DEPARTAMENTO
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CONTRIBUCIÓN AL ESTUDIO DE LA APLICACIÓN DE ULTRASONIDOS DE ALTA INTENSIDAD EN PROCESOS DE SECADO A BAJA TEMPERATURA

TESIS DOCTORAL

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Que la memoria titulada "CONTRIBUCIÓN AL ESTUDIO DE LA APLICACIÓN DE ULTRASONIDOS DE ALTA INTENSIDAD EN PROCESOS DE SECADO A BAJA TEMPERATURA", presentada por D. Juan Vicente Santacatalina Bonet para aspirar al grado de Doctor en Ciencia, Tecnología y Gestión Alimentaria y realizada bajo nuestra dirección en el Departamento de Tecnología de Alimentos de la Universitat Politècnica de València, cumple las condiciones adecuadas para su aceptación como Tesis Doctoral, por lo que

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Al interesado a su presentación en el Departamento de Tecnología de Alimentos de la Universitat Politècnica de València.

Y para que conste a los efectos oportunos, presentamos la referida memoria firmando el presente certificado en Valencia a 28 de octubre de 2015.

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ABSTRACT

Dehydration is one of the most commonly used operations in the food industry, and although its aim is to extend the shelf life of foods by reducing their water activity, it could also involve quality degradation. Vacuum freeze-drying may be considered one of the best drying methods for the purposes of preserving the organoleptic and nutritional properties of the fresh product, but its high processing cost limits its use to high value-added products. Convective drying at low temperatures could be considered an alternative means of obtaining high quality products at lower cost. However, the low drying rates at low temperatures (T<20ºC) and atmospheric pressure makes its industrial application difficult. In this sense, high intensity ultrasound (US) has been used to intensify mass transfer phenomena in food processing. It could be of great interest to apply US in low temperature drying because the ultrasonic effects are mainly mechanical (non-thermal).

In this context, the main aim of this thesis was to determine the feasibility of US application in low temperature drying, addressing the effect on both the drying kinetics and the quality of the obtained products. For this purpose, apple, eggplant and cod samples were dried at different temperatures (-10, -5, 0, 5 and 10ºC), air velocities (1, 2, 4 and 6 m/s) and applying different ultrasonic powers (0, 25, 50 and 75 W). Diffusion models were used to describe the drying kinetics and to quantify the influence of the process variables. Moreover, different quality parameters (rehydration capacity, texture, antioxidant capacity...) of the dried products were determined.

The application of US significantly ($p<0.05$) shortened the drying time under every drying condition and with each product tested, reducing the drying time by up to 80, 87 and 60% in apple, eggplant and cod samples, respectively. Thus, the greater the ultrasonic power applied, the shorter the drying time. The drying temperature and air velocity influenced the US efficiency and the best performance was achieved at the lowest drying temperatures and air velocities.

In general terms, the diffusion model adequately fitted the drying kinetics of the three products tested. Although, in the case of US assisted drying, a better fit of the experimental data was obtained when the external resistance to water transfer was considered. The URIF (Uniformly Retreating Ice Front) model successfully fitted the atmospheric freeze drying kinetics. This model was validated under different experimental conditions.

As regards the effect of the process variables on the quality parameters, in overall terms, it was observed that neither the US application nor the air velocity greatly influenced the quality of the obtained products. However, the temperature affected some quality parameters, such as rehydration capacity and color, especially at temperatures below the samples' freezing point.

Finally, as a technology employed for the purposes of obtaining porous food matrices to be used further in the development of functional foods, US-assisted low temperature drying could be considered of great potential. Thus, from dried apple samples impregnated with olive leaf extract, it was observed that US application during drying did not significantly ($p<0.05$) influence the infusion capacity but did increase the antioxidant capacity of the final product.

Therefore, high intensity ultrasound could be considered an interesting technology with which to speed-up the low temperature drying processes without greatly affecting the quality of the dried product.

Contribución al estudio de la aplicación de ultrasonidos de alta intensidad en procesos de secado a baja temperatura

RESUMEN

La deshidratación, una de las operaciones más utilizadas en la industria agroalimentaria, mejora la estabilidad de los alimentos al reducir su actividad de agua, aunque puede afectar a su calidad. Entre las diferentes técnicas de secado existentes, destaca la liofilización a vacío por ser una de las que mejor conservan las propiedades organolépticas y nutricionales de los productos. Sin embargo, esta operación resulta muy cara y sólo se utiliza en productos de alto valor añadido. El secado convectivo a baja temperatura (T<20ºC) representa una alternativa para obtener productos de alta calidad a menor coste aunque su baja velocidad de proceso dificulta su implementación a nivel industrial. En este sentido, los ultrasonidos de alta intensidad (US) se han aplicado para intensificar operaciones de transferencia de materia en diferentes procesos agroalimentarios. Sus efectos son principalmente mecánicos (no térmicos), por lo que su uso en el secado a baja temperatura resulta altamente interesante.

En este contexto, el objetivo general de la presente tesis doctoral fue determinar la viabilidad de la aplicación de US en procesos de secado a baja temperatura, abordando tanto su efecto en la cinética como en la calidad de los productos obtenidos. Para ello, se deshidrataron muestras de manzana, berenjena y bacalao a diferentes temperaturas (-10, -5, 0, 5 y 10ºC) y velocidades de aire (1, 2, 4 y 6 m/s) y aplicando diferentes niveles de potencia acústica (0, 25, 50 y 75 W). Se utilizaron modelos difusivos para describir las cinéticas de secado y cuantificar la influencia de las variables de proceso. Además, se determinaron diferentes parámetros de calidad (capacidad de rehidratación, textura, capacidad antioxidante,…) de los productos deshidratados.

La aplicación de US permitió reducir significativamente ($p<0.05$) el tiempo de secado en todas las condiciones experimentales y productos analizados, obteniendo reducciones de tiempo de secado de hasta el 80, 87 y 60% en manzana, berenjena y bacalao, respectivamente. La reducción del tiempo de secado fue mayor cuanto mayor fue la potencia acústica aplicada. La temperatura

y la velocidad del aire de secado influyeron en la efectividad de la aplicación de US, siendo mayor el efecto de los US a las temperaturas y velocidades más bajas.

En general, la teoría difusional describió adecuadamente la cinética de secado de los tres productos estudiados. En las experiencias con aplicación de US se obtuvo un mejor ajuste a los datos experimentales cuando se consideró la resistencia externa en el modelo. Asimismo, en condiciones de liofilización a presión atmosférica, el modelo URIF (Uniformly Retreating Ice Front) se ajustó adecuadamente a los datos experimentales. Además, este modelo se validó en diferentes condiciones experimentales.

Respecto al efecto de las variables de proceso en los parámetros de calidad, en general, se observó que ni la aplicación de US ni la velocidad de aire influyeron de manera importante en la calidad de los productos obtenidos. En cambio, la temperatura afectó de manera relevante a parámetros como la capacidad de rehidratación y el color, especialmente a temperaturas por debajo del punto de congelación de las muestras.

Por otro lado, el secado a baja temperatura asistido con US tiene un alto potencial para la obtención de matrices porosas alimentarias para su posterior utilización en el desarrollo de alimentos funcionales. Así, en muestras de manzana deshidratada e impregnada con extracto de hoja de olivo, se observó que la aplicación de US durante el secado no afectó significativamente ($p<0.05$) a la capacidad de impregnación, pero sí incrementó la capacidad antioxidante del producto obtenido.

Por lo tanto, los ultrasonidos de alta intensidad se pueden considerar como una tecnología interesante para acelerar los procesos de secado a baja temperatura sin afectar en gran medida a la calidad del producto obtenido.

Contribució a l'estudi de l'aplicació d'ultrasons d'alta intensitat en processos d'assecatge a baixa temperatura

RESUM

La deshidratació, una de les operacions més utilitzades en la indústria agroalimentària, millora l'estabilitat dels aliments en reduir la seua activitat d'aigua, encara que pot afectar-ne la qualitat. Entre les diferents tècniques d'assecatge que hi ha, destaca la liofilització al buit per ser una de les que millor conserven les propietats organolèptiques i nutricionals dels productes, però aquesta operació resulta molt cara i només s'utilitza en productes d'alt valor afegit. L'assecatge convectiu a baixa temperatura (T<20ºC) representa una alternativa per a obtenir productes d'alta qualitat a menor cost. No obstant això, la baixa velocitat d'assecatge dificulta la seua implementació a nivell industrial. En aquest sentit, els ultrasons d'alta intensitat (US) s'han aplicat per a intensificar operacions de transferència de matèria en diferents processos agroalimentaris. El seu ús en l'assecatge a baixa temperatura resulta altament interessant pel fet que els seus efectes són principalment mecànics (no tèrmics).

En aquest context, l'objectiu general de la present tesi doctoral va ser determinar la viabilitat de l'aplicació d'US en processos d'assecatge a baixa temperatura, abordant tant l'efecte en la cinètica del procés com en la qualitat dels productes obtinguts. Amb aquesta finalitat, es van deshidratar mostres de poma, albergínia i bacallà a diferents temperatures (-10, -5, 0, 5 i 10ºC) i velocitats d'aire (1, 2, 4 i 6 m/s) i aplicant diferents nivells de potència acústica (0, 25, 50 i 75 W). Es van utilitzar models difusius per a descriure les cinètiques de l'assecatge i quantificar la influència de les variables del procés. A més, es van determinar diferents paràmetres de qualitat (capacitat de rehidratació, textura, capacitat antioxidant...) dels productes deshidratats.

L'aplicació d'US va permetre reduir significativament ($p<0.05$) el temps d'assecatge en totes les condicions experimentals i tots els productes analitzats; es van obtenir reduccions de temps de fins al 80%, 87% i 60% en pomes, albergínies i bacallà, respectivament. La reducció del temps d'assecatge va ser més alta com més alta va ser la potència acústica aplicada. La temperatura i la velocitat de l'aire de

l'assecatge van influir en l'efectivitat de l'aplicació d'US, sent major l'efecte dels US a les temperatures i velocitats més baixes.

En general, la teoria de la difusió va descriure adequadament la cinètica de l'assecatge dels tres productes estudiats. En les experiències amb aplicació d'US es va obtenir un millor ajust a les dades experimentals quan es va considerar la resistència externa en el model. Així mateix, en condicions de liofilització a pressió atmosfèrica, el model URIF (Uniformly Retreating Ice Front) es va ajustar correctament a les dades experimentals. A més, aquest model es va validar en diferents condicions experimentals.

Respecte a l'efecte de les variables del procés en els paràmetres de qualitat, en general, es va observar que ni l'aplicació d'US ni la velocitat de l'aire van influir de manera important en la qualitat dels productes obtinguts. En canvi, la temperatura va afectar de manera rellevant a paràmetres com la capacitat de rehidratació i el color, especialment a temperatures per davall del punt de congelació de les mostres.

D'altra banda, l'assecatge a baixa temperatura assistit amb US presenta un alt potencial per a obtenir matrius poroses alimentàries per a la posterior utilització en el desenvolupament d'aliments funcionals. Així, en mostres de poma deshidratada i impregnada amb extracte de fulles d'olivera, es va observar que l'aplicació d'US durant l'assecatge no va afectar significativament ($p<0.05$) la capacitat d'impregnació, però sí que va incrementar la capacitat antioxidant del producte obtingut.

Per tant, els ultrasons d'alta intensitat es poden considerar com una tecnologia interessant per a accelerar els processos d'assecatge a baixa temperatura sense afectar de manera rellevant la qualitat del producte obtingut.

1. Introducción

1.1 Generalidades secado

La reducción del contenido de agua es un procedimiento para la conservación de los alimentos que se ha utilizado desde la antigüedad y que en la actualidad continua siendo una de las operaciones unitarias más relevantes (Mulet et al., 2005). Se puede considerar deshidratación el proceso de eliminación del agua del producto mediante cualquier técnica o método, mientras que el término secado es más concreto ya que contempla la deshidratación con cambio de fase (Garcia-Perez, 2007). Además de prolongar la vida útil, el secado proporciona otras ventajas adicionales, como son la disminución del peso y del volumen del producto, lo que implica una reducción tanto del espacio de almacenamiento como de los costes de transporte (Ozuna et al., 2011). Los numerosos métodos que existen para extraer el agua de los alimentos se pueden clasificar en dos grandes grupos: métodos mecánicos (prensado o centrifugación) y métodos físico-químicos (secado con aire caliente, secado a baja temperatura, uso de radiación infrarroja, aplicación de ultrasonidos de potencia, CO_2 supercrítico,...) (Vega-Mercado et al., 2001). Por otro lado, cabe destacar que el secado es una operación que requiere un aporte importante de energía, representando en algunos casos el 15% del uso de la energía total empleada en la industria (Mulet et al., 2011). Además, y en términos generales, son procesos con una eficiencia energética relativamente baja que oscila entre el 25 y el 50% (Mujumdar, 2007).

El secado incrementa la estabilidad de los alimentos porque reduce su actividad de agua, limitando así su disponibilidad para el desarrollo de microorganismos y minimizando los cambios físicos y químicos que se producen durante el almacenamiento (Mayor y Sereno, 2004). Sin embargo, también produce una pérdida de calidad en el producto debido a que induce cierto colapso estructural y cambios bioquímicos. Obviamente, la degradación de la calidad del alimento depende de la técnica y de las condiciones de secado (tiempo, temperatura) empleadas (Garau et al., 2006).

El secado por aire caliente es una de las tecnologías de deshidratación más utilizadas en la industria alimentaria porque es una operación sencilla y requiere inversiones iniciales relativamente bajas. Con esta técnica se obtienen productos deshidratados bastante homogéneos y con una larga vida útil. El aumento de la

temperatura del aire constituye la alternativa tradicional para incrementar la baja velocidad de secado y disminuir los tiempos de proceso. Sin embargo, esta estrategia puede afectar negativamente a la calidad del producto final debido a las altas temperaturas utilizadas. La pérdida de agua y el calentamiento producen estrés en la estructura celular del alimento provocando cambios en su microestructura (como por ejemplo la formación de poros) y el encogimiento de las muestras. Además, el tratamiento térmico que supone este tipo de secado puede inducir la degradación de los componentes termolábiles de los alimentos como los compuestos polifenólicos con capacidad antioxidante.

1.2 Secado a baja temperatura

Una alternativa para mejorar la calidad de los productos deshidratados es la utilización de bajas temperaturas durante la operación de secado. Se considera secado a baja temperatura aquel que se realiza a una temperatura por debajo de las condiciones ambientales estándar (20ºC) (Ozuna et al., 2014a). Las bajas temperaturas producen una menor degradación del alimento y permiten obtener productos deshidratados de alta calidad debido a que se conservan mejor las propiedades organolépticas y nutricionales, especialmente las relacionadas con componentes termolábiles. Sin embargo, su principal inconveniente es que los tiempos de proceso son muy largos, mucho mayores que los del secado por aire caliente.

