g/g dm)

Samples

Chapter 1:

U	untreated sample
F20	sample frozen at –20 °C
F80	sample frozen at –80 °C
FLN	sample frozen by liquid nitrogen immersion
UD	untreated sample dried at 50 °C and 1 m/s
F20D	sample frozen at –20 °C and dried at 50 °C and 1 m/s
F80D	sample frozen at –80 °C and dried at 50 °C and 1 m/s
FLND	sample frozen by liquid nitrogen immersion and dried at 50 °C and 1 m/s

Chapter 2:

R	raw sample
F	sample frozen at –20 °C
R0	raw sample dried without ultrasound application
R1	raw sample dried with ultrasound application 1
R2	raw sample dried with ultrasound application 2
F0	sample frozen at –20 °C and dried without ultrasound application
F1	sample frozen at –20 °C and dried with ultrasound application 1
F2	sample frozen at –20 °C and dried with ultrasound application 2

Chapter 3:

5 °C AIR	sample dried at 5 °C without ultrasound application
10 °C AIR	sample dried at 10 °C without ultrasound application
15 °C AIR	sample dried at 15 °C without ultrasound application
5 °C AIR+US	sample dried with ultrasound application
10 °C AIR+US	sample dried with ultrasound application
15 °C AIR+US	sample dried with ultrasound application

INTRODUCTION

1. Intensification of the drying process

Fruits and vegetables are quickly perishable due to their high moisture, acidity and carbohydrate levels (Nanda, Reddy, Hunter, Dalai, and Kozinski, 2015). Drying is perhaps the oldest and widely used method of postharvest food preservation. It consists of the reduction, in the solid product, of the water activity, by removing the majority of its water content. Water activity is a measure of available water in a system to support biological and chemical reactions (Oliveira, Brandão, and Silva, 2016). Thus, after drying, the solid product obtained might have a low water activity in order to avoid microbial growth under room temperature (Oliveira et al., 2016). Moreover, drying improves postharvest handling and packaging, increases the ease of product transportation and improves other processing operations such as milling and mixing (Onwude et al., 2017). As an important unit in postharvest operation, especially for food and agricultural processing industries, it remains an area of incessant interest for food research.

Several drying methods have been proposed to preserve fruits and vegetables. The most antique and traditional drying method consists of placing the agricultural products on beaten earth, floor covering or floor exposed to sun. Although sun energy-based methods present economic advantages, being for this reason largely used in tropical countries, the product quality and food safety-related issues become often difficult to monitor and control. The products are vulnerable to contaminations by dirt and dust, insects infestation and loss by birds and animals (Janjai and Bala, 2012). Moreover, required drying time and the final moisture content of the product could not be estimated easily.

The foremost used drying techniques promote water vaporization from a food product by using heat through conduction, convection and radiation, being the formed vapour subsequently removed through forced air (Oliveira et al., 2016). Convective drying reduces drying time and provides homogeneous and better dried products when utilizing optimum conditions.

However, depending on the drying process conditions (temperature, air velocity, and relative humidity, among others), drying time and important product characteristics, such as texture, colour, antioxidant activity and the content of different bioactive compounds as carotenoids, phenolics, etc. could be affected (Onwude et al., 2017). Therefore, studies about the drying process are fundamental to provide increasingly a wider variety of fruits and vegetables with extended shelf life and with appreciable quality (Brasil and Siddiqui, 2018).

Chou and Chua (2001) reported that, nowadays, drying process research is mainly focused on its intensification. The drying process intensification should involve the mass transfer enhancement, which is related to energy consumption and cost reduction, together with the final quality of the product. In the literature, there have been significant developments in using novel techniques in the drying of agricultural crops in terms of pre-treatment or in combination with conventional techniques that will increase process efficiency and enhance the quality of the final dried products (Onwude, Hashim, and Chen, 2016).

1.1. Convective drying process

The convective drying process of food materials is based on the sample surface water evaporation due to a forced air flow with low relative humidity and its consequent water transport removal from the inside of the solid, which promotes the sample dehydration.

1.1.1. Transport phenomena

The process of food materials drying is complex, involving coupled transport phenomena of heat, mass and momentum transfer processes accompanied by physical, chemical and phase change transformation (Sabarez, 2012) as it is represented in Figure 1. Basically, the convective drying system consists of a gas phase (the air) and a solid phase (the sample being dried). Thus, the main different transport phenomena taking place simultaneously are:

- Heat transfer from the drying air to the solid promoting the solid heating and the surface water evaporation.
- Mass transfer of the water from the interior of the solid to its surface and then to the drying air in gas phase.
- Momentum transfer as a consequence of the air speed gradients created when the air goes around the solid.

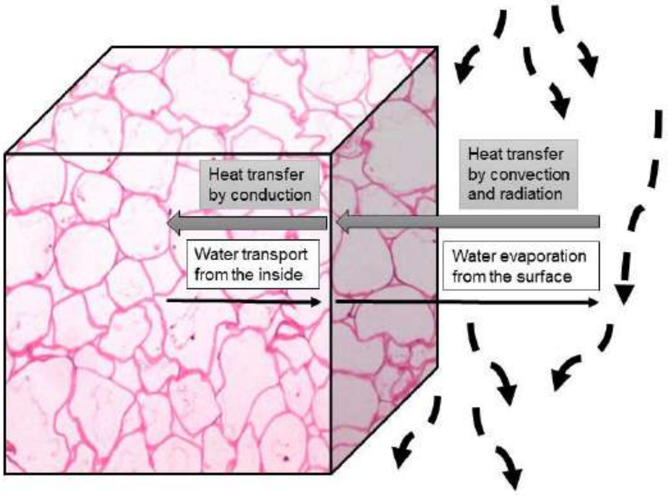

Figure 1. Mass and heat transfer processes during food materials drying

Due to the high latent heat of vaporisation of water and the inherent inefficiency of using air as the drying medium, convective drying is a highly energy-consuming unit operation (Sabarez, 2015). Therefore, the three modes of energy transfer (convection, conduction and radiation) may be used alone or in combination to supply heat from the heat source to the solid.

The global rate of the process would be defined by the respective rates of those transfers. However, it is frequently considered that the mass transfer is the main transport phenomenon of the drying process because the heat and the momentum transfers are usually faster than the mass transfer.

On the one hand, the water movement through the solid depends on the characteristics of the solid and its moisture content and temperature. On the other hand, the surface water removal depends on the temperature, relative humidity and drying air flow together with the solid exposed surface and the pressure.

1.1.2. Transport resistances of the mass transfer

During a drying process, the mass transfer takes place until the equilibrium is reached when the chemical potentials differences are cancelled. When the concentration profile is represented along the distance, an interphase discontinuity between the solid and the gas phases is observed as it is presented in Figure 2. Thus, equilibrium does not mean that both phases have equal concentrations but it means that equal chemical potentials are reached. The interphase resistance to mass transfer is commonly neglected. Therefore, two resistances to water transport are observed, an internal resistance in the solid phase and an external resistance in the gas phase. The relative significance of both resistances would affect the global mass transfer process. In the case of higher significance of one of the resistances, the global process would be limited by this resistance. Thus, the process analysis may just consider this limiting resistance.

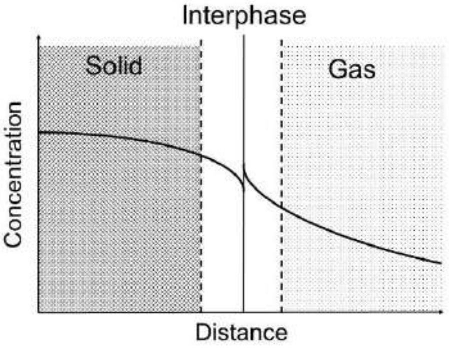

Figure 2. Mass transfer between two mediums. Double resistance concept

The internal resistance is related to the water transfer into the solid which is a complex process. It may be a combination of different mechanisms, such as capillary flow, surface diffusion or liquid diffusion, generating the total mass flow through the internal phase. In the literature, the internal mass transfer is frequently represented by the Fick's law (Equation 1) which considers the diffusive mechanism as the main one (Crank, 1979). In Fick's law, the mass flow (m_x) is related to the water diffusion coefficient (D_e) and the moisture content gradient.

$$m_x = -D_e \frac{\partial W}{\partial x} \quad \text{Eq.1}$$

In the literature, the diffusion coefficient (D_e) is usually considered as an effective parameter, representative of all the mechanisms involving the mass transfer through the solid (García-Pérez, Rosselló, Cárcel, De la Fuente, and Mulet, 2006). In general, the effective diffusion coefficient (D_e) varies with the temperature change, following an Arrhenius type equation (Gamboa-Santos, Montilla, Cárcel, Villamiel, and Garcia-Perez, 2014) (Equation 2), although it may also vary with other variables as the moisture content (Váquiro, Mulet, García-Pérez, Clemente, and Bon, 2008; Rodríguez, Llabrés, Simal, Femenia, and Rosselló, 2015).

$$D_e = D_0 e^{\left(\frac{-E_a}{RT}\right)} \qquad \text{Eq.2}$$

The external resistance is linked to the water transfer from the solid surface to the fluid which is in contact with, thus, from the sample being dried to the air of its surroundings. It consists of a turbulent convective transport whose vapour flow (m_v) per area unit could be expressed as in Equation 3 (Bird, Stewart, and Lightfoot, 2007).

$$m_v = h_m(\varphi_s - \varphi_\infty) \qquad \text{Eq.3}$$

In equation 3, the vapour flow is related to the external mass transfer coefficient (h_m) and the difference between the relative humidity on the solid surface and in the drying air, considering constant properties of both the solid surface and the drying air. The external mass transfer coefficient depends on the flow rate, the direction and the properties of the drying air together with the solid geometry and dimensions. The external mass transfer coefficient can be empirically estimated (Perry and Green, 2008; Castell-Palou et al., 2012) or experimentally determined (Cárcel, García-Pérez, Riera, and Mulet, 2011; Rodríguez et al., 2014).

1.1.3. Drying curve

The drying curve is defined as the relationship between the average moisture content of the solid (kg water/ kg dm) and the drying time, which is the time while the solid is in contact with the air flow at a certain velocity, temperature and relative humidity. Thus, the drying rate at each drying time could be obtained as the derivative of the drying curve. In the convective drying, several drying periods can be observed regarding the drying rate with the decrease of the average moisture content of the solid. The following figure shows a typical drying rate curve for constant drying conditions (Figure 3).

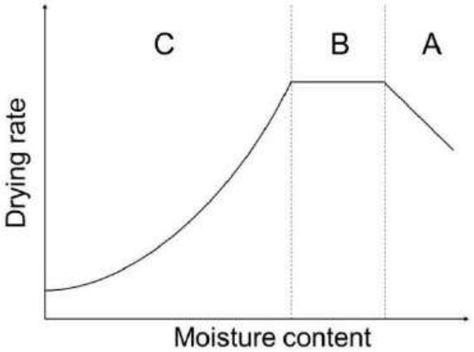

Figure 3. Representation of the drying rate vs the average moisture content of the solid. Drying periods: (A) Induction drying period; (B) constant rate drying period; (C) falling rate drying period

In the first drying moments, the solid sample is adapting to the drying conditions. Thus, during the induction period (A) the drying rate increases as the temperature of the solid rises and the water evaporation of the surface of the solid begins. Usually, this first period is undetectable in food materials drying.