En cuanto a las técnicas de secado que utilizan bajas temperaturas se puede diferenciar entre las que utilizan temperaturas por encima del punto de congelación y las que utilizan temperaturas por debajo del mismo (Ozuna et al., 2014a). En el primer caso, la eliminación del agua se produce por evaporación. El empleo de estas temperaturas puede resultar muy interesante ya que no se requiere la congelación previa de la muestra. De este modo, se evita la degradación de la estructura que conlleva el crecimiento de los cristales de hielo durante el proceso de congelación y se evita el consumo energético necesario para el mismo. En el segundo caso, la salida de agua del alimento se produce por sublimación y, de manera general, al proceso se le denomina liofilización. En su aplicación convencional, la más extendida, la sublimación se realiza a vacío

(Fissore et al., 2011). Se utilizan temperaturas de secado muy bajas y un ambiente con ausencia de oxígeno, lo que ayuda a mejorar la calidad y el valor nutritivo de los productos deshidratados (Wu et al., 2007). Sin embargo, esta técnica requiere de una elevada inversión inicial en equipamiento. Además, presenta un elevado coste de operación debido, entre otras cosas, a la baja velocidad de secado y a la necesidad de trabajar a vacío y en discontinuo (Claussen et al., 2007a). Éstas son las principales razones por las que, aun siendo un proceso muy extendido en la industria farmacéutica y biotecnológica, su uso queda restringido en la industria agroalimentaria al procesado de productos de muy alto valor añadido. Por otro lado, la liofilización a vacío puede producir importantes pérdidas de compuestos volátiles, lo que hace que los productos liofilizados a veces se cataloguen como insípidos (Lin et al., 1998).

Una alternativa a la liofilización convencional es el secado convectivo a baja temperatura. En estas condiciones la sublimación es posible si se utiliza un aire de secado con una temperatura por debajo del punto de congelación del producto y ésta se facilita si la humedad relativa del aire es muy baja. Esta técnica, denominada liofilización a presión atmosférica (Claussen et al., 2007a), permite obtener productos de mayor calidad que los obtenidos con el secado por aire caliente pero con un coste menor que con la liofilización a vacío (Alves-Filho et al., 2007). Así, puede considerarse una técnica interesante con la que obtener productos deshidratados que mantengan bien las características nutricionales y organolépticas del producto fresco a precios más económicos. Sin embargo, el principal inconveniente de esta técnica es también los largos tiempos de proceso que se necesitan debido a que la sublimación a presión atmosférica es muy lenta (Garcia-Perez et al., 2012).

1.3 Tecnologías para la intensificación del proceso de secado

El procesado de alimentos evoluciona constantemente debido a la búsqueda continua de nuevos productos que se adapten a las cambiantes necesidades de los consumidores y de técnicas de procesado que sean más eficientes y respetuosas con el medio ambiente. En este sentido, la intensificación de procesos tiene como objetivo mejorar los procesos tradicionales y desarrollar nuevas

tecnologías que permitan incrementar el rendimiento y la seguridad del proceso, mejorar la calidad del producto y disminuir el consumo de energía (Benali y Kudra, 2010). Este es el caso del secado por aire caliente, donde se ha planteado el empleo de nuevas tecnologías para asistir el proceso y en busca de su intensificación (Benali y Kudra, 2010) sin repercutir en la calidad del producto deshidratado. Entre estas nuevas tecnologías se encuentran las microondas, la radiación infrarroja, la radiofrecuencia y los ultrasonidos de potencia (Mulet et al., 2010).

Las microondas son ondas electromagnéticas con una longitud de onda comprendida entre 1 mm y 1 m y cuya frecuencia se encuentra entre 300 y 300000 MHz (Orsat et al., 2007). Cuando se aplican sobre un alimento causan el movimiento de las moléculas de agua y de las moléculas con carga eléctrica. Este movimiento genera calor debido a la fricción y es función de la temperatura y las características del material. De esta manera, se provoca una diferencia de presión de vapor entre la superficie y el interior del producto que facilita una rápida transferencia de humedad hacia la superficie de los alimentos (Zhang et al., 2010). Así, mediante el secado convectivo (40ºC) asistido por microondas (100 W), Chua y Chou (2005) obtuvieron una reducción en el tiempo de secado del 42% en patata y un 31% en láminas de zanahoria (4 mm de espesor, 20 mm de longitud y 20 mm de anchura). Por lo tanto, es una técnica prometedora en términos de acortamiento de tiempos de secado. Sin embargo, su implantación a nivel industrial es escasa debido a las dificultades técnicas para realizar un control preciso de la aplicación que evite el sobrecalentamiento de los alimentos (Ratti, 2001; Vadivambal y Jayas, 2009). Otros inconvenientes que presenta esta técnica son el calentamiento no uniforme de los materiales, su baja eficiencia energética y la aparición de daños en la textura, que incluso pueden llegar a la rotura del material cuando se utilizan altos niveles de potencia.

Las ondas de radio, al igual que las microondas, son ondas electromagnéticas. Sus aplicaciones más frecuentes se dan a frecuencias comprendidas entre 10 y 100 MHz (Chou y Chua, 2001) y se basan en el calentamiento de todo el volumen del producto a secar debido al fenómeno de la rotación dipolar (campo alterno) y a los efectos de conducción (campo continuo). El calentamiento de la muestra

reduce el tiempo de secado (Wang et al., 2014). Su utilización para intensificar procesos de secado ha sido menor que en el caso de las microondas.

La radiación infrarroja presenta longitudes de onda entre las microondas y la luz visible. Su aplicación contribuye a la reducción del tiempo de proceso por aporte de calor sensible durante el secado de alimentos (Riadh et al., 2015). Las principales ventajas de esta tecnología son la limitada transmisión de calor al medio por el cual se transmite la radiación, la fácil direccionalidad de la energía, la consecución de elevados coeficientes de transferencia de calor, la facilidad de incorporación de dicha tecnología a los secaderos convencionales y los rápidos tiempos de respuesta que facilitan el control del proceso (Doymaz, 2015). Así, Mihindukulasuriya y Jayasuriya (2015) consiguieron reducir el tiempo de secado un 30 y un 40% en el secado de chile a 70 y 50ºC, respectivamente, empleando una combinación de radiación infrarroja y aire caliente.

De lo expuesto anteriormente, se puede concluir que los efectos sobre la velocidad de secado de la aplicación de radiación infrarroja, microondas y ondas de radio se basan principalmente en incrementar el calentamiento del material a secar. Es decir, son tecnologías que aportan una energía adicional al proceso de secado en forma de energía térmica. Esto, aunque contribuye a la reducción de tiempo de secado, puede afectar significativamente a la calidad del producto deshidratado (Schössler et al., 2012a). Para evitar y/o reducir esta degradación térmica es necesario realizar un control cuidadoso del aporte de energía que evite fenómenos de sobrecalentamiento (Riera et al., 2011).

Otra opción interesante radica en el uso de ultrasonidos de potencia o de alta intensidad. Esta tecnología basa su capacidad de intensificación de la transferencia de materia en que genera principalmente efectos mecánicos, no térmicos. Por lo tanto, además de preservar la calidad de los productos, también puede ser una alternativa capaz de reducir el consumo energético y hacer al proceso de secado más respetuoso con el medio ambiente (Gallego-Juárez et al., 2010).

1.4 Ultrasonidos

1.4.1. Generalidades

Las ondas sonoras o acústicas son oscilaciones mecánicas que tienen lugar en el seno del material por el que se propagan (Cárcel, 2003). Por lo tanto, y a diferencia de las ondas electromagnéticas que pueden transmitirse por el vacío, las ondas acústicas son ondas elásticas que necesitan un medio material para su propagación. Los ultrasonidos son ondas acústicas de frecuencia superior a 20 kHz, valor que representa el límite de audición humano (Raj et al., 2004). La fuente de producción de ultrasonidos suele ser un cuerpo vibrante, cuyo movimiento de vibración se transmite a las partículas que lo rodean. Éstas, a su vez, comienzan a oscilar y transmiten el movimiento oscilante a las partículas vecinas, y así sucesivamente.

El "rastreador de ecos" (eco-sounder) fue la primera aplicación comercial de ultrasonidos. Este equipo fue diseñado y construido por Langevin en 1917 y posteriormente dio lugar al SONAR (SOund Navegation And Ranking), que fue empleado en la II Guerra Mundial. Otras aplicaciones ultrasónicas han sido el microscopio ultrasónico de barrido, aplicaciones médicas de inspección no destructivas (ecografías), supervisión de soldaduras y detección de grietas.

Como cualquier tipo de onda, los ultrasonidos se caracterizan por varios parámetros, entre los que destacan principalmente la frecuencia, la velocidad acústica, la longitud de onda, la amplitud, la intensidad acústica, la potencia acústica, la impedancia acústica y la atenuación:

- La **frecuencia** (f, Hz) se define como el número de ciclos o vibraciones que dicha onda completa en una unidad de tiempo. Al inverso de la frecuencia se le denomina periodo y se define como el tiempo necesario para que una onda complete un ciclo.
- La **velocidad** acústica (v, m/s) se define como la velocidad de propagación de una onda. Es característica del medio de propagación y, en general, puede considerarse constante para un medio determinado. Sin embargo, puede verse afectada por la temperatura y por la presión.
- La **longitud de onda** (λ, m) se define como la distancia entre dos planos en los que las partículas se encuentran en el mismo estado de vibración. Se

puede determinar a partir del cociente entre la velocidad acústica y la frecuencia.

- La **amplitud** (A, m) de la onda es el máximo desplazamiento de la partícula desde la posición de equilibrio.
- La **intensidad** (I, W/m^2) de una onda acústica se define como la energía media transmitida por unidad de tiempo a través de una unidad de área perpendicular a la dirección de propagación de la onda.
- La **potencia** acústica (P, W) es la energía total irradiada por la fuente ultrasónica por unidad de tiempo. Puede calcularse multiplicando la intensidad acústica por el área de la superficie radiante.
- La **impedancia** acústica (Z, MRayl) se define como la relación entre la presión acústica y la velocidad de vibración de la partícula. Se puede calcular a partir del producto de la velocidad acústica y la densidad del medio. Cuando la onda ultrasónica llega a una interfase, una parte es reflejada y otra transmitida. La proporción de energía reflejada depende en gran medida de la diferencia de impedancia entre los dos medios, de manera que cuanto mayor sea esta diferencia, mayor será la energía reflejada y menor la transmitida. Por lo tanto, esta característica presenta una gran importancia en las aplicaciones de los ultrasonidos. Si la proporción de energía reflejada es mayor que la transmitida los efectos de los ultrasonidos podrían ser más intensos en la interfase. Si ocurre lo contrario, se incrementan los efectos en el interior del segundo medio (Garcia-Perez, 2007).
- La **atenuación** se define como la pérdida de energía (disminución de la intensidad) que sufre una onda al atravesar el medio de propagación (Povey y McClements, 1988). La atenuación depende de la distancia a la fuente que produce la onda y es debida a reflexión, dispersión y/o difracción de la onda durante su propagación, así como a la conversión de parte de la energía cinética en calor. Es un parámetro importante ya que determina la cantidad de energía que recibe la muestra con respecto a la que inicialmente se generó.

1.4.2. Clasificación

Los ultrasonidos se pueden clasificar, de una manera arbitraria, en función de su frecuencia e intensidad (Awad et al., 2012). Esta clasificación también define sus posibles aplicaciones. Así, se denomina ultrasonidos de baja intensidad, de alta frecuencia o de señal a aquellos que presentan intensidades inferiores al 1 W/cm^2 y frecuencias comprendidas entre 100 kHz y 20MHz. Las aplicaciones de los ultrasonidos de señal se basan en la información que se puede extraer de los cambios que sufre la onda acústica cuando atraviesa un material. Esto es debido a que algunos parámetros ultrasónicos (fundamentalmente velocidad y atenuación) varían en función de las propiedades físicas del medio (Awad et al., 2012; Corona et al., 2014). Por este motivo, son empleados como técnica no invasiva para el análisis y la evaluación de la calidad de productos (Cárcel et al., 2014). Así, entre otras aplicaciones, han sido usados para la caracterización de productos cárnicos (Corona et al., 2013), para la estimación del contenido de grasa solida y el estado físico de la grasa (Awad, 2004; Santacatalina et al., 2011), para la evaluación de la calidad de frutas y vegetales (Mizrach, 2008) o para el control de procesos de fermentación durante la fabricación de pan (Ross et al., 2004).

Por otro lado, se denominan ultrasonidos de alta intensidad, de baja frecuencia o de potencia a aquellos que se aplican con intensidades superiores a 1 W/cm^2 y frecuencias comprendidas entre 20 y 100 kHz. En este caso, los ultrasonidos se utilizan para provocar cambios en los productos o procesos en los que son aplicados (Chemat et al., 2011; Picó, 2013). En este trabajo se han utilizado ultrasonidos de potencia, por lo que en los siguientes apartados se profundizará en aspectos como su generación, en los efectos que producen y en sus principales aplicaciones.

1.4.3. Efectos de la aplicación de ultrasonidos de potencia

La propagación de los ultrasonidos de potencia depende en gran medida del medio donde las ondas se propagan. Además, los efectos producidos por los ultrasonidos y la magnitud de los mismos dependen de las características de dicho medio (líquido, sólido, gas), de las variables de proceso (temperatura, presión, intensidad) y de la estructura del producto a tratar (Mason et al., 2005).

Efectos en medio líquido

Las ondas acústicas inducen sucesivas compresiones y descompresiones que, en los medios líquidos, provocan movimientos moleculares que originan variaciones de presión, velocidades oscilantes y generación de microcorrientes que pueden facilitar los procesos de transferencia de materia y energía. Además, cuando la energía ultrasónica aplicada alcanza un cierto umbral, durante la fase de descompresión se puede llegar a romper la continuidad del medio apareciendo las burbujas de cavitación (Soria y Villamiel, 2010). Dichas burbujas pueden permanecer estables, oscilando en las sucesivas compresiones y descompresiones (cavitación estable), o pueden crecer hasta alcanzar un tamaño inestable y, entonces, implosionar (cavitación inestable). Esta implosión de las burbujas de cavitación libera una gran cantidad de energía y produce efectos mecánicos (turbulencias) y térmicos (aumento de temperatura) (Cárcel et al., 2012). Si el colapso se produce cerca de una superficie sólida, la implosión es asimétrica y se genera una corriente de líquido (microjet) que golpea la superficie del sólido. Este fenómeno puede incrementar la transferencia de materia entre el líquido y el sólido, pero también puede alterar la estructura del sólido, especialmente en su superficie.

En medio líquido, la aplicación de ultrasonidos de potencia resulta relativamente sencilla porque las propiedades acústicas de los emisores ultrasónicos (metales) no son excesivamente diferentes a los líquidos. Por esta razón, las aplicaciones en medios líquidos son más frecuentes que en otros medios (Araujo et al., 2013; Chemat et al., 2011).

Efectos en medio sólido

Cuando las ondas ultrasónicas atraviesan un medio sólido producen una serie de contracciones y expansiones alternantes. Este fenómeno es conocido como “efecto esponja” debido a que a nivel microscópico se asemeja a lo que le ocurre a una esponja cuando se comprime y se relaja repetidamente. Esta tensión alterna facilita la transferencia de materia con el medio que rodea al sólido. Por otro lado, este estrés mecánico puede inducir la formación de microgrietas o microcanales en el interior del sólido que también facilitan los procesos transferencia de materia.

Además, la alta intensidad de las ondas acústicas puede producir cavitación en la fase líquida de la matriz sólida. Aunque es difícil que se produzca por el nivel de energía necesario, la cavitación dentro de la partícula podría contribuir a mejorar la transferencia de materia entre el sólido y el medio circundante, provocando incluso la eliminación de las moléculas de agua más fuertemente adheridas a la matriz sólida (Mulet et al., 2003).

Efectos en medio gaseoso

La aplicación de ultrasonidos de potencia en medios gaseosos es especialmente interesante por los efectos intensos que pueden provocar en las interfases sólido/gas, tales como variaciones de presión, velocidades oscilantes y generación de microcorrientes. Estos efectos pueden contribuir a la disminución del espesor de la capa límite de difusión, y por tanto a la reducción de la resistencia externa a la transferencia de materia y energía (Mulet et al., 2010). Sin embargo, la aplicación de ultrasonidos en medios gaseosos, como el aire, es menos frecuente que en otros medios debido a la dificultad de transmisión de la energía acústica desde la superficie del emisor hasta la muestra, causada por la diferencia de impedancia acústica entre los emisores, normalmente metales o cerámicas, y el gas. Además, los medios gaseosos son altamente atenuantes lo que limita la cantidad de energía que finalmente llega a las muestras (Garcia-Perez et al., 2009). Por lo tanto, para obtener una eficiente transmisión de energía y producir campos acústicos de elevada intensidad es necesario conseguir una buena adaptación de impedancia entre el emisor y el aire, grandes amplitudes de vibración y una elevada concentración de energía (Gallego-Juárez, 1999). El desarrollo de nuevos sistemas de aplicación con estas características que se ha producido en los últimos años, principalmente debido a los trabajos realizados por el Grupo de investigación de “Ultrasonidos de Potencia” del ITEFI (CSIC, Madrid) (Gallego-Juárez et al., 2007), ha posibilitado el incremento en las aplicaciones de ultrasonidos en medios gaseosos como es el caso del secado. En las siguientes secciones, se describirán en detalle estos sistemas y su aplicación al secado convectivo de alimentos.

1.4.4. Sistemas de generación y aplicación de ultrasonidos de potencia

En general, la producción de ultrasonidos consiste en la conversión de cualquier otro tipo de energía en energía acústica (Carlin, 1972). Un sistema de generación de ultrasonidos está constituido por tres elementos fundamentales: generador, transductor y emisor (Figura 1.1). El generador es el encargado de proporcionar la energía necesaria al sistema. Dado que en la mayor parte de las aplicaciones industriales se utiliza energía eléctrica, el generador transforma la señal eléctrica de la red a otra con la frecuencia deseada. El transductor, que suele ser un cuerpo vibrante, es el equipo encargado de la conversión de la señal eléctrica de alta frecuencia en vibraciones mecánicas. Por último, el emisor irradia la energía acústica generada por el transductor al medio a tratar (Cárcel et al., 2012).

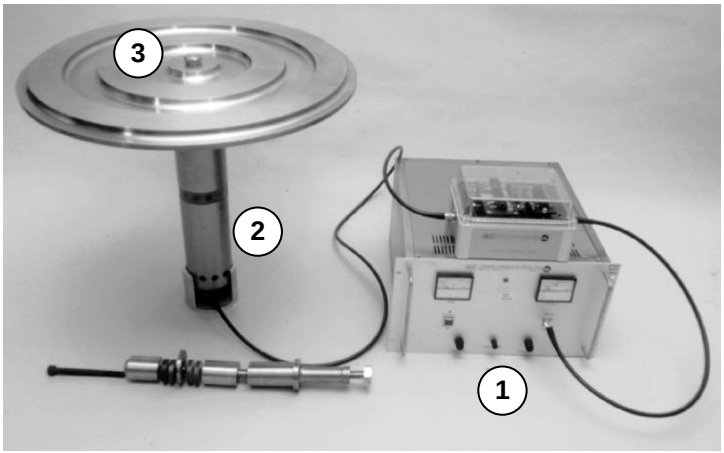

Figura 1.1. Sistema de aplicación de ultrasonidos**.** 1. Generador/Amplificador, 2. Transductor piezoeléctrico, 3. Emisor de placa escalonada.

Los tipos de transductores más utilizados a nivel industrial son los magnetoestrictivos y, principalmente, los piezoeléctricos. Los primeros están construidos a partir de aleaciones metálicas de alta resistencia y presentan la ventaja de ser capaces de alcanzar niveles altos de intensidad acústica (>150 W/cm^2). Además, son muy estables y duraderos. Sin embargo, su utilización está muy limitada debido a que no pueden generar frecuencias superiores a 100 kHz y a que su eficiencia eléctrica es muy baja. Esto conlleva importantes pérdidas de energía en forma de calor que además obliga a incluir sistemas de refrigeración de los transductores (Sabarez et al., 2012).

Los transductores piezoeléctricos se basan las propiedades piezoeléctricas que presentan algunos cristales. Él efecto piezoeléctrico aparece al ejercer una presión sobre el cristal que genera una carga de sentido contrario en cada cara del mismo pero de igual intensidad. El efecto piezoeléctrico inverso ocurre cuando al aplicar una carga, igual pero de sentido contrario, en ambas caras del cristal, éste se contrae o se expande en función de la polaridad de las cargas. Si se aplica una corriente eléctrica alterna de elevada frecuencia se puede provocar el cambio alternante de tamaño del material y, por lo tanto, una vibración. Esta vibración genera una onda mecánica que a la frecuencia adecuada se denomina onda ultrasónica. Los transductores piezoeléctricos son los más utilizados en la actualidad debido a que son capaces de suministrar elevadas potencias cubriendo todo el rango de frecuencias y a que presentan factores de conversión de energía eléctrica muy elevados. Su principal limitación es el paulatino envejecimiento que sufren las cerámicas con el tiempo de trabajo y su despolarización cuando trabajan a las elevadas temperaturas (Cárcel et al., 2014).

Existen diferentes tipos de sistemas de aplicación de ultrasonidos de potencia en función del medio en el que se van a utilizar y de los efectos que se quieren producir en el mismo. Como se ha comentado anteriormente, conseguir un buen acople entre el sistema de aplicación y el medio resulta de gran importancia para que el sistema sea eficiente, haciendo llegar así la mayor cantidad posible de energía a la muestra a tratar. Los principales sistemas comerciales de aplicación de ultrasonidos en medio líquido son los baños de ultrasonidos (sonicación indirecta) y los sistemas tipo sonda (sonicación directa). Los baños de ultrasonidos (Figura 1.2) son posiblemente los sistemas de aplicación de ultrasonidos de potencia más utilizados debido a que son equipos simples, compactos y económicos. Incluyen el sistema de generación-emisión y los transductores se encuentran acoplados en la base y/o paredes de un recipiente de acero inoxidable. Así, cuando todos ellos vibran en fase transmiten la vibración al recipiente y éste al líquido que contiene.

Los baños ultrasónicos se han utilizado para, entre otras aplicaciones, limpieza de material de laboratorio, disgregación celular, solubilización y mejora de procesos de transferencia de materia (Mason, 1998). También se han empleado como tratamiento previo al secado de banana, piña o manzana (Azoubel et al., 2010;

Fernandes et al., 2008; Nowacka et al., 2012). Los principales inconvenientes que presentan estos sistemas son la heterogeneidad del campo acústico generado, el difícil control de la temperatura y, en general, la baja potencia suministrada al medio (Cárcel et al., 2012).

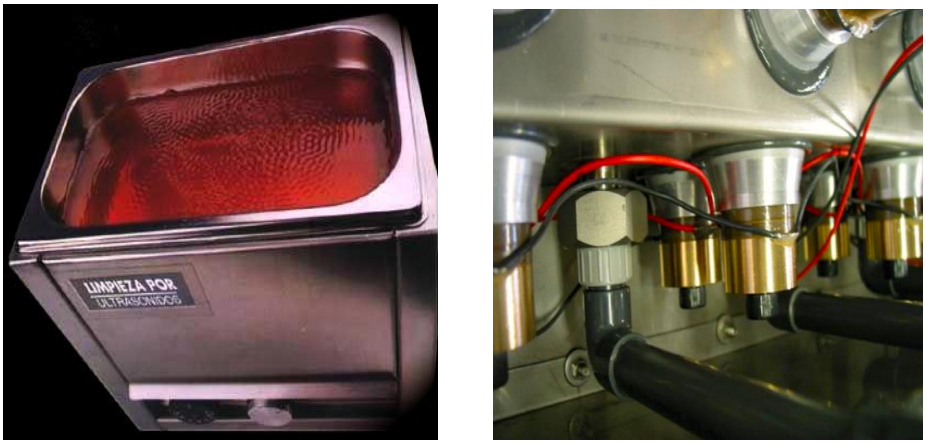

Figura 1.2. Baño ultrasónico.

Los sistemas tipo sonda están constituidos por un transductor acoplado a un emisor metálico cilíndrico o cónico que transmite la vibración directamente al líquido (Figura 1.3). Generalmente, tanto el diseño como la forma del emisor tienen una gran importancia. Una sonda con forma cilíndrica sin variación de diámetro a lo largo de su longitud, se limita únicamente a la transmisión de la energía al medio. Por el contrario, una reducción del diámetro a lo largo de la misma, conlleva un aumento de la amplitud de la vibración (Kutruff, 1991). El material empleado para la fabricación de las sondas debe tener una alta resistencia a la erosión que produce la cavitación, resistencia a la fatiga y bajas pérdidas acústicas (Cárcel, 2003). La sonicación directa se ha utilizado en procesos de deshidratación osmótica de frutas (Cárcel et al., 2007a), de extracción sólido/líquido (Ahmad-Qasem et al., 2013), durante el escaldado de vegetales (Gamboa-Santos et al., 2012), como tratamiento previo al secado convectivo (Kek et al., 2013), para la mejora de la transferencia de materia en el salado en salmuera de carne (Cárcel et al., 2007b) o en la inactivación de enzimas como la polifenoloxidasa de champiñones (Cheng et al., 2013).

Figura 1.3. Sistema tipo sonda.

En cuanto a los sistemas utilizados para la aplicación de ultrasonidos en medios gaseosos, destacan los emisores de placa escalonada, rectangular o circular, (Figura 1.4) y los emisores de cilindro vibrante (Figura 1.5) diseñados por el Grupo de Ultrasonidos de Potencia (ITEFI, CSIC). Estos sistemas se han utilizado para aplicaciones tan diferentes como el desespumado o la aglomeración de partículas sólidas en humos de combustión (Riera et al., 2006; Rodríguez et al., 2010). Una de sus principales aplicaciones ha sido en la intensificación del secado convectivo de alimentos. Así, los emisores de placa escalonada se han utilizado con contacto directo entre emisor y el producto (Figura 1.4). Esta configuración facilita la transferencia de energía acústica, proporcionando una mejora en su transmisión y propagación, sin embargo, es de difícil adaptación a los secaderos convectivos industriales (Garcia-Perez et al., 2009). Por tanto, resulta necesario adaptar los sistemas de ultrasonidos de potencia a los procesos de secado convectivo y para ello se han desarrollado sistemas con emisores eficientes sin que exista necesidad de contacto directo entre el elemento vibrante y el producto. En la Figura 1.5, se muestra un emisor ultrasónico donde las propias paredes de la cámara de secado (cilíndrica) vibran e irradian la energía acústica al medio generando un campo

acústico intenso en su interior, donde se encuentran las muestras que se pretende secar (Garcia-Perez, 2007).

Figura 1.4. Placa escalonada circular utilizada para la aplicación de ultrasonidos por contacto directo entre el emisor y el alimento.

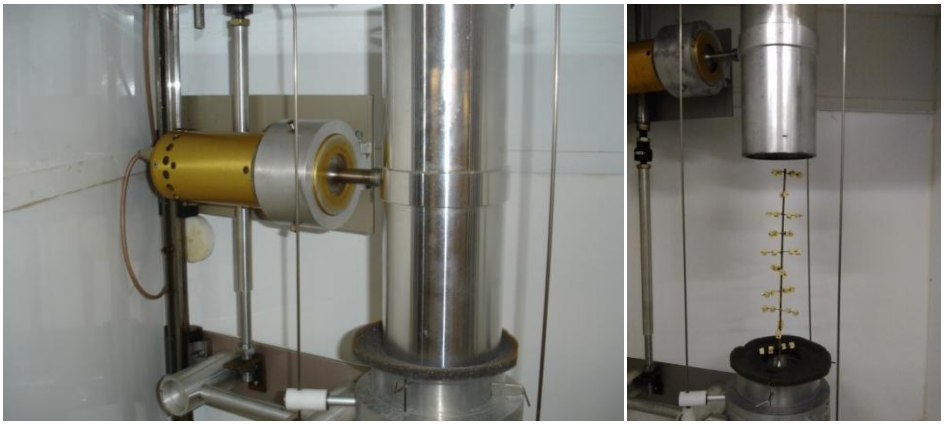

Figura 1.5. Cámara de secado cilíndrica utilizada para la aplicación de ultrasonidos sin contacto directo entre el emisor y el alimento.

1.4.5. Aplicación de ultrasonidos de potencia en el secado convectivo

La aplicación de ultrasonidos de potencia en el proceso de secado pretende facilitar la salida del agua de los materiales y conseguir así la reducción del tiempo de secado y del consumo energético de la operación, sin provocar un calentamiento significativo del producto y evitar así su degradación. El proceso de secado de un alimento está limitado por dos resistencias al transporte del agua: una resistencia interna y una resistencia externa. La resistencia interna define el movimiento del agua dentro del material, siendo una característica intrínseca del alimento. Por contra, la resistencia externa controla el movimiento del agua entre la superficie del sólido y el aire y depende del espesor de la capa límite de difusión que se establece entre estos medios (Mulet et al., 2011). La aplicación de ultrasonidos de potencia durante el secado convectivo puede afectar a ambas resistencias debido a los efectos que inducen tanto en la interfase entre el medio que rodea el alimento (medio gaseoso) como en el propio alimento (medio sólido) (Garcia-Perez, 2007; Riera et al., 2011).