Afterwards, the constant drying rate period starts (B). In this period, the drying rate is equal to the water evaporation rate and the energy is spent in the water phase change. Thus, the external mass transfer is the controlling resistance. This period continues until the moisture content of the solid decreases to the critical moisture content of the product. This critical moisture content is normally close to the initial moisture content of the product in food materials (Park et al., 2007). Consequently, this period is very short or non-existent.

When the moisture content is under the critical moisture content, the drying rate decreases until the equilibrium moisture content is reached in the falling rate period (C). During this period, the amount of water moved from inside of the solid to its surface can be smaller than the amount of water evaporated from the surface and transferred to the gas. Therefore, a moisture gradient is developed from the centre of the solid (with the maximum moisture content) to the solid surface (with the minimum moisture content which can reach the equilibrium moisture content).

1.1.4. Volume shrinkage

According to Mayor and Sereno (2004), one of the most important physical changes that food suffers during drying is the reduction of its external volume. The loss of water and the heating cause stresses in the cellular structure of the food leading to change in shape and decrease in dimension. These stresses in the cellular structure due to the loss of water and heating could be observed in the product microstructure as cell walls folding and tissue compression (Lewicki and Pawlak, 2003; Ramos, Silva, Sereno, and Aguilera, 2004; Mayor, Silva, and Sereno, 2005). Therefore, shrinkage of the dried products could be evaluated through sample microstructure observations by light microscopy (Bancroft, 2019) or by Scanning Electron Microscopy (SEM) (Reimer, 2013).

Moreover, the reduction of its external volume is related to the reduction of the transfer area of the solid which may affect the moisture removal from the solid surface. The moisture transport from the inside of the solid is also affected by the reduction of the solid dimensions. Therefore, both internal and external resistances are affected. Consequently, the study of the shrinkage is useful when modelling the drying transport phenomenon.

Volume shrinkage correlations could be theoretically or experimentally estimated. For instance, Rodríguez, Eim, Simal, Femenia, and Rosselló (2013) determined the area changes of the apple sample faces by using an image acquisition system and image analysis in order to measure the alterations of the sample dimensions during drying at different pre-set times. A linear correlation was obtained between the nominal dimension ratio and the average moisture content. Then, the shrinkage correlation could be considered as part of the mathematical model (De Lima, Queiroz, and Nebra, 2002; Ruiz-López and García-Alvarado, 2007; Eim et al., 2013; Rodríguez et al., 2013).

Among the factors affecting the volume shrinkage, according to Mayor and Sereno (2004), the main ones in convective drying are:

- The amount of water removed. As water is removed from the solid, the structural tensions increase. In some cases, the volume contraction is similar to the amount of water removed and an equilibrium is almost reached.

- The solid matrix mobility. The mobility of the solid structure is related to its physical properties under the drying conditions. A high mobility is presented when the solid has a viscoelastic behaviour and a low mobility is observed in a glassy performance. At the beginning of the drying process, the high moisture content is associated with a rubbery state and the moisture content decrease is balanced out by the volume contraction decreasing linearly. However, at low moisture content values, the material tends to present a rigid state and the contraction rate diminishes significantly.

- The drying rate. The drying rate is related to the solid properties and the drying conditions (temperature, air velocity and air relative humidity, among others) which may affect the moisture movement into the solid creating gradients. When significant moisture content gradients are promoted, the surface has a significantly lower moisture content than the interior of the solid. In this case, a quick transformation from a rubbery state to a rigid state of the exterior of the sample occurs, crusting of the sample is observed and pores can appear. Consequently, the volume of the sample is fixed and the drying of the interior of the sample, which is still in a rubbery state, is more difficult. However, when the moisture profiles into the solid tend to be less pronounced or nearly linear, the material decreases its volume almost constantly during the process.

1.2. Drying kinetics modelling and simulation

Although the traditional production methods are based on the experience through the years, nowadays the society demands new production methods which ensure safety, quality and health. Therefore, the prediction and control of the production results is now a requirement in every factory, especially when food products are manufactured. Thus, a mathematical model constitutes an essential tool which allows the analysis, estimation and control of the production processes. Therefore, the mathematical modelling of the processes represents a basic factor in new production systems in order to estimate the process development (Bon, Rosselló, Femenia, Eim, and Simal, 2007). According to Rathnayaka Mudiyanselage, Karunasena, Gu, Guan, and Senadeera (2017), numerical modelling is an effective resource to investigate the fundamental mechanisms of plant cellular structures and their dynamics. However, the modelling of drying processes becomes a challenge when biological materials are dried due to their heterogeneity, complexity and sensitivity (Chou and Chua, 2001). The level of the model complexity should be equalized to the cost and time needed to develop and set it up and, at the same time, a suitable accuracy must be reached. A model could be too much simple and represent an unlikely situation or it could be too much complex and become a useless application.

Modelling could be done through two different approaches: by using empirical equations or by using equations based on fundamental physics. An empirical approach consists of the simple fitting of the experimental observations. The most known empirical models used to simulate the drying curves of fruits and vegetables are logarithmic, Page, Newton and Weibull models, all of them widely applied in convective drying (Simal, Femenia, Garau, and Rosselló, 2005; Tzempelikos, Vouros, Bardakas, Filios, and Margaris, 2015; Zhang et al., 2016; Salehi, Kashaninejad, and Jafarianlari, 2017). Frequently, they do not allow the simulation of experiments under conditions different to those used to identify the model parameters but, they provide relatively good results for engineering applications in the food industry.

Otherwise, models based on fundamental laws of conservation of heat, mass and momentum are the classical methods which compromise the real mechanisms which occur during the drying process. These models usually involve the determination of a certain number of parameters and a high mathematical complexity. Therefore, sometimes they could be unsuitable for practical purposes. Consequently, different simplifications might be considered in order to minimize computational time (Kiranoudis, Maroulis, and Marinos-Kouris, 1992). Afterwards, the convenience of these simplifications should be evaluated depending on the model adequacy to the real system behaviour. Thus, some simplifications should be changed or discarded and some simplifications might be added in the model for further computational time minimization until a reasonable accuracy is reached.

1.2.1. Modelling steps in a diffusion model

According to Sabarez (2015), modelling of drying processes as well as modelling of other processes involves several steps as it is represented in Figure 4, including model conceptualisation, mathematical formulation, determination of model parameters, methods of solution and experimental validation.

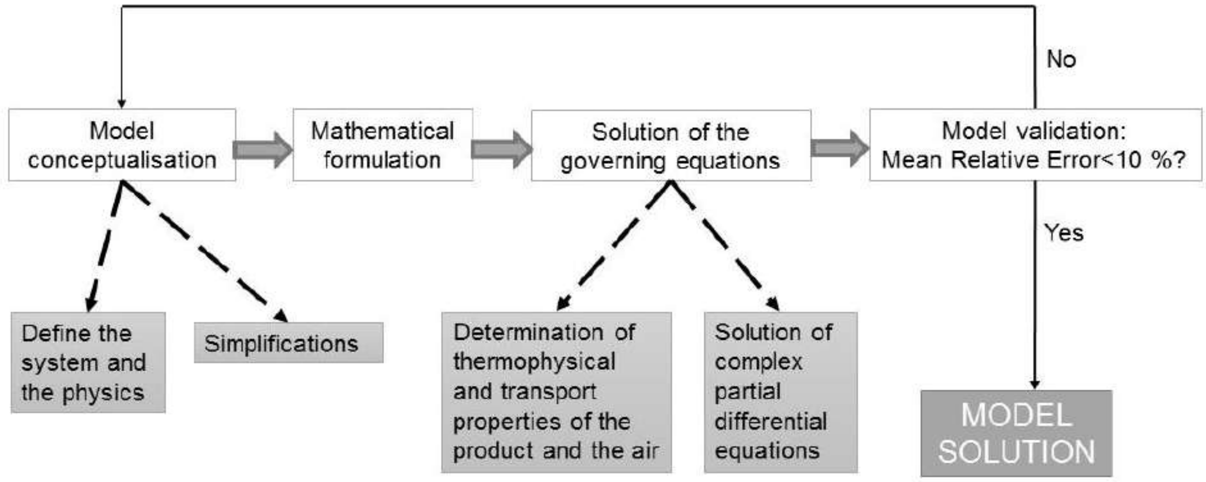

Figure 4. Modelling steps scheme

The conceptualisation of the model is to define the system and the physics of the process as a computational domain depending on the geometry and other characteristics. In this step, it is important to define the detailed simplifications considered in order to reach a practical solution and satisfy the need of the application obtaining the required information level. The simplifications formulation should be done taking into account the system characteristics and the relative importance of each partial process occurred in the moisture removal of the drying process. Thus, in the convective drying process, the main transport phenomenon considered could be the mass transfer, which may be controlled by the internal and/or the external resistances as it was mentioned below. Moreover, the shrinkage could be considered additionally (Castro, Mayorga, and Moreno, 2018). If the simplifications considered turned to be inadequate, they should be reformulated with the aim of fitting the model to the reality.

In the convective drying process, the main transport phenomenon considered could be the mass transfer, which may be controlled by the internal and/or the external resistances as it was mentioned below. However, in the falling rate period, which is the larger period in the convective drying of fruits and vegetables, the internal resistance is usually considered as a determinant resistance. In the internal resistance, the water movement into the solid is frequently considered as a liquid diffusion mechanism based on the molecular movements of the water and it is defined by the second Fick's law (Equation 1). Thus, in the conceptualisation of the model of the convective drying process, it is defined as a diffusion model.