Actualmente, hay muy pocos grupos trabajando en la aplicación de ultrasonidos de potencia en el secado a baja temperatura de alimentos. En general, un grupo de trabajos publicados se basan en la adaptación de transductores comerciales, y por lo tanto diseñados para otros usos, para su utilización en procesos de secado (Bantle y Eikevik, 2011; Schössler et al., 2012a, 2012b y 2012c). Los resultados obtenidos con estos sistemas se encuentran en torno al 10% de reducción de tiempo de secado. Otro grupo de trabajos publicados se basan en los sistemas de emisión de amplia superficie radiante descritos en el apartado anterior, placas escalonadas (Figura 1.4) y cilindro vibrante (Figura 1.5). Estos sistemas han sido diseñados específicamente para aplicaciones en medios gaseosos y muestran una eficiencia mucho mayor en la transmisión de la energía acústica al medio. Ambos sistemas han sido principalmente utilizados en procesos de secado por aire caliente de alimentos. Su aplicación en procesos de secado a baja temperatura todavía no ha sido abordada en profundidad. Así, los sistemas de placa escalonada se han utilizado en aplicaciones con (De la Fuente et al., 2006; Figura 1.4) y sin contacto directo (Sabarez et al., 2012) con el alimento. En cuanto a los emisores de cilindro vibrante, se han empleado en el secado convectivo de diversos alimentos como piel de limón (Garcia-Perez et al., 2009), caqui (Cárcel et

al., 2007c), piel de naranja (Ortuño et al., 2010), berenjena (Garcia-Perez et al., 2011), zanahoria (Cárcel et al., 2011), patata (Ozuna et al., 2011) o manzana (Rodríguez et al., 2014). En todos los casos, se ha alcanzado una reducción significativa del tiempo de secado que oscila entre el 30 y el 75 %. Recientemente, este sistema se ha modificado para poder utilizarse en el secado a baja temperatura de alimentos, concretamente en liofilización a presión atmosférica (Garcia-Perez et al., 2012), obteniendo resultados muy prometedores con reducciones del tiempo de secado de hasta un 70%.

A partir del estudio de la bibliografía, se puede observar que la eficacia de la aplicación de ultrasonidos para intensificar procesos de secado depende en gran medida de las variables del proceso, tales como la temperatura y la velocidad del aire de secado o la potencia acústica aplicada. Así, diferentes autores han observado que la influencia de los ultrasonidos de potencia es más importante a temperaturas de secado moderadas (<40ºC) que a temperaturas más elevadas (>60ºC) (Garcia-Perez et al., 2006a; Rodríguez et al., 2014; Sabarez et al., 2012). Esto se puede atribuir a que, a altas temperaturas, la gran disponibilidad de energía térmica en el sistema enmascara los efectos producidos por los ultrasonidos. Éstos sí se observan a menores temperaturas ya que, en esas condiciones, la energía térmica disponible es menor. Este hecho vuelve a poner de manifiesto el gran potencial que presentan los ultrasonidos de potencia para acelerar largos procesos de secado a baja temperatura.

En cuanto a la velocidad del aire de secado, se ha demostrado que la eficacia de los ultrasonidos es mayor cuando se utilizan bajas velocidades (≤4 m/s) (Cárcel et al., 2007c; Garcia-Perez et al., 2006b). El aumento del flujo puede crear turbulencias que distorsionan el campo acústico disminuyendo su intensidad. Esto reduce la energía acústica que llega a la muestra y que, por lo tanto, está disponible para intensificar el secado.

La potencia acústica aplicada también afecta al grado de intensificación conseguido. Así, se ha observado que una mayor potencia aplicada provoca una mayor reducción del tiempo de secado (Garcia-Perez et al., 2011; Sabarez et al., 2012). Algunos autores han encontrado un aumento proporcional entre la potencia acústica y la difusividad efectiva durante el secado, siendo necesario en algunos

productos superar un umbral de potencia para producir efectos significativos (Garcia-Perez et al., 2009).

1.5 Modelización del proceso de secado

La modelización matemática de procesos constituye una herramienta básica para los nuevos sistemas de producción ya que permite estimar, controlar, predecir y optimizar el comportamiento del proceso bajo diferentes condiciones de operación (Bon et al., 2007). Así, para optimizar el funcionamiento de un proceso agroalimentario se requiere del desarrollo de modelos matemáticos que simulen dicho funcionamiento y que permitan formular y establecer las mejores condiciones de operación (Váquiro, 2009). El desarrollo de modelos presenta una complejidad adicional cuando se trabaja con productos biológicos debido a su carácter heterogéneo, complejo y delicado (Chou y Chua, 2001). Por lo tanto, la modelización constituye una herramienta necesaria para analizar el proceso de secado y la influencia de las condiciones de operación sobre el mismo (Mulet et al., 2010). Para ello, se pueden utilizar dos tipos de modelos, los teóricos o los empíricos. Aunque ambos se formulan teniendo en cuenta una serie de simplificaciones de la realidad, presentan importantes diferencias. Así, los primeros proporcionan información útil sobre los mecanismos que intervienen en el proceso. Estos modelos son desarrollados a partir de principios físicos, basándose en diferentes hipótesis y consideraciones, y son capaces de describir cuantitativamente un proceso particular. La opción más empleada para la modelización de los procesos de secado es la teoría difusional.

Los modelos empíricos son modelos obtenidos a través del análisis matemático o estadístico de datos experimentales y su único objetivo es describir el proceso de manera precisa. Entre otros, destacan los modelos de Newton, Weibull, Page, Henderson y Pabis y Wang y Singh (Rodríguez et al., 2013). A diferencia de los modelos teóricos, éstos carecen de significado físico al no proporcionar ninguna información sobre los mecanismos que intervienen en el proceso (Datta, 2007a,b).

El secado es un proceso complejo en el que se produce una transferencia simultánea de materia y de energía, acompañada de cambios físicos y estructurales en el producto. Por ello, en la modelización de un proceso de secado

se puede diferenciar varias etapas. En primer lugar, se debe realizar la identificación de los fenómenos de transporte controlantes y/o de la resistencia a la transferencia que controla el proceso. Así, se debe definir si la velocidad del proceso está controlada por la transferencia de calor, por la de materia, o por ambas (Garcia-Perez, 2007). Cuando ambos fenómenos sean significativos, el modelo deberá incluir ecuaciones que consideren la transferencia simultánea. Si se considera la transferencia de materia como factor limitante del proceso de secado, será necesario identificar si es el transporte interno o externo el responsable de controlar la velocidad de secado. Seguidamente, se procede a la selección del mecanismo de transferencia de materia que explique el transporte. Como se ha comentado, en operaciones de secado, es la difusión el mecanismo más comúnmente utilizado. Éste considera que la transferencia de materia dentro del alimento se produce únicamente por los gradientes de humedad (Ortuño et al., 2010), es decir por la diferencia de humedad entre la parte interna y externa del sólido. Una vez identificado el mecanismo controlante, se plantea el modelo matemático y se obtiene la ecuación de gobierno del proceso. Para poder abordar su resolución, es necesario considerar ciertas hipótesis simplificadoras y definir una serie de condiciones iniciales y de contorno. Entre algunas de las suposiciones que se pueden adoptar, destacan las siguientes:

- La isotropía y homogeneidad del sólido.
- La simetría del sólido.
- El contenido de humedad inicial y la temperatura del sólido son homogéneos en toda la muestra.
- El tamaño y forma de la muestra permanece constante durante el proceso de secado.

Una vez formulado el problema, se procede a la resolución del modelo matemático. En determinados casos, las ecuaciones planteadas posibilitan que la resolución se pueda realizar de manera analítica. En otros, es necesario recurrir a resoluciones de tipo numérico. Entre los métodos numéricos de resolución destacan el de diferencias finitas (Garau et al., 2006; Mulet et al., 2005) y el de elementos finitos (Váquiro et al., 2009).

En función del objetivo de la modelización, se pueden plantear modelos con diferentes grados de complejidad en su resolución (Simal et al., 2005). Tras la obtención de la solución del modelo, es conveniente realizar la validación del mismo con el objetivo de demostrar su fiabilidad (Castell-Palou et al., 2011). Una manera de validar el modelo consiste en la extrapolación de los resultados obtenidos a los obtenidos en otras condiciones experimentales y comprobar que la capacidad de ajuste en las nuevas condiciones es correcta (Bon et al., 1997).

1.5.1. Modelos utilizados en el secado a baja temperatura

Los modelos difusionales son relativamente fáciles de formular y suelen proporcionar resultados razonables. Su principal inconveniente se encuentra en que las suposiciones consideradas para su resolución se acerquen más o menos a la realidad, lo que puede suponer implementar mayor o menor complejidad al modelo. Una de estas hipótesis simplificadoras que se puede asumir es la relacionada con la resistencia externa a la transferencia de materia. Así, se pueden plantear modelos puramente difusivos que no consideran la resistencia externa a la transferencia de materia. Éstos asumen que el proceso de secado depende únicamente del transporte interno de agua a través del sólido, manteniéndose la superficie del producto en equilibrio con el aire de secado desde el inicio del proceso. La resolución de este modelo permite obtener los valores de la difusividad efectiva (D_e), un parámetro que, en este caso, incluye todos los factores que influyen en la cinética del proceso (Garcia-Perez, 2007) y que resulta esencial para abordar la optimización del mismo (Hassini et al., 2007). Estos modelos son adecuados cuando las condiciones de flujo de aire de secado son suficientemente elevadas como para admitir que el proceso está principalmente controlado por la resistencia interna.

Por otro lado, se pueden desarrollar modelos difusivos que consideran a ambas resistencias, externa e interna, como factores limitantes de la transferencia de materia durante el proceso de deshidratación. Su resolución proporciona los valores de las dos variables cinéticas que intervienen en el proceso, la difusividad efectiva (D_e) y el coeficiente de transferencia de materia (k). Constituyen una aproximación más cercana a la realidad que los modelos puramente difusionales,

especialmente cuando la cinética de secado es dependiente de la velocidad del aire (velocidades de aire bajas).

Ambos tipos de modelo, el puramente difusivo y el difusivo considerando la resistencia externa, han sido utilizados para describir cinéticas de secado a baja temperatura (-14ºC) de diferentes productos como manzana, berenjena y zanahoria (Garcia-Perez et al., 2012). En experiencias de secado de manzana a temperaturas entre -16 y 22ºC, Li et al. (2008) además del modelo difusivo con resistencia externa, también consideraron el encogimiento de las muestras.

En el caso de las operaciones de secado que tienen lugar a temperaturas por debajo del punto de congelación (liofilización a presión atmosférica) el modelo difusivo se convierte en un modelo empírico. En estas condiciones, durante el secado, se pueden distinguir dos zonas diferenciadas en el producto, una capa externa deshidratada y una interna totalmente congelada. Por lo tanto, una de las principales suposiciones del modelo difusivo, que es la isotropía del material, no se cumple. Para este caso, se pueden encontrar en la bibliografía otros modelos que describen de manera más precisa lo que ocurre en el interior del alimento cuando se deshidrata. Así, Claussen et al. (2007b) utilizaron un modelo basado en la ecuación de Lewis cuya precisión depende en gran medida de una correcta estimación de las propiedades térmicas del producto seco. Rahman (2009) también desarrolló un modelo basado en las propiedades térmicas del producto y usó la analogía entre los números de Nusselt y Sherwood para predecir la velocidad de secado. Una aproximación similar fue considerada por Li et al. (2007), que desarrollaron un modelo en CFD para cinéticas de liofilización atmosférica de manzana.

El modelo más utilizado para describir el proceso de liofilización a presión atmosférica es el denominado modelo URIF (Uniformly Retreating Ice Front) (Claussen et al., 2007a), publicado por primera vez por Wolff y Gibert (1990a, 1990b). Estos autores obtuvieron una solución al modelo combinando la teoría URIF y las leyes de la transferencia de materia y energía. Dicho modelo considera que durante el secado el producto presenta 2 capas: una capa externa seca y una interna congelada. Así, en la muestra congelada el frente de sublimación avanza de forma uniforme desde la superficie hacia el centro de la misma a medida que

transcurre el secado. Por el contrario, el vapor de agua difunde hacia la superficie a través de la capa seca que se va generando. Por tanto, el proceso de secado está controlado por la difusión interna. En un estudio publicado recientemente, Warning et al. (2015) introducen algunas variaciones a este modelo al considerar que el producto no está formado sólo por dos capas sino por tres: la interna congelada, la externa seca y una intermedia parcialmente congelada. Además, estos autores consideran que el frente de sublimación no retrocede uniformemente y que el frente de congelación no es totalmente paralelo a la superficie.

1.6 Parámetros de calidad

La calidad es un concepto abstracto, difícil de definir, donde la aceptabilidad por parte del consumidor es el principal elemento para su evaluación. Hoy en día, los consumidores demandan alimentos que mantengan las características naturales del alimento fresco. Así, algunos de los atributos fundamentales de la calidad de un alimento son la textura, el aroma, el sabor, el valor nutritivo y el aspecto, que engloba tamaño, color y forma (Jarén, 2005). En este contexto, la obtención de nuevos productos deshidratados de calidad y atractivos para el consumidor es necesaria para diversificar mercados (Askari et al., 2009). Por otra parte, existe la necesidad de obtener un equilibrio entre el coste operativo y la calidad del producto deshidratado, ya que ésta es normalmente menor que la del producto fresco (Ratti, 2001). Por tanto, es necesario investigar cómo las condiciones de secado afectan a diversos parámetros de calidad con el fin de optimizarlos y obtener productos de calidad a un precio lo más bajo posible.

La mayoría de los productos deshidratados se rehidratan antes de ser consumidos. La rehidratación es un proceso complejo que contribuye a restaurar parcialmente las propiedades del alimento fresco anteriormente deshidratado (Hogekamp y Schubert, 2003). Los alimentos deshidratados en condiciones óptimas son los que se deterioran menos, rehidratan de forma rápida y son capaces de alcanzar el contenido inicial de humedad (Weerts et al., 2006). Dado que el secado provoca daños celulares debido al estrés al que son sometidas las células por la eliminación del agua de su interior (Schössler et al., 2012c), se puede considerar a la capacidad de rehidratación como una medida del daño que

sufre el alimento durante la deshidratación. La velocidad de rehidratación también puede constituir una medida de calidad del producto final obtenido. La rehidratación se realiza llevando a cabo una inmersión del producto en agua, aunque también se han utilizado otros medios como soluciones azucaradas (glucosa, sacarosa, trehalosa), leche, zumos de frutas y verduras, extractos, o incluso aceite, etc. (Rastogi et al., 2004). De hecho, la inmersión en aceite puede proporcionar información sobre variaciones estructurales del alimento. Entre otros, permite evaluar la creación de microcanales como consecuencia del proceso de secado y detectar diferencias en la velocidad de reconstitución debido a la viscosidad. Además, en productos con fibra, permite evaluar la influencia del secado en la capacidad de absorción de aceite, parámetro importante para productos que van a ser cocinados, ya que está directamente relacionado con la cantidad de aceite necesario para un proceso de fritura.

La evaluación textural es otro aspecto muy importante en las etapas de control de calidad durante el desarrollo de nuevos productos. El ablandamiento y la pérdida de la textura original es uno de los principales problemas que aparecen en los productos rehidratados, y tienen una gran importancia en la aceptabilidad final del producto (Duan et al., 2013; Ozuna et al., 2014b). Para evaluar las propiedades texturales de los productos rehidratados se puede recurrir a determinaciones instrumentales como el análisis del perfil de textura que proporciona medidas objetivas del daño sufrido por los tejidos durante la operación de secado.

El color es otro de los parámetros importantes que influyen en la aceptabilidad del producto por parte del consumidor. El producto deshidratado debe mantener el color del producto fresco en la medida de lo posible, y por lo tanto, se debe evitar la aparición de pardeamientos, tanto de carácter enzimático como no enzimático (Sagar y Kumar, 2010). En el primer caso, las enzimas presentes de manera natural en los productos se inactivan mediante calor o mediante la inmersión del producto en soluciones de ácido cítrico, fosfórico o ascórbico. En cuanto a las reacciones de pardeamiento no enzimático, hay que señalar que las altas temperaturas favorecen las reacciones de Maillard originando productos más oscuros. En este caso, el secado a baja temperatura puede ser una alternativa de secado interesante para mejorar el color del producto obtenido. Una manera objetiva de evaluar el color de un producto es a partir la determinación de las

coordenadas del espacio de color CIE L*a*b* (Bai et al., 2013) mediante colorímetros.

En cuanto a la determinación de la calidad nutricional, uno de los parámetros utilizados, especialmente en frutas como la manzana, está relacionada con el potencial antioxidante. Éste depende en gran medida de su contenido de compuestos fenólicos, ya que los polifenoles presentan una elevada capacidad antioxidante. Sin embargo, se ha observado que el secado de los alimentos causa una reducción significativa de los mismos (Tiwari y Cummins, 2013) y dicha reducción depende de la variables de proceso (Stawczyk et al., 2007; Vega-Gálvez et al., 2012). Por tanto, resulta de especial interés la determinación de las mejores condiciones de secado que permitan optimizar el potencial antioxidante de los productos obtenidos.

1.7 Conclusiones

A partir de la revisión bibliográfica mostrada, se ha identificado el gran potencial que tienen los ultrasonidos de potencia para intensificar los procesos de transferencia de materia, como es el caso del secado de productos agroalimentarios. Sin embargo, su aplicación en el secado a baja temperatura todavía no ha sido estudiada en profundidad. Por lo tanto, sería de gran interés determinar los efectos de los ultrasonidos, no sólo en la cinética del proceso de secado a baja temperatura, sino también establecer su influencia en distintos parámetros de calidad del producto deshidratado.

2. Objetivos

El objetivo general de la presente tesis doctoral es determinar la influencia de la aplicación de ultrasonidos de potencia en procesos de secado a baja temperatura, tanto en la cinética del proceso como en la calidad de los productos deshidratados. Para alcanzar este objetivo se plantearon los siguientes objetivos específicos:

- Determinar el efecto de las principales variables de proceso (temperatura, velocidad de aire y potencia acústica aplicada) en las cinéticas de secado a baja temperatura de diferentes alimentos (manzana, berenjena y bacalao).
- Determinar la influencia del secado a baja temperatura en parámetros de calidad (capacidad de rehidratación, textura, color, microestructura, capacidad antioxidante) de muestras de manzana, berenjena y bacalao deshidratadas en diferentes condiciones de proceso (temperatura, velocidad de aire y potencia acústica aplicada).
- Cuantificar la influencia de la aplicación de ultrasonidos en las cinéticas de secado a baja temperatura de diferentes productos.
- Modelizar las cinéticas de secado a baja temperatura utilizando modelos difusivos, teniendo en cuenta diferentes hipótesis como la inclusión o no de la resistencia externa.
- Determinar la mejora en la modelización de las cinéticas de liofilización a presión atmosférica que supone la utilización de un modelo difusivo que considere el avance del frente de sublimación y validar dicho modelo.
- Evaluar una posible aplicación del secado a baja temperatura asistido con ultrasonidos como es el desarrollo de matrices alimentarias porosas en las que posteriormente se incorporen extractos con actividad antioxidante.

3. Plan de trabajo

El plan de trabajo de la presente tesis doctoral (Figura 3.1) se elaboró en base a los objetivos planteados en el apartado anterior. Así, la programación experimental se organizó en 3 principales apartados que dieron lugar a los 3 capítulos en los que se divide la sección de resultados.

El primer apartado (**Capítulo 1**) comprende el estudio de la influencia de las variables de proceso en el secado a baja temperatura asistido con ultrasonidos de potencia (US) de diferentes alimentos, estudiando su efecto tanto en la cinética de secado como en la calidad del producto obtenido. En primer lugar, se estudió el efecto de la temperatura en el secado de una matriz vegetal, como es el caso de la manzana. Para ello, se deshidrataron muestras cúbicas (8.8 mm de lado) de manzana (*Malus domestica* cv. Granny Smith) a 5 temperaturas distintas (10, 5, 0, -5 y -10ºC), con (50 W, 21.9 kHz) y sin aplicación de US. Todas las experiencias de secado se realizaron con una velocidad de aire constante (2 m/s) y una humedad relativa inferior al 10%. Se utilizó un modelo difusivo para describir las cinéticas de secado y cuantificar la influencia de la temperatura y de la aplicación de US en parámetros como la difusividad efectiva de agua y el coeficiente de transferencia de materia. Con el objetivo de evaluar el efecto de las condiciones de secado en la calidad del producto deshidratado, se realizaron medidas del contenido en polifenoles y flavonoides y de la capacidad antioxidante de la manzana deshidratada.

En segundo lugar, también se analizó en el capítulo 1 el efecto de la temperatura, en el secado de una matriz proteica (bacalao) y en la calidad del producto obtenido. Así, se realizaron experiencias de secado de láminas (50x30x5 mm) de bacalao desalado (*Gadus morhua*) a una velocidad de aire constante (2 m/s), diferentes temperaturas (10, 0 y -10ºC), con (50 W, 21.9 kHz) y sin aplicación de US. Tras el secado, las láminas de bacalao deshidratado fueron rehidratadas en agua destilada a 25ºC. Para describir las cinéticas de secado y rehidratación se utilizaron modelos difusivos. Finalmente, se realizaron medidas de color y textura (dureza) tanto de las muestras secas como de las rehidratadas.

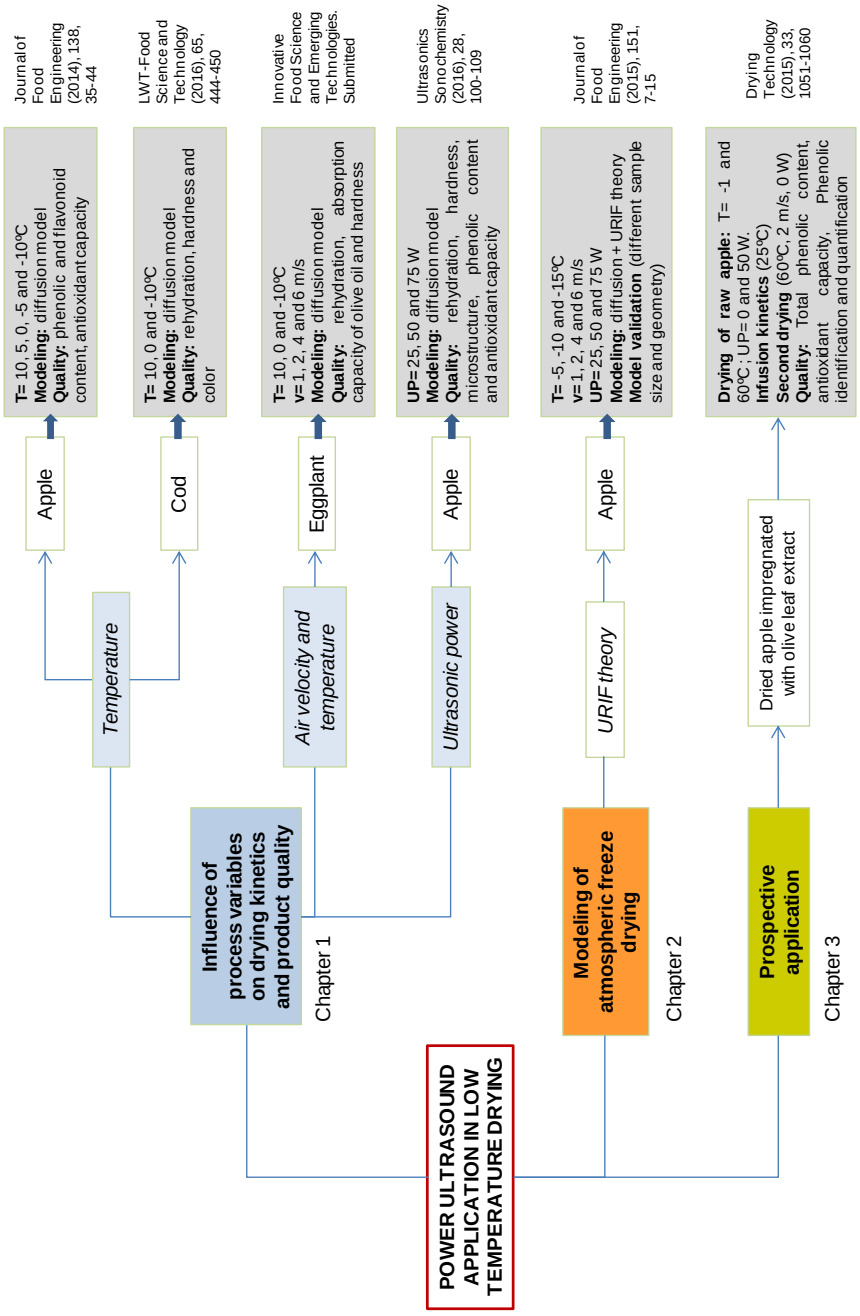

Figura 3.1. Plan de trabajo (Working plan). T=temperature; v= air velocity; UP= ultrasonic power

En tercer lugar, se evaluó en el capítulo 1 el efecto combinado de la temperatura y velocidad del aire en otro producto vegetal con una estructura diferente a la de la manzana, como es el caso de la berenjena. Para ello, se determinó la cinética de secado de cubos (8.6 mm de lado) de berenjena (*Solanum melongena* var. Black Enorma) a diferentes velocidades de aire (1, 2, 4 y 6 m/s) y temperaturas (-10, 0 y 10ºC), con (50 W, 21.9 kHz) y sin aplicación de US. Las cinéticas de secado y de rehidratación obtenidas experimentalmente fueron nuevamente modelizadas utilizando modelos difusivos. En cuanto a la calidad del producto obtenido, en este caso se analizó la capacidad de rehidratación, la capacidad de absorción de aceite de oliva y la dureza de las muestras rehidratadas.

La última variable de proceso evaluada en el capítulo 1 fue la potencia acústica aplicada durante el secado a baja temperatura. En este caso, se realizaron experiencias de secado de muestras cúbicas de manzana (8.8 mm de lado) a velocidad de aire constante de 2 m/s, a dos temperaturas diferentes (10 y -10ºC), con (25, 50 y 75 W) y sin aplicación de US. Con el fin de cuantificar las diferencias entre las distintas condiciones experimentales ensayadas, se recurrió a la modelización de las cinéticas de secado mediante modelos difusivos. La evaluación del impacto de la potencia acústica utilizada en la calidad de la manzana deshidratada se realizó mediante la determinación de la capacidad de rehidratación, la dureza, el contenido fenólico, la capacidad antioxidante y el análisis de la microestructura.

En el siguiente apartado (**Capítulo 2**) se abordó más en profundidad la modelización de las cinéticas de secado en condiciones de liofilización a presión atmosférica, que corresponden con temperaturas de secado por debajo del punto de congelación del producto. En estas condiciones, el modelo difusivo utilizado en el capítulo 1, se convierte en un modelo empírico al perderse la homogeneidad de las partículas. Por ello, se decidió evaluar un modelo difusivo de tipo URIF (Uniformly Retreating Ice Front) que considera el avance del frente de sublimación durante el secado. Este modelo se ajustó a las cinéticas de secado de cubos de manzana realizadas a diferentes velocidades de aire (1, 2, 4 y 6 m/s), temperaturas (-5, -10 y -15ºC), con (25, 50 y 75 W) y sin aplicación de US, para estimar los valores de difusividad efectiva y cuantificar la influencia de las distintas variable de proceso en vistas a una posible optimización del mismo. Además, se

realizaron nuevas experiencias de secado con muestras de manzana de diferente tamaño (cubos de 17.5 mm de lado) y geometría (cilindros) para validar dicho modelo.

Finalmente, en el último apartado de la tesis (**Capítulo 3**), y como prospección de la aplicación potencial del secado a baja temperatura asistido con US, se evaluó la viabilidad de su utilización en el desarrollo de un alimento funcional. En este sentido, el desarrollo de matrices alimentarias porosas en las que posteriormente se incorporen extractos con actividad antioxidante puede ser una vía interesante para obtener productos de una elevada calidad nutricional. Por este motivo, muestras de manzana deshidratada en diferentes condiciones experimentales, a 60 y -1ºC de temperatura, con (50 W) y sin aplicación de US, fueron impregnadas con extracto de hoja de olivo. Posteriormente, estas muestras fueron deshidratadas (60ºC, 0 W) de nuevo para obtener un producto estable. Se determinó el contenido fenólico y la capacidad antioxidante del producto deshidratado para evaluar el efecto del secado de la manzana fresca en ambos parámetros. Por medio de cromatografía líquida de alta eficacia (HPLC) se identificaron y cuantificaron los principales polifenoles presentes en el producto final, mayoritariamente añadidos con la impregnación, y evaluar así la influencia del procesado en la calidad final del producto obtenido.

En los diferentes capítulos del apartado de resultados se describe con más detalle la metodología empleada, la materia prima, los equipos y los modelos matemáticos utilizados en cada uno de los trabajos realizados.