The mathematical formulation of the model consists of the formulation of the mathematical equations needed to describe the drying process. When the mathematical model is formulated, the assumed approaches would depend on the problem being considered. Thus, the equations considered to describe the process are designed as governing equations and they are usually partial differential equations. In a diffusion model, the microscopic balance can be combined with the Fick's diffusion law (Equation 4) taking into account the geometry of the system in order to obtain the governing equation of the system.

$$\frac{\partial W_l}{\partial t} = \nabla(D_e \nabla W_l) \qquad \text{Eq.4}$$

For instance, the governing equation for a three-dimensional parallelepipedal geometry, considering that the solid is homogeneous and isotropic with regard to mass transfer, is presented in Equation 5.

$$\frac{\partial W_l}{\partial t} = D_e \left(\frac{\partial^2 W_l}{\partial x^2} + \frac{\partial^2 W_l}{\partial y^2} + \frac{\partial^2 W_l}{\partial z^2} \right) \qquad \text{Eq.5}$$

Afterwards, the initial and boundary conditions should be defined. The initial condition usually considered is that initially, the solid moisture is homogeneous and equal to the initial average moisture content of the sample in all its points (Equation 6).

$$W_{l(x,y,z)}\Big|_{t=0} = W_0 \qquad \text{Eq.6}$$

The boundary conditions are regarded to the limits of the system. Thus, in the geometric centre of the solid, due to the symmetry, no mass transfer is considered (Equation 7); and on the surface of the solid, the external mass transfer can be considered as it was expressed in equation 3 if the corresponding resistance is considered to be important (Equation 8) (Simal, Femenia, Garcia-Pascual, and Rosselló, 2003).

$$\left.\frac{\partial W_{l(x,y,z)}}{\partial x}\right|_{x=0} = \left.\frac{\partial W_{l(x,y,z)}}{\partial y}\right|_{y=0} = \left.\frac{\partial W_{l(x,y,z)}}{\partial z}\right|_{z=0} = 0 \qquad \text{Eq.7}$$

$$\begin{aligned} -D_e \rho_{dm} \left.\frac{\partial W_l}{\partial x}\right|_{x=L,t>0} &= h_m(\varphi_e - \varphi_\infty) \\ -D_e \rho_{dm} \left.\frac{\partial W_l}{\partial y}\right|_{y=L,t>0} &= h_m(\varphi_e - \varphi_\infty) \qquad \text{Eq.8} \\ -D_e \rho_{dm} \left.\frac{\partial W_l}{\partial z}\right|_{z=L,t>0} &= h_m(\varphi_e - \varphi_\infty) \end{aligned}$$

Therefore, the product isotherm and the psychrometric data should also be contemplated. Moreover, the shrinkage could be considered additionally (Castro et al., 2018).

The solution of the governing equations requires the knowledge of the thermophysical and transport properties of the product and the air. Some of these parameters might be considered constant through the drying process but some others would depend on different variables such as the temperature or the moisture content (Váquiro, Rodríguez, Simal, Solanilla-Duque, and Telis-Romero, 2016; Defraeye and Verboven, 2017). These parameters might be physically measured or theoretically estimated.

Subsequently, the modelling resolution involves the solution of complex partial differential equations, which can be solved by several numerical and analytical methods (Castro et al., 2018). The discretization of the geometry in finite elements allows the numerical solution of these complex systems. The most commonly used numerical methods are finite differences, finites elements and finite volumes.

The finite differences method approximates the differential equations to difference equations in which finite differences approximate the derivatives. Meanwhile, finite elements or volumes methods approximate the differential equations to algebraic equations approximating the unknown function over the domain. Thus, it subdivides a large system into smaller, simpler parts and, therefore, it has been widely used in diffusion models resolution (Janjai et al., 2008; Váquiro, Clemente, García-Pérez, Mulet, and Bon, 2009; Eim et al., 2013; Rodríguez et al., 2015). The finite differences method has been used when a regular geometry is considered in a diffusion model with moving boundary conditions (Garau, Simal, Femenia, and Rosselló, 2006; Simal, Garau, Femenia, and Rosselló, 2006; Ozuna, Cárcel, García-Pérez, and Mulet, 2011).

The numerical methods provide solutions in steps, thus after each step the solution of one set of conditions is obtained and the repetition of the calculation expand the range of solutions. Finally, the mathematical model should be validated in order to asses if the mathematical description of the process captures reality. The obtained solution of the model must be comparable to the real system behaviour. Thus, differences between the predicted values and the experimental data are indicators of the considered simplification level of the problem. When the level of simplification and the level of accuracy are optimized, the real problem could be satisfactorily explained by the proposed model. Frequently, the percentage of mean relative error (MRE) between predicted and experimental values is calculated in order to evaluate the quality of the simulation provided by the drying model. For example, the model could be considered as acceptable if MRE is lower than 10% (Kaymak-Ertekin and Gedik, 2005).

When solving a model, it is frequent to unknown one or several parameters of the model, in the present case, both the effective diffusion and external mass transfer coefficients are unknown. Consequently, initial values of the unknown model parameters are supposed to solve the model and compare the results of the simulation with the experimental ones. By using an iterative method of identification, new figures for the model parameters are obtained for the resolution of the model in order to minimize the differences between the experimental and calculated drying curves. With the definitive model parameters, those which allow the minimization of differences between experimental and calculated drying curves (effective diffusion and external mass transfer coefficients), the percentage of mean relative error is calculated and the quality of the simulation is evaluated.

1.3. Quality parameters changes during convective drying

One of the main concerns after drying process is the loss of quality of the dried product compared with the fresh one. The food quality changes during drying may be classified in chemical and physical changes as it is represented in Table 1 Chua and Chou (2014).

Table 1. Food quality changes, adapted from Chua and Chou (2014)

Chemical changes	Physical changes
Vitamin and other bioactive compounds' losses	Colour loss
Antioxidant activity loss	Rehydration changes
Protein loss	Solubility changes
Lipid oxidation	Texture changes
Microbial survival	Shrinkage
Aroma degradation	Gelatinization
	Aroma volatilization

It is important to consider that degradation processes of food quality parameters during drying are mainly related to heat and time exposure (Chou and Chua, 2001). The increase of the temperature may promote nutrients losses due to the decomposition of different chemical compounds. Therefore, as the temperature increases, the degradation rate increases. Many different analytical methods are proposed in the literature for bioactive compounds contents determination as well as for its antioxidant activity (Madrau et al., 2008; Wojdyło, Figiel, and Oszmiański, 2009). Afterwards, the bioactive compounds contents and antioxidant activity changes could be expressed as the percentage of loss related to fresh sample.

The heat and air exposure could also enhance non enzymatic browning reactions (Maillard reaction, caramelization, and ascorbic acid browning) which may change the colour of the product (Hrynets, Bhattacherjee, and Betti, 2019). Food products colour is one of the main factors in consumers acceptance (Hutchings, 2011), therefore, it should be carefully determined and controlled in order to obtain a good product appearance.

One of the most used method for colour evaluation is the use of a colorimeter in order to obtain the CIELab colour coordinates (L*: whiteness or brightness/darkness, a*: redness/greenness and b*: yellowness/blueness) and determine the total colour change with regard to the fresh sample (Chong, Law, Figiel, Wojdyło, and Oziembłowski, 2013) or the browning index (Farokhian, Jafarpour, Goli, and Askari-Khorasgani, 2017) as in Equations 9 and 10.

$$\Delta\mathrm{E} = \sqrt{\Delta\mathrm{L}^{*2} + \Delta\mathrm{a}^{*2} + \Delta\mathrm{b}^{*2}} \qquad \text{Eq.9}$$

$$\mathrm{BI} = \frac{[100(x - 0.31)]}{0.17}, \text{ where } \quad x = \frac{(a^{*} + 1.75L^{*})}{(5.645L^{*} + a^{*} - 3.012b^{*})} \qquad \text{Eq.10}$$

At the same time, the moisture removal from the inside of the material may promote physical changes in the texture, hydration properties and fat adsorption capacity of the product which are also determinant in the quality evaluation (Garau et al., 2006). According to Wilkinson, Dijksterhuis, and Minekus (2000) texture perception takes place partly during the dynamic process of food breakdown in the mouth and is affected by oral processes, such as motility, saliva production and temperature. Texture changes may be evaluated through a wide range of methods, which provide time-series data of sample deformation, thereby allowing a wide range of texture attributes to be calculated from force–time or force–displacement data (Chen and Opara, 2013).

On the other hand, hydration properties and fat adsorption capacity are indicative of the product physiological functionality (laxative, reduction of blood cholesterol, blood glucose or the risk of chronic disorder) as well as its expected technical behaviour when it is incorporated in processed food and drink (Elleuch et al., 2011). Thus, they could be evaluated as a quality parameter of dried products (Femenia et al., 2009; Malik, Sharma, and Saini, 2017).

It should be taken into account that most of the changes promoted by convective drying, although observed at a macroscopic level, are caused by changes occurring at a microstructural/cellular level (Mayor, Pissarra, and Sereno, 2008). Thus, microstructural changes also need to be studied when fruits and vegetables are dried. The microstructure could be studied through light microscopy (Bancroft, 2019) and/or Scanning Electron Microscopy (SEM) (Reimer, 2013) as it has been reported in the food drying process literature (Mayor et al., 2008; Seremet, Botez, Nistor, Andronoiu, and Mocanu, 2016). Moreover, from the obtained light microscopy or SEM micrographs, the image analysis could be carried on by using an specific software of cell detection in order to quantify the microstructure features and compare them with that of the fresh sample. In the image analysis process, the cell cavities are detected and evaluated in terms of cell number, area, perimeter, roundness, axis length, elongation and compactness (Mayor et al., 2008; Ramírez, Troncoso, Muñoz, and Aguilera, 2011).

In conclusion, in convective drying processes, air temperature, humidity and velocity have significant effects on the drying kinetics and, consequently, on the quality of the final food products. Therefore, the minimization of the product quality degradation can be reached through the direct control of the drying parameters (Chua and Chou, 2014).

1.4. Low-temperature drying

In order to better preserve quality parameters, convective drying at low temperatures have been proposed as a novel technique (Ozuna, Cárcel, Walde, and Garcia-Perez, 2014). Low temperatures during drying process would reduce thermolabile compounds losses due to less thermal damages. Thus, low-temperature convective drying refers to the convective drying at air temperatures below 20 °C, which include figures below or close to the product's freezing point and at atmospheric pressure (Ozuna et al., 2014). Therefore, the drying air should present a low relative humidity (Moreno, Brines, Mulet, Rosselló, and Cárcel, 2017), below 35%.

When drying temperatures between 20 and 0 °C are used, the moisture removal is carried out by evaporation. Meanwhile, when drying temperature is lower than 0 °C the moisture removal consists of a sublimation process and the freezing of the sample is required (Santacatalina, Fissore, Cárcel, Mulet, and García-Pérez, 2015). In this last case, the drying technique is also called atmospheric freeze drying.

With regard to quality parameters, compared with convective drying at high temperatures, low-temperature drying at temperatures between 20 and 0°C has been reported to decrease the quality parameters losses. For instance, according to Santacatalina et al. (2014) and Rodríguez et al. (2014), the losses of some bioactive compounds (total polyphenols and flavonoids) in apple var. Granny Smith during convective drying were of 25% at 0 °C and 28% at 10 °C but of 39% at 30 °C. Furthermore, the loss of hardness of rehydrated eggplant after convective drying compared to that of the fresh sample, was of ca 68% when drying was at temperatures between 40 and 60 °C (Urun, Yaman, and Köse, 2015) but only of ca 45% when drying air was at a lower temperature (10 °C) (Santacatalina, Soriano, Cárcel, and Garcia-Perez, 2016).

Thus, low-temperature drying using temperatures between 20 and 0 °C could be a reasonable alternative to hot-air convective drying, in order to obtain high quality food products.

However, low-temperature drying usually presents a very low drying rate. For example, to reach an 80% of weight loss low-temperature drying (at 10 °C and 2 m/s) of apple cubes (8.8 mm side) required 17.1 h (Santacatalina, Contreras, Simal, Cárcel, and Garcia-Perez, 2016), meanwhile hot-air drying (at 70 °C and 1 m/s) of apple cubes (10 mm side) required only 1.92 h (Rodríguez et al., 2014). Therefore, low-temperature drying is prone to be intensified.

2. Drying pre-treatments: freezing pre-treatment

Different pre-treatments, such as chilling, blanching, osmotic dehydration, compression, ultrasonic bath and freezing, have been applied in order to enhance food drying process (Dandamrongrak, Young, and Mason, 2002; Arévalo-Pinedo and Xidieh Murr, 2007; Rodríguez et al., 2015; Ando et al., 2016; Wei, Liu, Li, Liu, and Jiang, 2017). Drying pre-treatments have been reported to promote different structural changes in the sample which ease the water removal during drying. These structural changes have been described as the injury to the cell membrane and the weak adhesion of cell walls by Ando et al. (2016). According to Wei et al. (2017), the structure collapse during pre-treatment processes facilitated heat and moisture transfer during drying.

Among the different pre-treatments, freezing has been reported to enhance the mass transfer process in vegetables and, therefore, promote higher drying rates (Lewicki, 2006). As it was observed by Dandamrongrak et al. (2002), freezing pre-treatment (at –34 ºC) enhanced better the drying process of banana at 50 ºC and 3.1 m/s than chilling (at 0 ºC for 24 h) or blanching (at 100 ºC for 3 min). Moreover, according to Ando et al. (2016), freezing pre-treatment (at –20 ºC) promoted a higher mass transfer enhancement than blanching (at 60-100 ºC for 5 min) in carrot root drying at 60 ºC and 0.83 m/s. One of the most important effects of freezing is the occurrence of tissue structure disorders due to the ice crystals formation (Bonat Celli, Ghanem, and Su-Ling Brooks, 2016).

2.1. Freezing pre-treatment characteristics

2.1.1. Freezing rate

According to Li, Zhu, and Sun (2018), the process of the ice crystals formation is regarded as one of the main factors affecting the cell structure during freezing, together with the water migration and the inherent characteristics of cell structure. Consequently, different freezing pre-treatments might have different effects depending on the freezing rate. Thus, the freezing pre-treatment characterization is usually done through the freezing rate or cooling rate which is defined as the average of the ratio between the temperature gap (from the initial ambient temperature to the final set temperature) and the global freezing time (Chassagne-Berces, Fonseca, Citeau, and Marin, 2010).

However, some other authors (Haiying, Shaozhi, and Guangming, 2007) reported that the ice crystals formation is mainly during the freezing plateau which is the temperature constant period starting from the initial freezing point. Therefore, the freezing rate could also be determined in this step of the freezing process.

In overall, it is accepted that faster freezing rates lead to less damage than slower freezing rates (Nowak, Piechucka, Witrowa-Rajchert, and Wiktor, 2016). However, the breakage of the product due to ice density differences with water can be provoked by too fast freezing (Chassagne-Berces et al., 2009).

2.1.2. Freezing equipment

Another important characteristic of the freezing pre-treatment are the specifications of the equipment used in the freezing process. Freezing chambers have some characteristic features which could also change the freezing process performance, such as the kind of air circulation. The heat transfer process is faster when the air is forced in the surroundings of the sample, enhancing the freezing rate, than when the air is naturally moved.

As it was reported by Nowak et al. (2016), when comparing freezing under natural convection at –20 °C with that under forced convection at –40 °C, freezing time was 7-15 times shorter and the cooling rate 4 times greater in the second case, which was not expected to be that high with regard to the temperature difference. Thus, the authors concluded that the freezing method resulted in diverse freezing intensity due to different air circulation, as well as freezing temperature difference.

To sum up, the freezing pre-treatment characterization is related to both the freezing rate and the freezing chamber features.

2.2. Freezing pre-treatment and material structure

As it was reported by Li et al. (2018) the inherent characteristics of cell structure are also important with regard to freezing process effects on the materials. Unfortunately, only few studies of different freezing treatments have been found and only for one product at a time: apple (Chassagne-Berces et al., 2009), carrot (Kidmose and Martens, 1999), and strawberry (Delgado and Rubiolo, 2005), or for different products but subjected to only one freezing treatment (green asparagus, zucchini and green beans frozen at –40 °C) (Paciulli et al., 2015). The only found exception was the study of Chassagne-Berces et al. (2010) which evaluated the effect of different freezing treatments (–20 °C, –80 °C and liquid nitrogen immersion) of mangoes and apples of different varieties and ripeness, concluding that the quality parameters analysed (texture, colour, soluble solids and water content) changed differently depending on the freezing protocol and the product nature and state.

Thus, there is still a claim for a better understanding of the complex mechanisms that take place during freezing which are not only affected by the freezing velocity but also by the structure of the sample submitted to freezing process.

2.3. Freezing pre-treatment effects on drying kinetics

It seems that freezing process modifies the structure and results in better water diffusion since it contributes to an easier water removal and, consequently, shorter drying times. Significant drying time reductions have been reported in the literature when different freezing pre-treatments were applied, compared with untreated samples. Thus, drying time of banana (at 50 ºC and 3.1 m/s) (Dandamrongrak et al., 2002) and apple (at 60 °C and 1.2 m/s) (Ramírez et al., 2011) after freezing pre-treatment at –34 ºC and at –30 ºC, respectively, were significantly shorter (46 and 28% shorter, respectively) in comparison with those of unfrozen samples. Moreover, freezing pre-treatment at –20 °C promoted reductions of the drying time by 32% (at 70 °C and 2 m/s), 13-20% (60-80 ºC) and 40% (60 ºC and 0.81 m/s) on the drying kinetics of beetroot, blueberries and carrots, respectively (Shynkaryk, Lebovka, and Vorobiev, 2008; Zielinska, Sadowski, and Błaszczak, 2015; Ando et al., 2016). Drying time of cape gooseberry (60 ºC and 2 m/s) was shortened by freezing pre-treatment of the samples at –18 °C (13%) and by liquid nitrogen immersion (20%) (Junqueira, Corrêa, de Oliveira, Ivo Soares Avelar, and Salles Pio, 2017).

Due to the drying time reduction, freezing pre-treatment has been reported to decrease specific energy consumption by up to 27% in comparison with drying without pre-treatment when blueberries were frozen (at –20 °C) prior to drying at 60 and 80 °C (Zielinska et al., 2015).

2.4. Freezing pre-treatment effects on dried product quality

Different characteristics of the food products are determined by the structural organization at different levels; from molecular to tissue level (Chassagne-Berces et al., 2009). Thus, material tissue structure disorders due to ice crystals formation would lead to physico-chemical changes which could promote macroscopic effects on properties related to the colour, the texture, the bioactive compounds content and/or the antioxidant activity of the sample, among others. The quality of the frozen and dried product would depend on the extension of such changes. For instance, Shynkaryk et al. (2008) observed higher shrinkage during drying, slower rehydration kinetics after drying and lower stress-relaxation texture curves (in dried and rehydrated samples) in frozen beetroot samples (at –20 °C) than in untreated ones.

Moreover, in order to understand and predict the changes occurred in the physico-chemical properties at higher levels of structure, the knowledge of the microstructural changes is crucial (Mayor et al., 2008). Ramírez et al. (2011) observed a more damaged microstructure (analysed by light microscopy) in frozen apple samples (at –30 °C) than in untreated samples. In this study the disruption of the cell walls was observed after freezing treatment in the light microscope images. Therefore, in the light microscope image analysis of frozen samples, significantly higher mean cell area was determined than in those of untreated ones, due to larger cell cavities created after the cell wall breakage during freezing.

In overall, freezing pre-treatment may damage the product quality, but at the same time, the quality could be better preserved due to drying time shortening which minimizes thermal exposure of the material.

3. Energy assistance during drying process: ultrasound application

Convective drying is usually a high energy demanding operation. According to Chua and Chou (2014), by using combined methods, the drying time could be reduced while retaining most quality parameters. The combined methods could be thermal techniques, non-thermal techniques, or combination of both.

Thermal techniques are based on heating technologies which surmount the internal resistance to water transfer inherent to the agricultural products. These techniques could be based on microwave, infrared or radio-frequency energies, the three of them being reported as able to reduce the time and energy consumption of fruits and vegetables drying (Onwude et al., 2016). However, they are based on the product heating which may induce higher quality parameters losses compared to conventional convective drying due to the higher temperatures reached by the sample being dried. Therefore, non-thermal techniques could be considered instead.

Non-thermal techniques include ultraviolet radiation, pulsed electric fields and ultrasound energies (Onwude et al., 2017). They do not involve the generation of heat; thus, they do not depend on the temperature of source and they could be effective at room or less intense temperatures.

Ultraviolet radiation energy has been used as a medium of disinfection, inactivation of microorganisms in liquid food and as a post-harvest treatment of fruits and vegetables (Pataro, Sinik, Capitoli, Donsì, and Ferrari, 2015). It seems that, when applying ultraviolet radiation energy during drying, the injured reproductive systems of cells lead to the death of cells increasing the pore formation and the rate of moisture transfer (Phimphilai, Maimamuang, and Phimphilai, 2014). Thus, it has been reported to reduce drying time up to 38% compared with convectional convective drying of mistletoe at 60-80 °C and 0.5-1.5 m/s (Köse and Erentürk, 2010). However, it can be said that ultraviolet radiation energy drying mechanism is still in the early stages of investigation (Onwude et al., 2017).

Pulsed electric fields energy should be applied on materials with low electrical conductivity, high electrical resistivity and free of bubbles. Thus, it is not suitable for all materials. Significant drying time reductions were reported when combining pulsed electric fields with convective drying. Wiktor et al. (2013) reported a drying time reduction by 12% when applying pulsed electric fields in apple drying at 70 °C and 2 m/s. However, pulsed electric field energy application has also been reported to electrically increase product damage presenting increased resistance of smaller cells (Onwude et al., 2017).

Finally, ultrasound energy is based on sound waves with frequencies higher than 20 kHz which is the upper audible limit of human hearing (Rodriguez et al., 2018).

3.1. Ultrasound characteristics

3.1.1. Ultrasound waves

Ultrasound waves could be characterized by the following parameters (Cárcel, García-Pérez, Riera, Rosselló, and Mulet, 2014):

- Frequency (Hz) is the number of cycles or vibrations completed in a unit of time. The inverse of the frequency is the period (T, s) which is defined as the time needed for a wave to complete a cycle.
- Speed (m/s) is the propagation velocity of the wave. It is usually characteristic of the material medium. However, it could be affected by the temperature or the pressure.
- Wavelength (m) is the distance between two planes in which the particles are in the same state of vibration. It is calculated by the quotient of the acoustic speed over the frequency.
- Amplitude (m) is the maximum movement of the particle from the equilibrium position.
- Intensity (W/m^2) is defined as the average energy transmitted per unit of time through a unit of area perpendicular to the propagation direction.