4. Resultados

Chapter 1

Influence of process variables on drying kinetics and product quality

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ULTRASONICALLY ENHANCED LOW-TEMPERATURE DRYING OF APPLE: INFLUENCE ON DRYING KINETICS AND ANTIOXIDANT POTENTIAL

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ULTRASONICALLY ENHANCED LOW-TEMPERATURE DRYING OF APPLE: INFLUENCE ON DRYING KINETICS AND ANTIOXIDANT POTENTIAL

Abstract

Low-temperature air drying represents an alternative means to hot air drying of better retaining the sensory, nutritional and functional properties of foods. However, reducing the air temperature to figures below the product's freezing point involves low drying rates, which largely places constraints on any further industrial application. The main aim of this work was to evaluate the feasibility of using power ultrasound to improve the low-temperature drying of apple, considering not only the kinetic effects but also the influence on the antioxidant potential of the dried apple.

For that purpose, apple (*Malus domestica* cv. Granny Smith) cubes (8.8 mm side) were dried (2 m/s and a relative humidity of under 10%) at low temperatures (10, 5, 0, -5 and -10ºC) with (20.5 kW/m^3) and without ultrasound application. The drying kinetics were modeled by considering the diffusion theory, negligible shrinkage and cubic geometry. In the dried apple, total phenolic and flavonoid contents and antioxidant capacity were measured.

The application of power ultrasound sped up the drying kinetics at every temperature tested, achieving drying time reductions of up to 77%, which was linked to the improvement in diffusion and convective mass transport. In overall terms, ultrasound application involved a greater degradation of polyphenol and flavonoid contents and a reduction of the antioxidant capacity, which was related to the cell disruption caused by the mechanical stress of acoustic waves.

Keywords: Dehydration; Ultrasound; Modeling; Antioxidant capacity

1. Introduction

Food drying is an ancient and widely used preservation method that allows for greater flexibility in the availability of food products, regardless of the season. Nowadays, dried products occupy an important place within the food industry (Vega-Gálvez et al., 2012). Drying involves the reduction of moisture in the product and so, the slowing down of its microbial and chemical deterioration. Moreover, a reduction in the product volume and weight makes the transport and storage easier (Doymaz and Pala, 2003). Nowadays, there is an increasing demand for high-quality dried products whose nutritional and sensory properties have only been minimally altered if compared to the fresh product (Mayor and Sereno, 2004). However, drying provokes a series of changes in materials, such as oxidation, color change, shrinkage or loss of texture and nutritional-functional properties (Vega-Gálvez et al., 2009). These changes are greatly dependent on the drying technique applied or the temperature used (Heras-Ramírez et al., 2012; Vega-Gálvez et al., 2012). In fact, severe drying conditions, like high temperatures, could imply the greatest degradation.

Low-temperature drying may be defined as the water removal process carried out at temperatures below standard room conditions, e.g. below 20ºC. This technique includes a wide range of processing conditions and temperatures both below and above the product's freezing point. The main exponent of low-temperature drying is vacuum freeze drying or lyophilization, in which the total or partial reduction of vapor pressure leads to an increase in the water removal rate and keeps the temperature of the wet product low (Ratti, 2001). Drying below freezing point can also be performed at atmospheric pressure, which consists of blowing low temperature air through the product. In this way, high quality products can also be obtained and continuous processing is feasible (Stawczyk et al., 2007), thus reducing the processing cost compared to vacuum freeze drying. However, working at atmospheric pressure and low temperatures leads to very low drying rates (Garcia-Perez et al., 2012a). Therefore, there is a particular interest in intensifying this low-temperature drying process, thereby making its application in the food industry feasible.

Power ultrasound (PU) has been applied to the hot air drying of different products, such as several fruits and vegetables, leading to shorter drying times (Gallego-Juárez et al., 2007; Garcia-Perez et al., 2007). The mechanical energy introduced by PU into the drying medium could help to reduce both the external and the internal mass transfer resistance without introducing a high amount of thermal energy during drying (Riera et al., 2011). Therefore, the use of PU to dry heat-sensitive materials or in low-temperature drying processes has great potential (Awad et al., 2012) that needs to be investigated. In this sense, ultrasound has been applied during the drying of apple, carrot and eggplant at -14ºC (Garcia-Perez et al., 2012a) and the drying time was shortened by between 65 and 70%. Therefore, to confirm the potential of applying PU during low-temperature drying, it should be investigated over a wide range of temperatures both above and below the sample freezing point and it should not only be the kinetics that are taken into consideration, but also issues of quality.

Dried apples can either be consumed fresh or used as a raw material in the processing of prepared foods, such as snacks, breakfast cereals and other functional foods (Akpinar et al., 2003). Furthermore, apple constitutes one of the main sources of polyphenols and flavonoids in the western diet (Boyer and Liu, 2004) and the antioxidant activity of apple is among the highest in commonly consumed fruits and vegetables (Lee et al., 2003; Van der Sluis et al., 2002; Vrhovsek et al., 2004). However, it has been observed that processing brings about a large reduction in both the total phenolic content and the antioxidant activity (Tiwari and Cummins, 2013; Van der Sluis et al., 1997 and 2002). Thus, it is important to define the drying conditions under which the characteristics of fresh apples can be better preserved. Nowadays, there are very few studies into the effect of low-temperature drying on the antioxidant activity of dried products, and no references have been found about how ultrasound can influence it. In this sense, apple is an all-year-round product with a homogeneous solid matrix and for these reasons it has been used in several studies into the influence of different drying process variables (Kaleta and Górnicki, 2010; Li et al., 2008; Stawczyk et al., 2007 and Vega-Gálvez et al., 2012). Therefore, the main aim of this work was to evaluate the feasibility of PU application as a means of improving the low-

temperature drying of apple, quantifying its influence on both the drying kinetics and antioxidant potential of the dried product.

2. Materials and methods

2.1. Raw material

Apples (*Malus domestica* cv. Granny Smith) were purchased in a local market (Valencia, Spain). Fruits were selected to obtain a homogeneous batch in terms of ripeness, size and color and held at 5ºC until processing. Cubic samples (8.8 mm side) were obtained from the flesh using a household tool. Samples dried at temperatures of 0ºC or above were immediately processed, while those dried at temperatures below 0ºC were wrapped in plastic film and frozen by placing in a freezing room at -18±1ºC until processing (at least 10 h). The initial moisture content was measured by placing samples in a vacuum oven at 70ºC and 200 mmHg until constant weight was reached, following the standard method 934.06 (AOAC, 1997).

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation (Figure 1), already described in the literature (Garcia-Perez et al, 2012a). The drying air temperature and velocity are controlled using a Proportional-Integral-Derivative (PID) algorithm. Air temperature control is achieved by coupling a cooling system and an electric resistance. Thus, a chiller (KAE evo-121, MTA, Italy) feeds a copper tube heat exchanger (area 13m^2, fin space 9 mm; Frimetal, Spain) with a glycol-water (45% v/v) solution at -22ºC, where the air flow is cooled down. Finally, acting over the electrical resistance, the air drying temperature is set to the desired value. In order to keep the relative humidity low, the air is forced to flow through a tray containing desiccant material, which is periodically regenerated. The drying chamber consists of a vibrating cylinder attached to a piezoelectric transducer (22 kHz). Thus, the walls of the cylinder radiate the ultrasonic energy into the air medium producing a sound pressure level of 154.3 dB (Riera et al., 2011). The samples are placed in a sample holder to be randomly distributed in the

drying chamber. The dryer is equipped with an industrial scale (VM6002-W22, Mettler-Toledo, USA) to weigh the samples automatically at preset times.

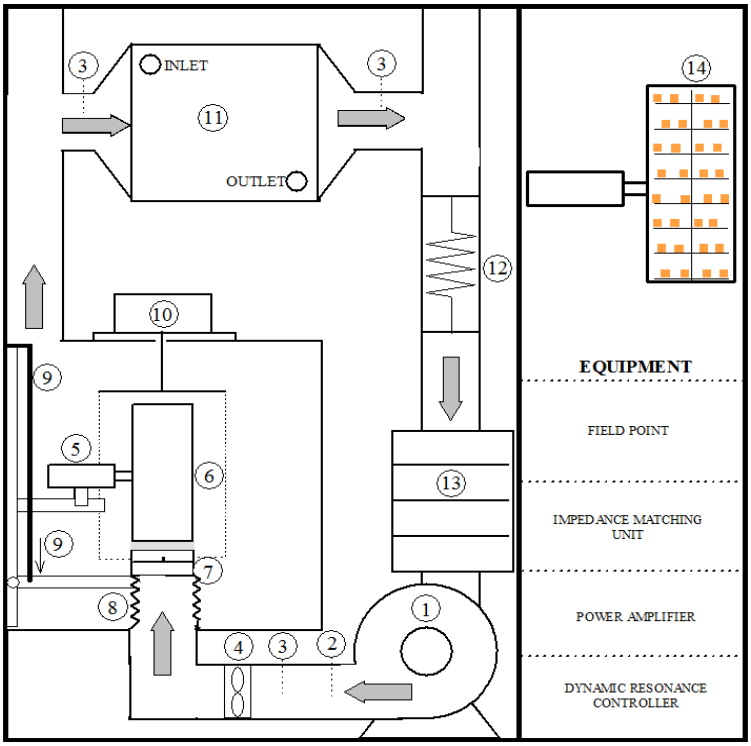

Figure 1. Diagram of the ultrasonically assisted convective dryer (Garcia-Perez et al., 2012a): 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer; 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe; 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13, desiccant tray chamber; 14, details of the sample load on the trays.

The drying tests (2±0.1 m/s air velocity and 7±4% relative humidity) were carried out at different temperatures (-10, -5, 0, 5 and 10ºC) with (AIR+US) and without (AIR) ultrasound application. An acoustic power density of 20.5 kW/m^3 was applied in the AIR+US experiments; this energy density is defined as the electric power supplied to the ultrasonic transducer (50 W) divided into the volume of the drying chamber (cylindrical radiator, 2.43 L). For each run, 40 cubic samples were processed and the initial mass load density was 9.5 kg/m^3. The drying experiments were extended until the samples lost 80% of the initial weight. At least four replicates were carried out for each drying condition tested.

2.3. Modeling of drying kinetics

A diffusion model was used to describe the drying kinetics. The governing diffusion equation was obtained by combining Fick's second law and the microscopic mass balance. For cubic geometry, considering the effective moisture diffusivity to be constant, the temperature uniform and the shrinkage negligible, the diffusion equation (Equation 1) is written as follows:

$$\frac{\partial W_p(x,y,z,t)}{\partial t} = D_e\left(\frac{\partial^2 W_p(x,y,z,t)}{\partial x^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial y^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial z^2}\right) \quad (1)$$

where W_p is the local moisture (kg water/kg dry matter, dm), t is the time (s), D_e is the effective moisture diffusivity (m^2/s) and x, y and z represent the characteristic mass transport directions in cubic geometry (m).

In order to solve Equation 1, the initial moisture was assumed to be uniform and the symmetry was considered in directions x, y, z. Two different approaches to the boundary condition on the interface were taken into consideration. As a first approach, the external resistance was considered negligible. Therefore, the surface moisture content suddenly reached equilibrium with the drying air, as reflected by Equation 2 for the x coordinate, and mass transfer was entirely controlled by internal diffusion (D model). The model's analytical solution, in terms of the average moisture content, is given by Equation 3 (Simal et al., 2005).

$$W_p(L,y,z,t>0) = W_e \quad (2)$$

$$W(t) = W_e + (W_0 - W_e)\left[\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(-\frac{D_e(2n+1)^2\pi^2 t}{4L^2}\right)\right]^3 \quad (3)$$

where W is the average moisture content (kg water/**k**g dm), L the half-length of the cube side (m) and subscripts 0 and e represent the initial and equilibrium states, respectively. Sorption data at 10ºC reported by Veltchev and Menko (2000) were used to estimate the equilibrium moisture content.

In a second approach, the external resistance to mass transfer was also considered. Therefore, the moisture transport was jointly controlled by diffusion and convection (D+C model), this being represented in the model by the boundary

condition shown in Equation 4, again for the x coordinate. The D+C model permits the quantification of both the effective diffusivity and the external mass transfer coefficient (k, kg water/m^2s):

$$t > 0 \qquad x = L \qquad -D_e \rho_{ds} \frac{\partial W_p(L,y,z,t)}{\partial x} = k(a_w(L,y,z,t) - \varphi_{air}) \qquad (4)$$

where ρ_{ds} is the dry solid density (kg dm/m^3) and φ_{air} is the relative humidity of the drying air. As mentioned previously, the water activity on the surface of the material (a_w (L,y,z,t)) was estimated from sorption isotherm data reported in the literature (Veltchev and Menko, 2000).

The D+C model was numerically solved by applying an implicit finite difference method (Garcia-Perez et al., 2012a), for which a computational algorithm in MATLAB 7.9.0 (The MathWorks, Inc., USA) was written. The application provided the local moisture distribution inside the solid and the average moisture content of the solid as a function of the drying time.

2.4. Model fitting

The D model was fitted to the experimental data in order to identify the effective moisture diffusivity (D_e). For that purpose, an optimization problem was defined. The objective function to be minimized was the sum of the squared differences between the experimental (W_{exp}) and calculated (W_{calc}) average moisture contents. The optimization was conducted by applying the generalized reduced gradient method available in the Solver tool (Microsoft Excel 2007).

In the case of the D+C model, kinetic parameters, k and D_e, were jointly identified by minimizing the same objective function as in the D model. In this case, the SIMPLEX method available in fminsearch function (MATLAB) was used for optimization. Both D and D+C models were fitted to each drying run and the kinetic parameters averaged.

Finally, the percentage of explained variance (%VAR, Equation 5) was calculated in order to determine the goodness of the fit to the experimental data.

$$\%VAR = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \quad (5)$$

where S_{xy} and S_y are the standard deviation of the estimation and the sample, respectively.

2.5. Antioxidant potential

The antioxidant potential content was measured by means of the Total Phenolic Content (TPC), the Flavonoid Content (FC) and Antioxidant Capacity (AC).

For that purpose, extracts of dried samples were prepared following the methodology proposed by Eim et al (2013), with some modifications. Samples (1.00±0.02 g) were placed into 20 mL of methanol (MeOH) (Scharlau, Barcelona, Spain) and homogenized at 4ºC using an Ultra-Turrax® (T25 Digital, IKA, Germany), at 13,000 rpm for 1 min. Then the homogenized solution was kept overnight in refrigeration. After that, the mixture was centrifuged at 4,000 rpm for 10 min and filtrated (Ederol filter paper No 202, J.C. Binzer, Hatzfeld, Germany); the extract was subsequently kept at 4ºC until analysis.

Total polyphenol and flavonoid contents were determined by means of the Folin-Ciocalteu and Aluminum chloride assays (Carbone et al., 2011; Leontowicz et al., 2003), respectively. The antioxidant capacity was determined by ABTS, FRAP, CUPRAC and DPPH assays, which provides a good estimation of the AC in different oxidative reactions. Table 1 briefly summarizes the above-mentioned assays, as well as showing recent references in which the different assays are described in detail. The absorbance measurement was taken at 25°C in a microplate spectrophotometer (MultiSkan® Spectrum, Thermo Scientific, USA).

For each drying run, a batch of fresh samples was separately analyzed and used as control to compare with the dried samples. From the standard curves, the absorbance results were expressed as mg of Gallic acid equivalent (GAE)/g dm and mg of Cathechin equivalent (CE)/g dm for the phenolic and flavonoid contents, respectively, while the AC was expressed as mg of Trolox/g dm. Every analysis was carried out in triplicate and the results were reported as mean ± standard deviation.

Table 1. Total phenolic content, flavonoid content and antioxidant capacity assays.

Determination	Assay	Reagents	λ (nm)	Reference
Polyphenol content	Folin Ciocalteu	[a]Folin Ciocalteu [e]Na_2CO_3 7.5%	745	(Carbone et al., 2011)
Flavonoid content	Aluminium chloride	[e]$NaNO_2$ 5% [d]$AlCl_3$*$6H_2O$ 10% [f]NaOH 1M	510	(Leontowicz et al., 2003)
Antioxidant capacity	ABTS	[c]ABTS 7 mM [a]$K_2S_2O_8$ 2.45mM	734	(Floegel et al., 2011)
	FRAP	[b]TPTZ 0.01M [a]$FeCl_3$*$6H_2O$ 0.02M [a]Acetate buffer (pH 3.6)	593	(Gonzalez-Centeno et al., 2012)
	CUPRAC	[a]$CuCl_2$*$2H_2O$ 10 mM [d]Neocuprine 7.5 mM [a]NH_4Ac Buffer 1.0 M	450	(Eim et al., 2013)
	DPPH	[d]DPPH 0.2 mM:	517	(Lo Scalzo et al., 2004)

[a]Purchased from Scharlau (Barcelona, Spain).
[b]Purchased from Acros Organics (New Jersey, USA).
[c]Purchased from Biochemica (Darmstadt, Germany).
[d]Purchased from Sigma-Aldrich (Steinheim, Germany).
[e]Purchased from Panreac (Barcelona, Spain).
[f]Purchased from Riedel-de Haën (Seelze, Germany).

The percentage of degradation for each parameter (%Degradation, Equation 6) was used in order to quantify the influence of both the drying temperature and PU application on each specific parameter:

$$\%\text{Degradation} = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (6)$$

where C_0 and C_f are the initial (fresh product) and the final concentration (mg/g dm) for each parameter.

2.6. Statistical analysis

In order to evaluate if PU application and air temperature had a significant influence on the kinetic parameters (D_e and k), an analysis of variance (ANOVA) was carried out and the least significant difference (LSD) intervals ($p<0.05$) were estimated using Statgraphics Plus software 5.1. (Statistical Graphics Corp., Rockville, USA). Likewise, the influence of the drying conditions on the antioxidant capacity and the polyphenolic and flavonoid contents of the dried samples were also compared by means of an analysis of variance and LSD intervals.

3. Results and discussion

3.1. Drying experiments

The drying kinetics of apple cubes without ultrasound application (AIR experiments) are shown in Figure 2A. It should be noted that when drying temperatures were above the sample's freezing point (0, 5 and 10ºC), the water was removed from the solid matrix by evaporation, while for temperatures below freezing point (-5 and -10ºC), it was removed by sublimation. In this last case, according to the "uniformly retreating ice front" theory (URIF) (Claussen et al., 2007), sublimation happens in the ice front and the water vapor moves through the dry layer to the sample surface. It can be observed that, at temperatures above freezing point (0, 5 and 10ºC), the lower the temperature used, the longer the drying time (Figure 2A), which is the typical behavior found in foodstuffs drying. Likewise, the drying process at -5ºC was faster than at -10ºC. However, when experiments below and above freezing point are compared, it was found that experiments carried out at -5ºC were faster than those carried out at 0 and 5ºC (Figure 2A) and the drying rate of experiments performed at -10ºC was quite similar to at 0ºC. This fact is probably linked to the degradation of the sample's structure produced by the prior freezing of samples dried at -5 and -10ºC, which can make the water removal easier. In this sense, Eshtiaghi et al. (1994) and Dandamrongrak et al. (2003) already reported that prior freezing of the raw material sped-up the drying of green beans, carrots, potatoes and bananas. In addition, the drying rate at 0ºC, and considering the temperature drop ascribed to water evaporation, could be also limited because part of the energy was used for providing the necessary latent heat for water freezing or thawing. A similar effect of the drying temperature was observed in experiments with ultrasound application (AIR+US, Figure 2B).

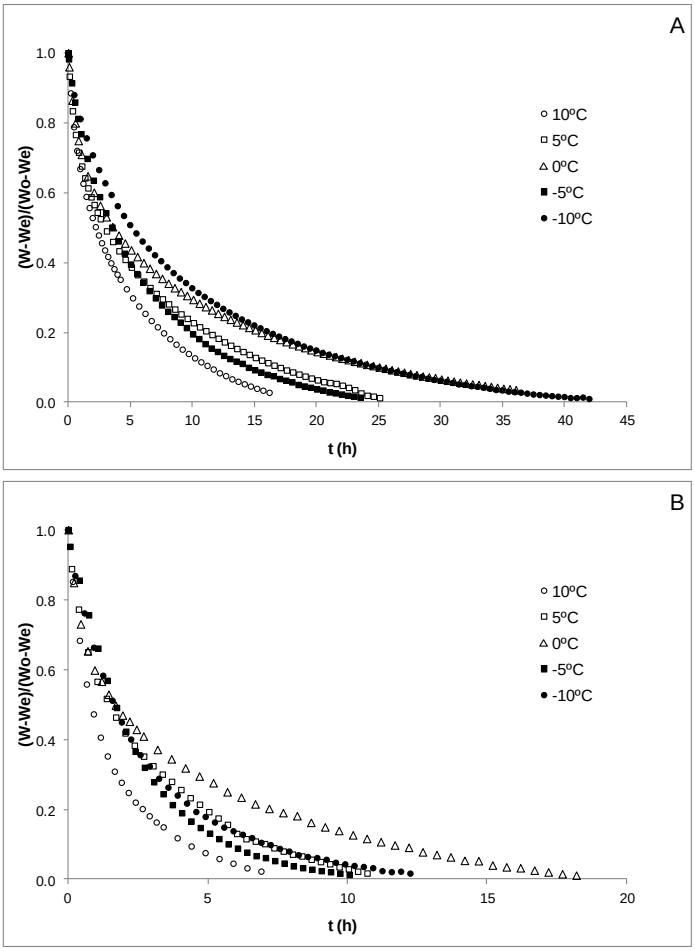

Figure 2. Experimental drying kinetics (10, 5, 0, -5 and -10ºC and 2 m/s) of apple. A: Convectional drying experiments (AIR) and B: Ultrasonically assisted drying experiments (AIR+US; 20.5 kW/m^3).

Applying PU greatly increased the drying rate of apples at all the temperatures tested. The reduction of the drying time brought about by PU application was similar in the experiments carried out at 10, 5, 0 and -5ºC (around 60%). However, an average drying time reduction of 77% was observed in the experiments performed at -10ºC (Figure 3), shortening the drying time from 43.8 (AIR) to 10.3 h (AIR+US). The drying time reduction may be ascribed to the mechanical effects associated with ultrasonic waves that cause a reduction of both the internal and external resistances to mass transfer. On the one hand, PU generates alternating expansions and contractions when travelling in a solid medium, this mechanical

stress helps to make the water movement towards the product surface easier. In addition, ultrasound may also promote water sublimation since, to a certain extent, the attenuation of the acoustic wave may provide the energy needed for the water to change state (Gallego-Juárez, 2010). On the other hand, the application of ultrasound in solid/gas systems also produces a mechanical stirring of the gas medium caused by the generation of oscillating velocities, micro-streaming and pressure variation on the interfaces, which reduces the boundary layer and, as a consequence, improves the movement of water from the solid surface to the air (Gallego-Juárez et al., 1999).

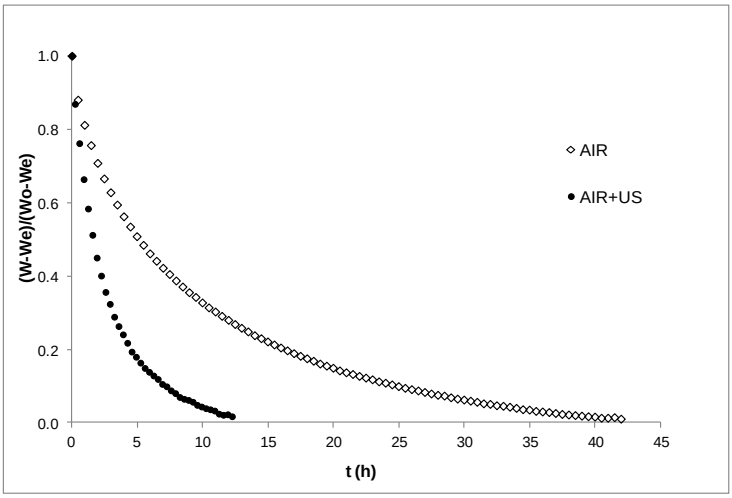

Figure 3. Experimental drying kinetics (-10ºC and 2 m/s) of apple. AIR: Convectional drying experiments and AIR+US: Ultrasonically assisted drying experiments (20.5 kW/m^3).

Schössler et al. (2012) developed a contact ultrasound system for the purpose of improving vacuum freeze-drying. It mainly constituted an ultrasonically activated meshed tray on which the samples were placed and the acoustic energy was directly transmitted from the vibrator to the sample. It is a very different system from the one used in this work, where an air-borne ultrasound application is performed. These authors found that ultrasound treatment led to an 11.5% reduction in the drying time required to reach a final moisture content of 10% (dry basis) when freeze-drying red bell pepper cubes. Bantle and Eikevik (2011) reported a maximum drying time reduction of around 10% when drying green peas at -3ºC using a commercial air-bone ultrasonic radiator (20kHz; DN 20/2000,

Sonotronic). Therefore, previous reported attempts at using ultrasound as a means of intensifying low-temperature drying were less satisfactory than the results obtained in this work.

3.2. Modeling of drying kinetics

Among other purposes, modeling aims to quantify the influence of both air temperature and ultrasound application on the drying kinetics of apple. In a first approach, the drying kinetics were modeled considering a pure diffusion model (D model, Table 2). First of all, it should be highlighted that the effective diffusivities identified for drying experiments carried out below and above the freezing point are not easily comparable. At -5 and -10ºC (atmospheric freeze drying) and assuming the URIF theory (Claussen et al., 2007), vapor diffusion is only restricted to the dry layer. As drying progresses, the ice core shrinks and the dry layer is made thicker. In the diffusion model, the characteristic dimension for diffusion is considered constant, and equal to the half-length (L) of the cubic sample; as a consequence, the effective diffusivities identified at -10 and -5ºC are overestimated due to the fact that the real characteristic dimension is always shorter than L. In the literature (Garcia-Perez et al., 2012a; Li et al., 2008), the general diffusion theory is mostly adopted to mathematically describe atmospheric freeze drying when modeling is not the final goal and the search for accurate diffusion coefficients is not required, such as in this work. Notwithstanding, further research should focus on developing and validating mechanistic models for atmospheric freeze drying. In addition, it should be emphasized that modeling assumed constant cubic shape and volume, which is a more reliable hypothesis in low-temperature than in hot air drying (Mayor and Sereno, 2004; Li et al., 2008).

The effective diffusivities obtained for AIR experiments ranged between $4.3 \cdot 10^{-11}$ m^2/s at -10ºC and $10.9 \cdot 10^{-11}$ m^2/s at 10ºC (Table 2). The identified D_e figures are consistent with previous results obtained in literature. Thus, Li et al. (2008) reported effective diffusivities of $1.0 \cdot 10^{-11}$ and $1.1 \cdot 10^{-11}$ m^2/s for apple drying at -8 and -4ºC, respectively. The influence of temperature on D_e can also be observed in Table 2. Thus, in the range from 0 to 10ºC, the higher the temperature used, the greater the identified effective diffusivity. Likewise, for drying temperatures below

freezing point, D_e at -5ºC was higher than at -10ºC. However, the values of D_e for the experiments at -5 and -10ºC were similar to those obtained at higher temperatures (5 and 0ºC, respectively) due mainly to the effects of freezing on the product structure.

Table 2. Results of the modeling of the drying kinetics of apple without (AIR) and with (AIR+US) ultrasound application (20.5 kW/m^3) using the diffusion model (D model). Average values and standard deviation are shown for effective moisture diffusivity (D_e). VAR (%) is the percentage of explained variance. ΔD_e shows (in percentage) the increase in effective moisture diffusivity produced by ultrasonic application.

		-10ºC	-5ºC	0ºC	5ºC	10ºC
AIR	D_e (10^{-11} m^2/s)	4.3±0.5 ^{c}	6.8±0.3 ^{b}	4.7±0.5 ^{c}	6.6±0.4 ^{b}	10.9±1.9 ^{a}
	VAR (%)	98.4	97.8	99.8	99.5	98.8
AIR+ US	D_e (10^{-11} m^2/s)	15.6±1.3 ^{y}	16.7±2.9 ^{y}	11.6±2.2 ^{z}	15.9±2.8 ^{y}	25.8±2.7 ^{x}
	VAR (%)	94.4	92.9	99.4	98.6	98.3
	ΔD_e(%)	267	146	148	141	136

Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of AIR and AIR+US experiments, respectively.

The application of PU during apple drying significantly ($p<0.05$) increased the effective moisture diffusivity at all the temperatures tested (Table 2). The increase in D_e produced by PU application was of the same order at the drying temperatures of 10, 5, 0 and -5ºC, around 140%. However, for drying experiments carried out at -10ºC, the increase was found to be much higher (267%). This could be explained by the fact that drying at temperatures below the product's freezing point, where sublimation is the predominant water removal mechanism, converts the material into a highly porous dried matrix, which is more prone to ultrasound application (Garcia-Perez et al., 2009; 2012a; Ozuna et al., 2014). The improvement in D_e found in this work was more marked than others reported in the literature due to the high efficiency of the electric/acoustic energy conversion of the transducer used (Gallego-Juarez, 2010). Thus, Bantle and Eikevik (2011) found an effective diffusivity increase of up to 14.8% in the ultrasonic assisted drying of green peas at -6ºC.