- Power (W) is the total beamed energy from the ultrasonic source per unit of time. It can be determined from the product of the intensity and the radiant surface area.
- Impedance (MRayl) is the relationship between the acoustic pressure and the vibration speed of the particle. It can be determined through the product of the speed and the medium density. When the acoustic wave goes through the interphase, a part of the wave is reflected and the other is transmitted. The reflected energy ratio depends on the impedance differences between both mediums. Thus, the bigger the impedance difference, the higher the reflected energy and the lower the transmitted one. Therefore, the impedance is an important factor in ultrasound applications. If the reflected energy ratio is higher than the transmitted one, the ultrasound effects would be higher in the interphase than in the second medium. However, if the reflected energy ratio is lower than the transmitted one, the effects would be higher in the second medium.
- Attenuation is the loss of energy (intensity) as the wave goes through the medium. The attenuation depends on the distance to the wave source and it is due to the reflection, dispersion or diffraction phenomena during the wave propagation as well as the transformation of kinetic energy to thermal energy. The attenuation establishes the proportion of the energy that it is generated and the amount of energy that the sample receives.

Ultrasound waves have the same properties as sound waves, thus, they are elastic waves and they have to be propagated through a material medium. The material medium could be solid, liquid or gas. Moreover, ultrasound propagates by longitudinal motion but not by transverse motion (Musielak, Mierzwa, and Kroehnke, 2016). Therefore, ultrasound waves promote mechanical compression (high pressure) and rarefaction (low pressure) cycles of the material medium which are key in their application.

Ultrasound waves are classified into low- and high-intensity ultrasound according to their different applications. Low-intensity applications use frequencies higher than 100 kHz at intensities below 10 kW/m^2 and their purpose is transmitting energy through a medium without causing a change in the state of the medium (Musielak et al., 2016). They are used as non- destructive characterization of the medium in medical diagnosis, depth sounding, acoustic spectroscopy and microscopy or industrial monitoring and control, for instance in the evaluation of frying oil degradation (Benedito, García-Pérez, Carmen Dobarganes, and Mulet, 2007).

High-intensity applications use frequencies between 20 and 100 kHz at intensities higher than 10 kW/m^2 and their objective is to induce changes in the products or processes (Cárcel, García-Pérez, Benedito, and Mulet, 2012).

3.1.2. High-intensity ultrasound equipment in drying process

The ultrasound application system consists of three main elements: generator, transducer and emitter, as it is represented in Figure 5. The generator transforms the electrical signal into the selected frequency; the transducer, which is a vibrating body, converts the frequency electrical signal into mechanical vibrations; and the emitter radiates the mechanical vibrations to the medium (Rodriguez et al., 2018).

If the energy source is electrical, there are two transducer types available: magnetostrictive and piezoelectric and they have both advantages and drawbacks (Cárcel et al., 2014). The magnetostrictive transducer is based on the changes of shape produced in some high-strength metallic alloys by a changing magnetic field, meanwhile, the piezoelectric transducer is composed of two contrary effects which promote different signs of the electrical charges and, consequently, the material contractions or expansions. Magnetostrictive transducers do not age and the acoustic field can be very intense, stable and reliable, meanwhile, piezoelectric ones have a short life-span and the acoustic field is less intense (Cárcel et al., 2014). However, piezoelectric transducers are very efficient (95%) compared with magnetostrictive ones (<50%) and magnetostrictive transducers need an external cooling, meanwhile, piezoelectric ones are air cooled. Therefore, piezoelectric transducers are widely used in convective drying process applications.

The emitters used in lab-scale drying processes with ultrasound application usually consist of open circular or rectangular plates (Gallego-Juárez, Rodriguez, Acosta, and Riera, 2010) but also consist of close cylindrical systems similar to that in Figure 5 (Cárcel, García-Pérez, Riera, and Mulet, 2007). In this system, the sample to be dried is located in the cylinder and the air flows through it. Other ultrasonic systems such as ultrasonic sieve (Schössler, Jäger, and Knorr, 2012) or ultrasonic-microwave cabinet dryer (Kowalski and Mierzwa, 2015) have also been reported in the literature.

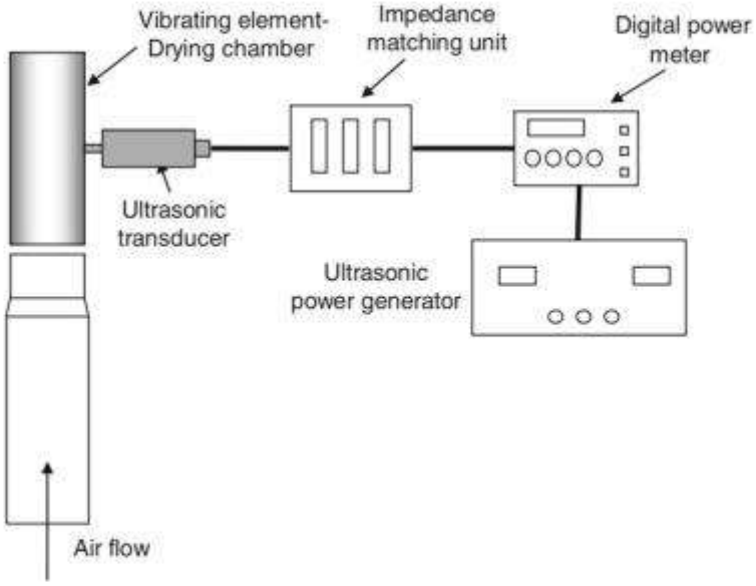

Figure 5. Ultrasound drying system in convective drying of fruits and vegetables, adapted from Cárcel et al. (2007)

3.2. High-intensity ultrasound and material structure during drying process

According to Kowalski and Rybicki (2017), the essential improvement of drying processes when using high-intensity ultrasound is regard to:

- Shortening of drying time
- Reduction of energy consumption
- Improvement of dried products quality

However, the effects of ultrasound application on the convective drying kinetics and the quality of the dried product vary according to the properties of the acoustic wave (frequency, power, attenuation, impedance) and the structure and the nature of the food product (Rodriguez et al., 2018).

Although ultrasound produces alternating compressions and expansions of the material in general, the effects are different when the material is fluid or solid (Cárcel et al., 2012). The effects of ultrasound application in fluid are pressure variations and stirring. However, the efficient transmission of the acoustic waves in fluid medium from the transducer is challenging due to the impedance mismatch and the ultrasonic attenuation. In solid materials, the effect of ultrasound application is similar to that observed when a sponge is squeezed and released repeatedly and the liquid is released from the inside. Thus, the forces involved in this mechanical effect could be higher than the surface tension of the water molecules inside the solid making easier the interchanges of matter (Cárcel et al., 2012).

In the ultrasound application during convective drying of solid samples, the efficiency of the ultrasound propagation through the air and the solid should be considered. The gases such as air are highly attenuating of the ultrasound waves because they absorb the acoustic energy preventing its transfer to the solids being treated (Cárcel et al., 2014). Moreover, the high impedance difference between the air and the solid emitters surface and between the air and the solid samples promotes the reflection of a high ratio of the acoustic signal with regard to the transmitted one (García-Pérez, Cárcel, De la Fuente-Blanco, and De Sarabia, 2006). Therefore, a proper application system should be designed in order to achieve an efficient ultrasound application.

3.3. High-intensity ultrasound effects on drying kinetics

The ultrasound application in gas-solid systems have been developed recently and the enhancement of the convective drying has been observed (Fan, Zhang, and Mujumdar, 2017). The effects of ultrasound application on hot-air convective drying have been observed at mild temperature (less than 50 °C) (García-Pérez, Rosselló, et al., 2006) and at low air velocities (less than 4 m/s) (Cárcel et al., 2007).

Ultrasound application effects during hot-air drying of different products have been previously studied. Reported drying time reductions (at 40 °C and 1 m/s of air velocity) due to ultrasound application (at power density of 37 kW/m^3 and 22 kHz of frequency) were between 32 and 72% on carrot cubes (García-Pérez, Cárcel, Riera, and Mulet, 2009) and eggplant cylinders (García-Pérez, Ozuna, Ortuño, Cárcel, and Mulet, 2011), respectively. As a consequence of the drying time reductions, significant energy reductions were reported when ultrasound was applied during hot-air drying, compared with drying without ultrasound application. Energy consumption reductions of 10-19% and 9-11% were reported by Kowalski, Pawłowski, Szadzińska, Łechtańska, and Stasiak (2016) and Szadzińska, Łechtańska, Kowalski, and Stasiak (2017) when applying ultrasound (at 100 and 200 W) on raspberries drying at 55 °C and on green pepper drying at 54 °C, respectively. Moreover, higher energy consumption reductions (42-54%) were reported in ultrasound assisted (75-90 W) drying of apples at 40 °C by Sabarez, Gallego-Juárez, and Riera (2012).

In low-temperature drying, 75% of drying time reduction was observed in apple cubes drying (at 10 °C and 2 m/s) (Santacatalina, Contreras, et al., 2016) when ultrasound was applied (at power densities of 20.5 kW/m^3 and 30.8 kW/m^3, respectively, and 22 kHz of frequency).

To sum up, in general, higher drying process enhancement was observed with ultrasound application (75% in apple drying at 10 °C and 2 m/s (Santacatalina, Contreras, et al., 2016)) than with ultraviolet radiation (38% in mistletoe drying at 60-80 °C and 0.5-1.5 m/s (Köse and Erentürk, 2010)) or pulsed electric fields (12% in apple drying at 70 °C and 2 m/s (Wiktor et al., 2013)) application. Therefore, it is a promising non-thermal combined method for drying process.

Furthermore, according to Onwude et al. (2017), the ultrasound effect seems to be higher at the beginning of the drying process. Therefore, it is suggested to apply the ultrasound energy at the first moments of the moisture removal in order to avoid further energy consumption and quality parameters losses due to the ultrasound extra application.

3.4. High-intensity ultrasound effects on dried product quality

Regarding quality parameters changes when ultrasound was applied during convective drying, Musielak et al. (2016) and Fan et al. (2017) compared a wide range of studies in their reviews and it was reported that, in general, the dried product quality was maintained or even enhanced with regard to some parameters (such as total phenolic content, flavonoid content, antioxidant activity) when ultrasound was applied during drying process because similar or lower losses were observed compared with drying process without ultrasound application. However, significant losses in dried product colour, water activity, porosity and hardness were usually reported after ultrasound application during drying, compared with drying process without ultrasound application. Rodriguez et al. (2018) particularizes that, at low temperatures (below 40-50 °C), the drying process shortening limited the oxidation reactions that maintain most of the bioactive compounds contents. But, at high temperatures (above 40-50 °C), the ultrasound application affected negatively the bioactive compounds contents as a result of the synergy between thermal and acoustic energy.

In fact, when ultrasound at 30.8 kW/m^3 was applied in hot-air convective drying experiments of apple at 30, 50 and 70 °C and 1 m/s (Rodríguez et al., 2014) and passion fruit peel at 40, 50, 60 at 70 °C an 1 m/s (Do Nascimento, Mulet, Ascheri, de Carvalho, and Cárcel, 2016) higher bioactive compounds contents and antioxidant activity losses were observed at high temperatures (above 50 °C) than at low temperatures (below 50 °C), compared with drying without ultrasound application.

In low-temperature drying (below 20 °C), equal or lower losses of hardness in rehydrated sample, total polyphenol content and antioxidant activity were reported after ultrasonically assisted (at 10.3, 20.5 and 30.8 kW/m^3) drying of apple cubes (8.8 mm side) at low-temperature drying (at 10 °C and 2 m/s), in comparison with changes after drying without ultrasound application (Santacatalina, Contreras, et al., 2016). Moreover, colour coordinates (CIELab scale) of cod slices dried (at temperatures of 0, 10 and 20 °C and air velocity of 2 m/s) with ultrasound application (at a power density of 20.5 kW/m^3 and frequency of 22 kHz) presented negligible differences to salted cod dried without ultrasound application (Ozuna et al., 2014; Santacatalina, Guerrero, Garcia-Perez, Mulet, and Cárcel, 2016). However, quality changes in food products during low-temperature drying with and without ultrasound application have been barely studied in the literature.

4. Overall perspective

From the literature review, an overall perspective could be obtained with the following bullet points:

- Drying process is commonly used to stabilise food materials due to their short shelf life promoted by their high moisture content.
- Convective drying intensification is mainly focused on mass transfer process enhancement, which is related to energy and cost savings, and quality retention.
- The drying of a solid may promote its shrinkage. Thus, the microstructure of the product is affected and the solid dimensions and the external transfer area are reduced.
- Drying process modelling is an essential tool with the objective of asses the system and predict its results. Modelling methods based on fundamental laws explain better the real system behaviour.
- Food quality involves bioactive compounds contents, antioxidant activity and physical evaluation (colour, texture, hydration properties and fat adsorption capacity, among others) as well as the product microstructure.
- Convective drying may induce important quality parameters losses in fruits and vegetables, the extension of these losses being related to drying time and temperature.
- Low-temperature drying at temperatures below 20 °C but above 0 °C may provide high quality products; however, it has a very low drying rate.
- Freezing pre-treatment modifies the product structure promoting the mass transfer enhancement during drying process.
- Ice crystals growing may induce different changes in quality parameters of the product depending on the freezing process parameters and the product characteristics.
- Ultrasound application eases the moisture removal process from the inside of the solid intensifying the drying process.
- Compressions and expansions cycles promoted by ultrasound may deteriorate, maintain or enhance product quality according to drying temperature and the product characteristics.

5. Research hypotheses

Taking into account the literature review, the following research hypotheses were stated as the initial point of the experimental work:

I. The application of freezing pre-treatments at different freezing temperatures may modify the drying kinetics and final quality and microstructure of food products.
II. Different effects due to the freezing rate and freezing equipment characteristics as well as the product characteristics could be expected.
III. The high-intensity ultrasound application during drying could enhance the convective drying process of fruits and vegetables. Furthermore, the moisture removal process could be further eased if a freezing pre-treatment is also applied.
IV. The ice crystals growing during the freezing pre-treatment and the compressions and expansions due to the ultrasound application during drying may affect the microstructure of the samples before and after drying as well as the quality parameters.
V. When the convective drying is carried out at low-temperature, high quality dried food products could be obtained. However, this process requires a long processing time which could be enhanced by using high-intensity ultrasound application during drying.
VI. The ultrasound compressions and expansions may induce samples microstructure damages which may be assessed through microscope observations, and also modify the final dried product quality.
VII. Mathematical modelling could help to evaluate the effects of both freezing pre-treatment application and drying assisted by ultrasound.

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OBJECTIVES

The work presented in this thesis was carried out within the framework of two research projects developed by the Agri-Food Engineering Group at the University of the Balearic Islands. These projects, financially supported by the Spanish government (MINECO) and the National Institute of Research and Agro-Food Technology (INIA) and co-financed with ERDF funds, were the following:

- “Aplicación de los ultrasonidos de potencia (UdP) en la intensificación de los procesos de secado a baja temperatura (DPI 2012-37466-C03-02)”.
- “Revalorización integral de subproductos en función de sus usos potenciales: Extracción de compuestos de interés mediante aplicación de US de potencia y estudios de bioaccesibilidad in vitro (RTA 2015-00060-C04-03)” within the coordinate project: “Gestión sostenible y revalorización de subproductos agroalimentarios para alimentación, energía y uso agronómico.”.

These projects were focused, on the ultrasound application in order to intensify the drying process at low-temperature; and on the sustainable management and revalorisation of agro-industrial by-products.

Within this context, the main aim of this work was, on the one hand, to study the drying process intensification at hot-air drying temperature by using freezing pre-treatments and ultrasound application; and on the other hand, also the intensification of the low-temperature drying process when ultrasound was applied. To these purposes, the effects on both the drying kinetics and the quality parameters were evaluated.

Thus, in order to achieve both general objectives, the following specific objectives were proposed:

- ➢ Evaluate the differences in hot-air drying of vegetable products with different initial microstructure (beetroot, apple and eggplant) when different freezing pre-treatments (at –20 °C, at –80 °C and by liquid nitrogen immersion) were applied and analyse the changes in microstructure, colour, texture, bioactive compounds contents (total polyphenol content) and antioxidant activity. This objective was developed in “Chapter I: Hot-air drying intensification by using freezing pre-treatments”.
- ➢ Evaluate the effects of both freezing pre-treatment (at –20 °C) and ultrasound application (at two power densities) on drying kinetics, microstructure, bioactive compounds contents (betalain and total polyphenol contents) and antioxidant activity of beetroot. This objective was worked out in “Chapter II: Hot-air drying intensification by using freezing pre-treatment and ultrasound application”.
- ➢ Asses the ultrasound application effects on low-temperature drying at different temperatures (at 5, 10 and 15 °C) of kiwifruit and mushroom and on their quality parameters such as microstructure, hydration properties, fat adsorption capacity, colour, bioactive compounds contents and antioxidant activity. This objective was developed in “Chapter III: Low-temperature drying intensification by ultrasound application”.

WORKING PLAN

The working plan of this doctoral thesis, presented in Figure 6, was set taking into account the objectives previously proposed. Thus, the experimental program was organized in three main parts which lead to the three chapters with the results obtained in each part.

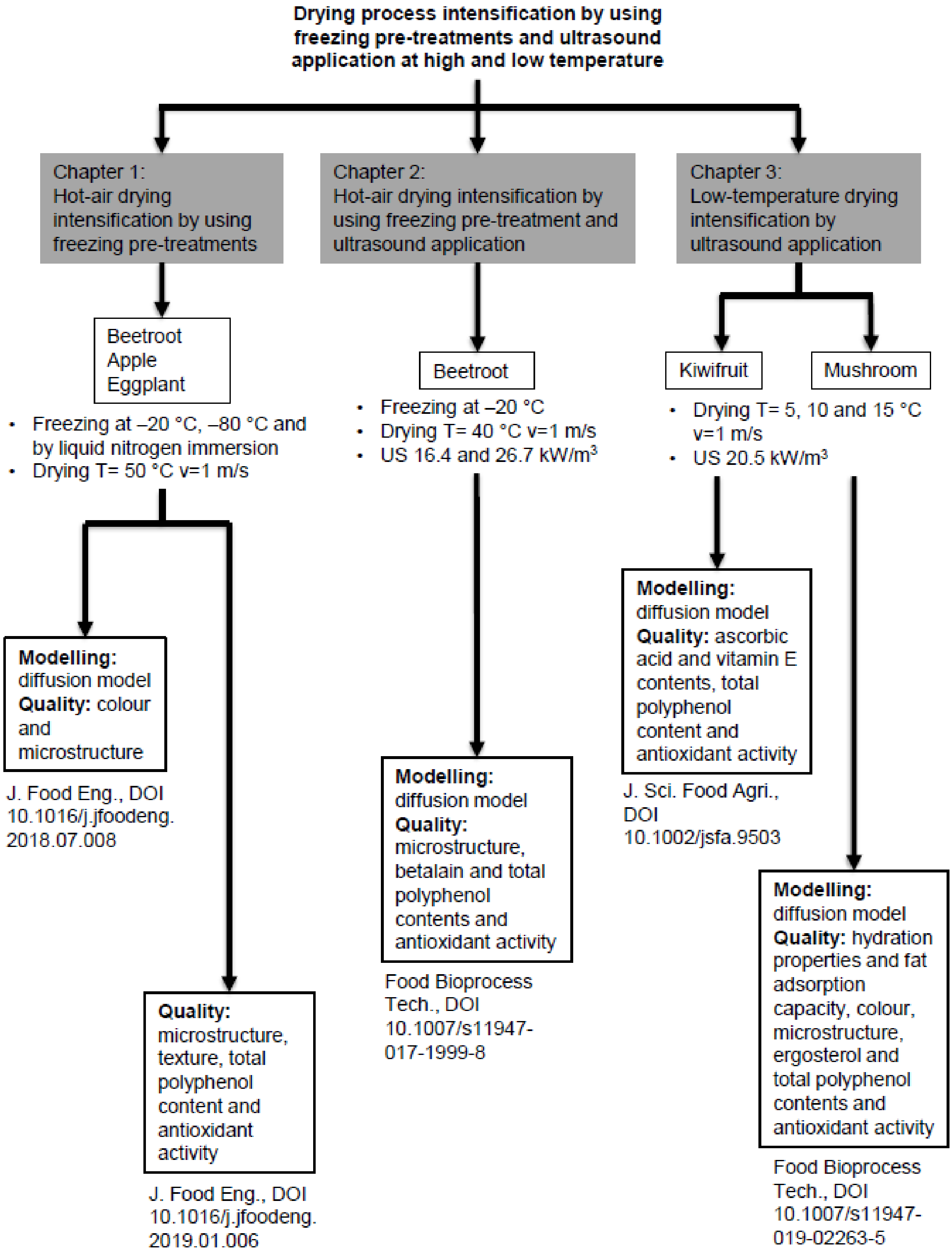

Figure 6. Working plan structure. Legend: T=temperature; v= air velocity; US=ultrasound power density.

The first part of the experimental plan (Chapter 1) consisted of the study of the effects of different freezing pre-treatments on the hot-air drying kinetics and the quality parameters of vegetal products with three different initial microstructures: beetroot (*Beta vulgaris* var. conditiva), apple (*Malus domestica* var. Granny Smith) and eggplant (*Solanum melongena* var. black enorma).

For this purpose, beetroot, apple and eggplant cubes (0.01 m side) were frozen at –20 °C, at –80 °C and by liquid nitrogen immersion. Then, untreated and frozen samples were convectively dried at air conditions of 50 °C and 1 m/s.

Firstly, the effects of freezing pre-treatments on the hot-air drying kinetics and quality parameters such as colour and microstructure were evaluated. A diffusional model, taking into account both internal and external resistances and solid shrinkage, was proposed in order to analyse the mass transfer intensification due to freezing pre-treatments. Colour and microstructure (Scanning Electron Microscopy, SEM) of untreated and frozen samples before and after drying were evaluated.

Secondly, microstructure, texture, bioactive compounds contents (TPC) and antioxidant activity (AA) changes due to freezing pre-treatments and drying were evaluated. Thus, microstructure micrographs, bioactive compounds contents (total polyphenol) and antioxidant activity of untreated and frozen samples before and after drying were analysed. Moreover, cell cavities throughout microstructure light micrographs (Light Microscopy, LM) and texture of untreated and frozen samples before drying was evaluated with the aim of observe the physical effects of freezing pre-treatments.

The subsequent part of the experimental plan (Chapter 2) proposed the evaluation of the effects, on both the hot-air drying kinetics and quality parameters of beetroot (*Beta vulgaris* var. conditiva), when samples were frozen prior to drying and/or ultrasound was applied during drying. Beetroot was chosen as a bioactive compounds’ rich product (total polyphenol and betalains content).

Therefore, beetroot cubes (0.008 m side) were frozen at –20 °C. Then untreated and frozen samples were convectively dried at 40 °C of air temperature and 1 m/s of air velocity with and without ultrasound application (at 16.4 and 26.7 kW/m^3).

A diffusional model, taking into account both internal and external resistances and solid shrinkage, was proposed in order to analyse the mass transfer intensification due to freezing pre-treatment and ultrasound application. Afterwards, microstructure (Light Microscopy, LM), bioactive compounds contents (betalains and total polyphenol) and antioxidant activity of both untreated and frozen samples before and after drying were analysed.

The last part of the experimental plan (Chapter 3) deal with the study of the effects of the ultrasound application on the low-temperature drying kinetics and quality parameters of kiwifruit (*Actinidia deliciosa* cv. Hayward) and mushroom (*Agaricus bisporus*), which are very appreciated but quickly perishable products.

For this purpose, kiwifruit parallelepipeds (0.01 x 0.01 x 0.005 m) and mushroom slices (0.005 m of thickness) were dried at 5, 10 and 15 °C of air temperature and 1 m/s of air velocity without and with ultrasound application (at 26.7 kW/m^3).

A diffusional model considering both internal and external resistances and solid shrinkage was proposed with the aim of evaluating mass transfer intensification due to ultrasound application during kiwifruit and mushroom drying.

Regarding kiwifruit, bioactive compounds contents, such as ascorbic acid, vitamin E and total polyphenol, and antioxidant activity were determined. Meanwhile, regarding mushroom, microstructure (Light Microscopy, LM), bioactive compounds contents, such as ergosterol and total polyphenol, antioxidant activity, colour, hydration properties and fat adsorption capacity were analysed.

RESULTS AND DISCUSSION

CHAPTER 1

Hot-air drying intensification by using freezing pre-treatments:

Freezing pre-treatments on the intensification of the drying process of vegetables with different structures

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Journal of Food Engineering
DOI: 10.1007/j.jfoodeng.2018.07.008
Accepted and published
Impact factor (2017): 3.197
Food Science & Technology (Q1)
https://www.sciencedirect.com/science/article/abs/pii/S0260877418302899

Effects of freezing treatments before convective drying on quality parameters: Vegetables with different microstructures

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Journal of Food Engineering
DOI: 10.1016/j.jfoodeng.2019.01.006
Accepted and published
Impact factor (2017): 3.197
Food Science & Technology (Q1)
https://www.sciencedirect.com/science/article/abs/pii/S0260877419300123

CHAPTER 2

Hot-air drying intensification by using freezing pre-treatment and ultrasound application:

Improvement of mass transfer by freezing pre-treatment and ultrasound application on the convective drying of beetroot (*Beta vulgaris L.*)

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Food and Bioprocess Technology
DOI: 10.1007/s11947-017-1999-8
Accepted and published
Impact factor (2017): 2.998
Food Science & Technology (Q1)
https://link.springer.com/article/10.1007/s11947-017-1999-8

CHAPTER 3

Low-temperature drying intensification by ultrasound application:

Ultrasound assisted low-temperature drying of kiwifruit. Effects on kinetics, bioactive compounds and antioxidant activity

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Journal of the Science of Food and Agriculture
DOI: 10.1002/jsfa.9503
Accepted and published
Impact factor (2017): 2.379
Food Science & Technology (Q1)
https://www.ncbi.nlm.nih.gov/pubmed/30471127

Intensification of low-temperature drying of mushroom by means of power ultrasound: effects on drying kinetics and quality parameters

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Food and Bioprocess Technology
DOI: 10.1007/s11947-019-02263-5
Accepted and published
Impact factor (2017): 2.998
Food Science & Technology (Q1)
https://link.springer.com/article/10.1007/s11947-019-02263-5

ADDITIONAL DISCUSSION

Diffusion models

In this study, diffusion models were formulated according to Fick's law combined with the microscopic balance according to the geometry of the sample. Thus, cubic, parallelepipedal and slab geometries were used. In all cases, both internal and external resistances to the moisture transfer were taken into account. Moreover, linear shrinkage experimental correlations were considered, except in Chapter 2 and Paper 1 of Chapter 3 in which the samples (beetroot and kiwifruit) dimensions were considered constant. In Chapter 1, the proposed shrinkage correlations were those presented in Table 1.

Table 1. Shrinkage correlations used in Chapter 1 for apple, eggplant and beetroot drying diffusion models

Product	**Shrinkage correlation**	**Reduction (%)**	**Reference**
Apple	$\frac{\mathrm{V}}{V_0} = 0.177 + 0.820\frac{W}{W_0}$	77	Schultz et al. (2007)
Eggplant	$\frac{\mathrm{V}}{V_0} = 0.112 + 0.929\frac{W}{W_0}$	65	García-Pérez, Ozuna, Ortuño, Cárcel, and Mulet (2011)
Beetroot	$\frac{\mathrm{V}}{V_0} = 0.093 + 0.964\frac{W}{W_0}$	88	Experimentally estimated

The shrinkage correlations were linear and very similar among them being slightly higher the slope figure in the low porosity product (beetroot) which corresponds to a high shrinkage. Meanwhile, the medium-high porosity products (apple and eggplant) presented a slightly lower slope figure which corresponded to a low shrinkage.

The mushroom slab geometry shrinkage of Chapter 3 was experimentally estimated as the thickness contraction and the face area contraction. Slab samples were dried at different times. Therefore, the shrinkage correlations were the relationship between the thickness or the face area changes and the moisture content, which are presented in Equations 1 and 2.

$$\frac{\mathrm{Th}}{Th_0} = 0.325 + 0.689\frac{W}{W_0} \qquad \text{Eq.1}$$

$$\frac{\mathrm{A}}{A_0} = 0.324 + 0.676\frac{W}{W_0} \qquad \text{Eq.2}$$

The proposed diffusion models allowed the proper evaluation of the different samples drying kinetics under the different conditions tested since the mean relative error (MRE) was lower than 5% and the percentage of explained variance (var) was higher than 99.5%.

From the obtained results, it could be concluded that freezing treatments at –20 °C, at –80 °C and by liquid nitrogen immersion before hot-air drying of beetroot, apple and eggplant at 40 °C enhanced drying process increasing the effective diffusion coefficient by up to 72%, compared with drying experiments of untreated samples. Moreover, both freezing pre-treatment and ultrasound application at low temperatures drying synergistically affected the mass transfer rate.

Comparing between beetroot hot-air drying at 50 and 40 °C when freezing pre-treatment were not applied, higher effective diffusion coefficient and higher external mass transfer coefficient were identified since faster internal mass transfer is observed.

Furthermore, the drying operation at low-temperature could be intensified by ultrasound application. Ultrasound application at 20.5 kW/m^3 during drying of kiwifruit and mushroom at low-temperature (5, 10 and 15 °C) enhanced mass transfer rate, increasing both the effective diffusion and the external mass transfer coefficients (76-184% and 61-231%, respectively), compared with the corresponding drying process without ultrasound application

Comparing between the identified parameters in low-temperature drying of kiwifruit and mushroom, higher effective diffusion coefficient and higher external mass transfer coefficient were observed in mushroom compared with kiwifruit when no ultrasound power density was applied. The initial food matrix of both products was different as well as the initial moisture content and the sample geometry. Therefore, faster drying kinetics were observed in mushroom drying than in kiwifruit drying and, consequently, higher parameters were identified in the diffusion model proposed.

Energy concerns

Additionally, drying process research focuses on different objectives. One of them is the reduction of the operating costs and the improvement of drying equipment capacity (Chua and Chou, 2014). Thus, to really ascertain the overall drying efficiency of freezing pre-treatments and ultrasound application, another important aspect to consider is the energy efficiency. Although freezing pre-treatment and ultrasound application required an additional power feed, a reduced drying time due to accelerated heat and mass transfer process may cause a corresponding reduction in the amount of energy required in comparison with conventional convective drying.

Therefore, as an additional information, the energy considerations of the experiments done in this doctoral thesis have been taken into account. However, it might be difficult to calculate an energy cost per kg of dry product so, an estimation of the specific energy consumption was done according to the equipment technical datasheet for each experiment and following the methodology proposed by Zielinska, Sadowski, and Błaszczak (2015).

Consequently, the specific energy consumption is expressed as kWh/ kg of water removed in the drying process.

Chapter 1: Hot-air drying intensification by using freezing pre-treatments

In this chapter, three different freezing pre-treatments at –20 °C, at –80 °C and by liquid nitrogen immersion were applied on beetroot, apple and eggplant drying at a temperature of 50 °C and 1 m/s of air velocity. The freezing process time of the three freezing pre-treatments (940, 1470 and 26 s for freezing processes at –20 °C, at –80 °C and by liquid nitrogen immersion, respectively) and the drying time have been taken into account. The results are presented in Table 2.

Specific energy consumption was significantly reduced when beetroot, apple and eggplant samples were frozen before drying in all experiments (between 12 and 33% compared with untreated sample specific energy consumption).

Zielinska et al. (2015) reported also that freezing pre-treatment decreased specific energy consumption by up to 27% in comparison with drying without pre-treatment when blueberries were frozen (at –20 °C) prior to drying at 60 and 80 °C. Similar energy consumption reductions (10-39%) were observed by Sripinyowanich and Noomhorm (2013) when freezing pre-treatment at –20 °C was applied in vibro-fluidized drying of rice at 110-185 °C.

Comparing among the different freezing pre-treatments, freezing pre-treatment at –20 °C was the one that presented higher specific energy consumption reductions in beetroot (15%), apple (26%) and eggplant (33%). This fact may be related to a significant drying time reduction and a short freezing process time.

Table 2. Energy consumptions and specific energy consumption of experiments carried out with beetroot, apple and eggplant in Chapter 1

Product	**Freezing pre-treatment**	**Freezing energy consumption (kWh)**	**Drying energy consumption (kWh)**	**Specific energy consumption (kWh/kg water removed)**	**Reduction (%)**
Beetroot	None		29.4	3.20	
	at -20 °C	0.2	24.7	2.71	15
	at -80 °C	0.7	24.5	2.74	14
	by liquid N_2		26.0	2.82	12
Apple	None		26.1	4.74	
	at -20 °C	0.2	19.0	3.50	26
	at -80 °C	0.7	19.0	3.59	24
	by liquid N_2		19.1	3.47	27
Eggplant	None		23.2	2.28	
	at -20 °C	0.2	15.4	1.53	33
	at -80 °C	0.7	18.0	1.84	19
	by liquid N_2		19.8	1.94	15

Chapter 2: Hot-air drying intensification by using freezing pre-treatment and ultrasound application

In this chapter, freezing pre-treatment at –20 °C was applied before beetroot drying at a temperature of 40 °C and 1 m/s of air velocity process assisted with ultrasound at two power levels (16.4 and 26.7 kW/m^3). In this case, the freezing process time (347 s) and the drying time have been taken into account. Moreover, ultrasound application time was equal to the drying time of the experiment. The results were presented in Table 3.

Freezing pre-treatment at –20 °C decreased the specific energy consumption by 46% when ultrasound was not applied which was slightly higher than the reported decreases by Zielinska et al. (2015) and Sripinyowanich and Noomhorm (2013) commented above.

Ultrasound application at 16.4 and 26.7 kW/m^3 on samples which were not pre-frozen, reduced specific energy consumption by 36 and 43%, respectively. Lower energy consumption reductions were reported by Kowalski, Pawłowski, Szadzińska, Łechtańska, and Stasiak (2016) and Szadzińska, Łechtańska, Kowalski, and Stasiak (2017) when applying ultrasound (at 100 and 200 W) on raspberries drying at 55 °C (10-19% of reduction) and on green pepper drying at 54 °C (9-11% of reduction), respectively. However, slightly higher energy consumption reductions (42-54%) were reported by Sabarez, Gallego-Juárez, and Riera (2012) in ultrasound assisted (75-90 W) drying of apples at 40 °C.

Table 3. Energy consumptions and specific energy consumption of beetroot experiments of Chapter 2

Product	**Freezing pre-treatment**	**US**	**Freezing energy consumption**	**Drying energy consumption (kWh)**	**US energy consumption (kWh)**	**Specific energy consumption (kWh/kg water removed)**	**Reduction (%)**
Beetroot	None	None		58.6		7.11	
		16.4 kW/m^3		37.6	0.1	4.58	36
		26.7 kW/m^3		33.3	0.2	4.05	43
	at -20 °C	None	0.1	31.5		3.83	46
		16.4 kW/m^3	0.1	26.3	0.1	3.21	55
		26.7 kW/m^3	0.1	24.5	0.1	3.00	58

Furthermore, when both freezing pre-treatment and ultrasound were applied, a reduction of the specific energy consumption by 55 and 58% was observed when acoustic densities of 16.4 and 26.7 kW/m^3 were applied, respectively. This specific energy reduction was higher than that observed when freezing pre-treatment and ultrasound were applied separately. Therefore, a synergistic effect was observed.

Chapter 3: Low-temperature drying intensification by ultrasound application

In the last chapter, ultrasound (20.5 kW/m^3) was applied on kiwifruit and mushroom low-temperature drying at 5, 10 and 15 °C. The drying time of each experiment has been taken into account and the ultrasound application time was considered equal to the drying process time. The results were presented in Table 4.

Specific energy consumption was reduced in kiwifruit and mushroom drying in a range between 6 and 68%. Specific energy consumption was significantly reduced when drying temperature was increased from 5 to 15 °C in kiwifruit (68%) drying but a lower decrease was observed in mushroom drying (14%).

When ultrasound was applied, specific energy reductions of 53-63% and 38-64% were obtained in kiwifruit and mushroom drying, respectively, compared with experiments without ultrasound assistance.

No bibliography was found about energy concerns of ultrasound application on low-temperature drying, thus, comparison with hot-air drying was done instead. The obtained results were similar to the obtained by Sabarez et al. (2012) when ultrasound (75-90 W) was applied on apple hot- air drying at 40 °C (42-54%).

Table 4. Energy consumptions and specific energy consumption of experiments carried out with kiwifruit and mushroom experiments in Chapter 3

Product	**Drying temperature**	**US**	**Drying energy consumption (kWh)**	**US energy consumption (kWh)**	**Specific energy consumption (kWh/kg water removed)**	**Reduction (%)**
Kiwifruit	5 °C	None	60.0		11.32	
	10 °C		34.0		6.42	43
	15 °C		19.0		3.58	68
	5 °C	20.5 kW/m^3	22.8	1.1	4.51	60
	10 °C		12.0	0.6	2.38	63
	15 °C		8.5	0.4	1.68	53
Mushroom	5 °C	None	21.4		1.97	
	10 °C		20.2		1.86	6
	15 °C		18.4		1.69	14
	5 °C	20.5 kW/m^3	12.6	0.6	1.22	38
	10 °C		8.6	0.4	0.83	55
	15 °C		6.3	0.3	0.61	64

In conclusion, ultrasound application in low-temperature drying of kiwifruit and mushroom presented higher specific energy reductions than freezing pre-treatment and/or ultrasound application in hot-air dying of beetroot, apple and eggplant.

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CONCLUSIONS

Based on the results obtained in this doctoral thesis, the following conclusions can be stated:

1. Freezing pre-treatment allowed the drying time shortening. However, both microstructure and quality were affected.

    1.1. Freezing treatments at –20 °C, at –80 °C and by liquid nitrogen immersion before hot-air drying of beetroot, apple and eggplant at 40 °C enhanced drying process reducing drying time by up to 34% and increasing the effective diffusion coefficient by up to 72%, compared with drying experiments of untreated samples.

    1.2. Microstructure, colour, texture, bioactive compounds and antioxidant activity of beetroot, apple and eggplant, before and after drying, were significantly affected by freezing at –20 °C, at –80 °C and by liquid nitrogen immersion, compared with those of untreated samples. It seemed that ice crystals growing promoted structure damage.

    1.3. Freezing affected differently depending on the porosity of the initial structure of the product. The original microstructure seemed to be more fragile in apple and eggplant but more compact in beetroot. Thus, freezing pre-treatment effects on drying rate, microstructure and quality parameters were more pronounced on medium-high porosity products (apple and eggplant) than on low porosity product (beetroot).

    1.4. Freezing pre-treatment rate affected the drying process. Freezing pre-treatments with a slow-medium freezing rate (at –20 °C and at –80 °C) had more impact on beetroot and eggplant drying rate, microstructure and quality parameters than freezing pre-treatment by liquid nitrogen immersion, which took place at a very fast rate. This fact could be related to the formation of bigger ice crystals in slow freezing rates than in fast ones.

2. Both freezing pre-treatment and ultrasound application during drying synergistically affected the mass transfer rate but also affected the microstructure, the bioactive compounds contents and the antioxidant activity.

    2.1. Freezing pre-treatment at –20 °C promoted beetroot hot-air drying at 40 °C time shortening by 46% and effective diffusion coefficient increment by 158%, compared with the raw sample, which can be related to sample tissue disorders due to ice crystals growing. Meanwhile ultrasound application at 16.4 and 26.7 kW/m^3 reduced drying time by 36 and 43%, respectively, and increased both effective diffusion and external mass transfer coefficients (60-73% and 28-49%, respectively) due to ultrasound mechanical effect. Moreover, when both freezing pre-treatment and ultrasound application at 16.4 and 26.7 kW/m^3 were applied, beetroot drying time was also shortened by 55 and 58%, respectively, and both effective diffusion and external mass transfer coefficients were also increased by 204-211% and 28-49%, respectively.

2.2. Although freezing pre-treatment and ultrasound application during drying could be used to increase the mass transfer rate in beetroot, processing affected the microstructure and the bioactive compounds contents and the antioxidant activity, especially when both were applied. Thus, disruptions and fissures were observed when freezing pre-treatment was applied due to ice crystals growing into the product structure and micro-channels were promoted by ultrasound compressions and expansions of the material. Moreover, significant reductions of bioactive compounds contents and antioxidant activity were observed after drying when freezing pre-treatment or/and ultrasound were applied (although betalains contents were preserved when freezing pre-treatment was applied).

3. The drying operation at low-temperature could be intensified by ultrasound application and it could help to preserve quality.

3.1. Ultrasound application at 20.5 kW/m^3 during drying of kiwifruit and mushroom at low-temperature (5, 10 and 15 °C) enhanced mass transfer rate, reducing drying time between 41 and 66%, and increasing both the effective diffusion and the external mass transfer coefficients (76-184% and 61-231%, respectively), compared with the corresponding drying process without ultrasound application. Thus, ultrasound compressions and expansions effect enhanced mass transfer process. These effects were lower as the temperature rose in kiwifruit drying but higher in mushroom drying. Consequently, different products presented different behaviours under ultrasound application at 20.5 kW/m^3 during drying at low-temperature (5, 10 and 15 °C).

3.2. Low-temperature drying assisted by ultrasound promoted greater microstructure changes. Mushroom microstructure exhibited shrinkage and hollows after drying which were wider as the temperature rose to 15 °C and presented also micro-channels when ultrasound was applied during drying due to ultrasound mechanical effect.

3.3. Loss of quality was observed when air drying temperature increased from 5 to 15 °C. In general, quality parameters of kiwifruit and mushroom, such as bioactive compounds contents, antioxidant activity, colour, hydration properties and fat adsorption capacity, were significantly affected by the rise of the drying temperature from 5 to 15 °C due to higher thermal degradation of the sample.

3.4. When drying at 5 °C, ultrasound application promoted important losses of quality parameters in kiwifruit and mushroom compared with drying without ultrasound application. However, drying at 15 °C with ultrasound application promoted lower kiwifruit and mushroom quality parameters losses compared with drying without ultrasound application, probably due to drying time shortening and consequent thermal and air exposure reduction. Therefore, it could be said that drying intensification was achieved under these conditions because significant drying process enhancement as well as quality parameters retention were observed.

RECOMMENDATIONS

Taking into account the conclusions obtained from this doctoral thesis, the recommendations for future studies are:

- Evaluate and quantify the changes in the microstructure, through image analysis, and other quality parameters of a wider range of fruits and vegetables products with high porosity figures and subjected to different low rate freezing pre-treatments and drying with ultrasound application at different power densities in order to better determine the relationship between the initial microstructure and the effects of the combined methods.

- Increase/decrease the ultrasound power density applied during low-temperature drying at temperatures between 10 to 20 °C of different fruits and vegetables in order to asses if the mass transfer could be further enhanced preserving the final product quality parameters and also with the aim of observe if the different initial microstructures may be affected differently by the ultrasound application at different temperatures.

- Analyse the use of the ultrasound application in intermittent acoustic drying processes at low temperature, evaluating the influence of the process variables on the quality of the final product. The ultrasound effect has been reported to be more important at the first moments of the drying process when the moisture content is high. The high free water content in the material at the beginning of the drying process aids the easy penetration and transmission of ultrasound waves inside the solid. Consequently, the pressure is increased and the cavitation take place. Moreover, further application of ultrasound could result in higher sample degradation which may be avoided by optimizing the ultrasound application period.

- Deeply determine the specific energy consumption of the system in order to evaluate more precisely the energy efficiency of the combined methods used and decide the optimal process conditions when applying freezing pre-treatments and/or ultrasound application.