In overall terms, D model fitted the AIR experiments well, with percentages of explained variance of over 97.8%. However, the modeling of the AIR+US

experiments was always less accurate and the explained variance fell to 94.4 and 92.9% in experiments carried out at -10 and -5ºC, respectively. These low values of %VAR indicate that the assumptions considered in the model formulation were not close to real behavior for these specific conditions, diffusion not being the only significant mass transport mechanism. Garcia-Perez et al. (2012a) had already observed this fact for apple, carrot and eggplant drying at -14ºC. These authors stated that, under these conditions, ultrasound application can modify the relative importance of convection in mass transport control. This is the reason why the drying kinetics were also modeled, including the external resistance to mass transfer (D+C model). In every case, the D+C model provided an accurate fitting of the drying kinetics, with explained variances of over 99.8% (Table 3). The different accuracy of D and D+C models is illustrated in Figure 4, where it is observed that the calculated moisture contents with D+C model were much closer to experimental values than those found with the D model. As regards the identified parameters (Table 3), PU application involved a significant ($p<0.05$) increase in the effective moisture diffusivity (D_e) and mass transfer coefficient (k). It was observed that ultrasound application at every temperature led to a greater increase in D_e than in k (Table 3). This fact was particularly noticeable at -5 and -10ºC, which suggests that ultrasound had a greater effect on internal transport than on external. Therefore, ultrasound reduced the role of diffusion in mass transport rate control and lent more significance to convection, which explains the fact that D model provided a poor fit at -5 and -10ºC in AIR+US experiments.

The improvement in D_e and k brought about by PU application in experiments performed at -10ºC (501 and 148%, respectively) was more marked than at -5ºC (263 and 96%); this could in all likelihood be explained by considering the more porous structure of the dried product when drying at -10ºC, because, at this temperature, the water was totally frozen. At -5ºC, however, the water of the apple samples would only be partially frozen since the freezing temperature of apple is around -5±0.3ºC (Cornillon, 2000) taking the ºBrix of fresh apple into account (12.2±0.6ºBrix). Therefore at -5ºC, a combined sublimation/evaporation could be found.

Table 3. Results of the modeling of the drying kinetics of apple without (AIR) and with (AIR+US) ultrasound application (20.5 kW/m^3) using the diffusion and convection model (D+C model). Average values and standard deviation are shown for kinetic parameters: effective moisture diffusivity (D_e) and mass transfer coefficient (k). VAR (%) is the percentage of explained variance. ΔD_e and Δk (in percentage) the increase in a kinetic parameter produced by ultrasonic application.

		-10ºC	-5ºC	0ºC	5ºC	10ºC
AIR	D_e (10^{-11} m^2/s)	3.5±0.4 ^{c}	6.6±1.0 ^{b}	3.3±0.4 ^{c}	4.8±0.4 ^{c}	8.8±2.0 ^{a}
	k (10^{-4} kg water/m^{2}s)	1.6±0.2 ^{D}	2.0±0.1 ^{D}	2.7±0.1 ^{C}	3.2±0.3 ^{B}	4.4±0.5 ^{A}
	VAR (%)	99.9	99.9	99.9	99.9	99.8
AIR+ US	D_e (10^{-11} m^2/s)	20.8±8.8^{xy}	24.0±8.4 ^{x}	8.6±2.1 ^{z}	12.5±2.6 ^{yz}	22.3±1.5 ^{x}
	k (10^{-4} kg water/m^{2}s)	3.9±0.6 ^{Z}	4.0±0.2 ^{Z}	5.4±1.1 ^{Y}	5.6±0.7 ^{Y}	9.1±1.4 ^{X}
	VAR (%)	99.9	99.8	99.9	99.9	99.9
	ΔD_e (%)	501	263	163	161	153
	Δk (%)	148	96	101	77	107

Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of AIR and AIR+US experiments, respectively.
Superscript letters (A, B, C, D) and (X, Y, Z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the k of AIR and AIR+US experiments, respectively.

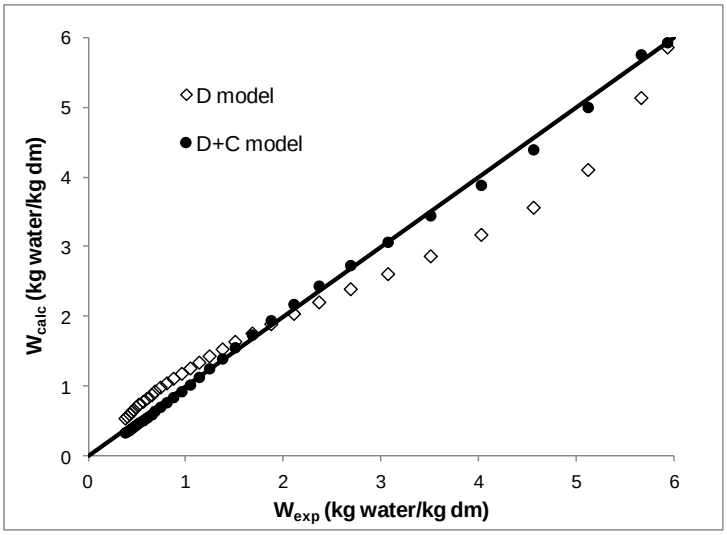

Figure 4. Experimental vs calculated moisture content evolution of apple with D and D+C model of an experimental drying kinetic (-5ºC and 2 m/s) assisted by power ultrasound (20.5 kW/m^3).

3.3. Antioxidant potential

In order to determine the influence of both PU application and the drying temperature on the antioxidant potential of the final dried product, the polyphenol and flavonoid content and the antioxidant capacity of dried samples were determined.

3.3.1. Polyphenol content

The total polyphenol content of fresh apples was 10.2±1.9 mg GAE/g dm. This value is in the range of those found by Vrhovsek et al. (2004) (7.8±0.5 mg GAE/g dm) and Heras-Ramírez et al. (2012) (11.9±1.0 mg GAE/g dm). AIR drying caused a reduction in the total polyphenol content regardless of the temperature used; thus, the degradation percentages ranged from 26.0±1.7% to 35.1±2.0% (Figure 5A). At temperatures above the freezing point, the higher the temperature used, the higher the degradation percentage observed; the lowest degradation was achieved at 0 and 5ºC. However, the degradation percentages found in the experiments carried out at -5 and -10ºC were significantly higher ($p<0.05$). This fact could be ascribed to the cell damage caused by freezing, which, among other things, aids the release of oxidative enzymes during thawing and extraction (Ahmad-Qasem et al., 2013). As for PU application during drying (AIR+US experiments), it brought about an average percentage of degradation of the total polyphenol content which was significantly ($p<0.05$) higher (40.8±3.5%) than those found in AIR experiments (30.5±3.6%) at every temperature tested. This fact could be linked to the structural damage of cells brought about by ultrasound (Garcia-Perez et al., 2012b; Puig et al., 2012). Therefore, the mechanical stress linked to ultrasonic wave propagation could aid the release of oxidative enzymes and intra-cellular compounds into the solvent, contributing to the degradation of polyphenol in a similar way to freezing. It should be noted that the degree of polyphenol degradation found in this work was greater than that reported by Stawczyk et al. (2007), who found an average reduction in the polyphenol content of only 20% in the convective drying of apple cubes (1 cm side) at -8 and -12ºC. The milder polyphenol degradation found by these authors could be explained by the fact that the samples were pre-treated in a 3% citric acid solution before drying. As regards

the effect of PU application during drying on TPC, Soria et al. (2010) did not found significant differences between the TPC of carrot samples freeze dried and those dried at 20ºC with PU application.

3.3.2. Flavonoid content

The total flavonoid content measured in fresh apple was 2.2±0.1 mg CE/g dm, which is in the range of the figures found by other authors, such as Leontowicz et al. (2003) (0.9±0.1 mg CE/g dm) and Heras-Ramírez et al. (2012) (5.3±0.5 mg CE/g dm) working with the Granny Smith variety . The influence of the drying air temperature and PU application on the degradation of the total flavonoid content (Figure 5B) was similar to that observed in the case of polyphenol degradation, since flavonoids are an important part of total polyphenols. Thus, in general terms, the drying process caused a reduction in the total flavonoid content at every drying temperature tested. In AIR experiments, the highest percentage of degradation was found at temperatures of -10ºC (33.9±1.8%) and -5ºC (32.3±1.7%), while the lowest degradation was found at 0ºC (24.2±2.1%) and 5ºC (26.3±2.3%). Heras-Ramírez, et al (2012) reported a flavonoid loss in the order of 50% in apple pomace dried at temperatures of 50, 60, 70, and 80ºC. At the different temperatures tested, these authors did not find any significant differences, but they suggested that blanching in a citric/ascorbic acid solution at 86ºC for 4 min before drying prevented degradation. Thus, considering the results of Heras-Ramírez et al. (2012), the low-temperature drying used in this study allowed for a better preservation of the flavonoid content in apples than hot-air drying. It could also be observed that in AIR+US experiments the degradation of the flavonoid content was significantly ($p<0.05$) greater than in AIR experiments (e.g. 44.7±2.1% and 34.7±1.5% for AIR+US experiments at -10 and 0ºC, respectively). It is worth mentioning that there are no published studies that relate the effect of PU application during low-temperature drying on the polyphenol and flavonoid content of fruits. However, Rodriguez et al. (2014) have studied the effect of ultrasonically assisted apple drying at 30, 50 and 70ºC on phenolic and flavonoid content. These authors observed that, in overall terms, the US application involved a lower TPC and FC in comparison to air dried apple samples.

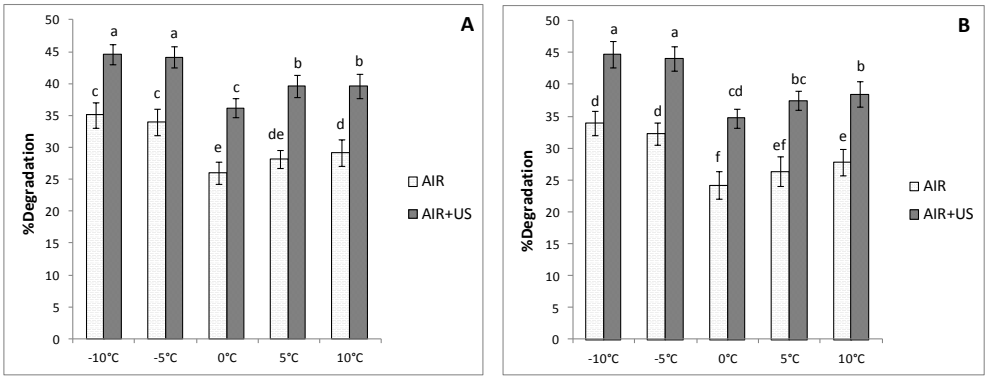

Figure 5. Degradation of total polyphenol (A) and flavonoid (B) content in apples during AIR and AIR+US drying. Different letters show significant differences according to LSD intervals ($p<0.05$).

3.3.3. Antioxidant capacity

In order to achieve a greater and more thorough understanding of the influence of drying temperature and PU application on bioactive compounds, four different assays of the antioxidant capacity were used in the present study: ABTS, CUPRAC, FRAP and DPPH. The antioxidant capacity measured for fresh apple was 12.9±1.8, 18.3±3.3, 8.0±1.7 and 29.2±5.5 mg Trolox/g dm using ABTS, CUPRAC, FRAP and DPPH assays, respectively. In every assay, the measurement is based on a single-electron-transfer, but the antioxidants present in the medium may be hydrophilic or lipophilic in nature and this will aid the reaction to a greater or lesser extent. It should be noted that, due to each assay being based on a different chemical system and/or reaction, the antioxidant activity values clearly varied for each sample extract depending on the method used (Gonzalez-Centeno et al., 2012).

The ABTS assay is based on the ability of antioxidants to quench the long-lived radical cation 2,2-azinobis-(3-ethylbenzothiazoline-6-sulphonate). Thus, ABTS allows the most preferably lipophilic fraction of polyphenols to be determined with AC (Buratti et al., 2001). AIR samples dried at -10 and -5ºC showed higher AC degradation figures ($p<0.05$) than those dried at higher temperatures (0, 5 and 10ºC) (Figure 6A). A higher degree of degradation was obtained in samples dried with PU application, a common fact at every temperature tested. However, these

differences between both drying techniques (AIR, AIR+US) were not significant ($p<0.05$) at drying temperatures below 0ºC.

The FRAP assay is based on the reduction of Fe (III)-Fe (II) in the presence of ferrous ion stabilizing ligand (TPTZ) allowing the AC of water-soluble antioxidants to be determined (Benzie and Strain, 1996). From the AC degradation measured by this method (Figure 6B), two observations could be made: the positive effect of the using low temperatures but the negative effect of freezing. Thus, the highest degree of degradation was found at -10ºC (50.2±2.1%) and the lowest at 0ºC (39.0±2.1%), showing a similar trend to TPC and FC. Significant ($p<0.05$) differences between the FRAP measurements in AIR and AIR+US samples were found only at -5ºC.

The CUPRAC assay is suitable as a means of analyzing biological samples due to the fact that the reaction is carried out at physiological pH (Apak et al., 2007) and it is used for the determination of both hydrophilic and lipophilic antioxidants. This assay (Figure 6C) exhibited the lowest degradation values of the different methods tested for measuring AC. In AIR experiments, a significant ($p<0.05$) influence of the drying temperature was observed and the highest degradation percentage was obtained at -10ºC and the lowest was attained at 0ºC. PU application during drying induced a greater AC degradation than those found in other AC assays. Thus, at every temperature tested, AIR+US samples showed a significantly ($p<0.05$) greater AC degradation than AIR ones. There are no previous data about the effect of PU application on the AC measured by CUPRAC. However, Eim et al., (2013) measured the effect of the drying temperature on the AC of carrots by means of the CUPRAC assay and reported an AC degradation of 70.2% and 45.3% for drying temperatures of 55 and 70ºC, respectively, which are much higher values than the ones found in this work for low-temperature AIR experiments .

The DPPH assay is based on the measurement of the scavenging ability of antioxidants towards the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH). The free radical DPPH is reduced to the corresponding hydrazine when it reacts with hydrogen donors (Sánchez-Moreno, 2002). Comparing all the AC measurements tested, the greatest degradation of the AC was found using the DPPH method (Figure 6D). Once again, it may be observed that the lowest degradation

percentage was found at 0ºC (59.8±2.9%). Stawczyk et al., (2007) reported lower figures of AC degradation for apples dried at -4ºC (19.4%) and -8ºC (20.0%) which had been pre-treated in a 3% acid citric solution. This fact could be explained by the fact that these authors only considered a 50% reduction of DPPH radicals, whilst the assay used in our study considered their total reduction (100%). At every temperature tested, the AIR+US samples presented a greater degradation than the AIR ones, although the differences were only significant ($p<0.05$) at 10ºC. This indicates that PU application has no effect on the AC degradation measured by the DPPH assay, except for experiments carried out at 10ºC.

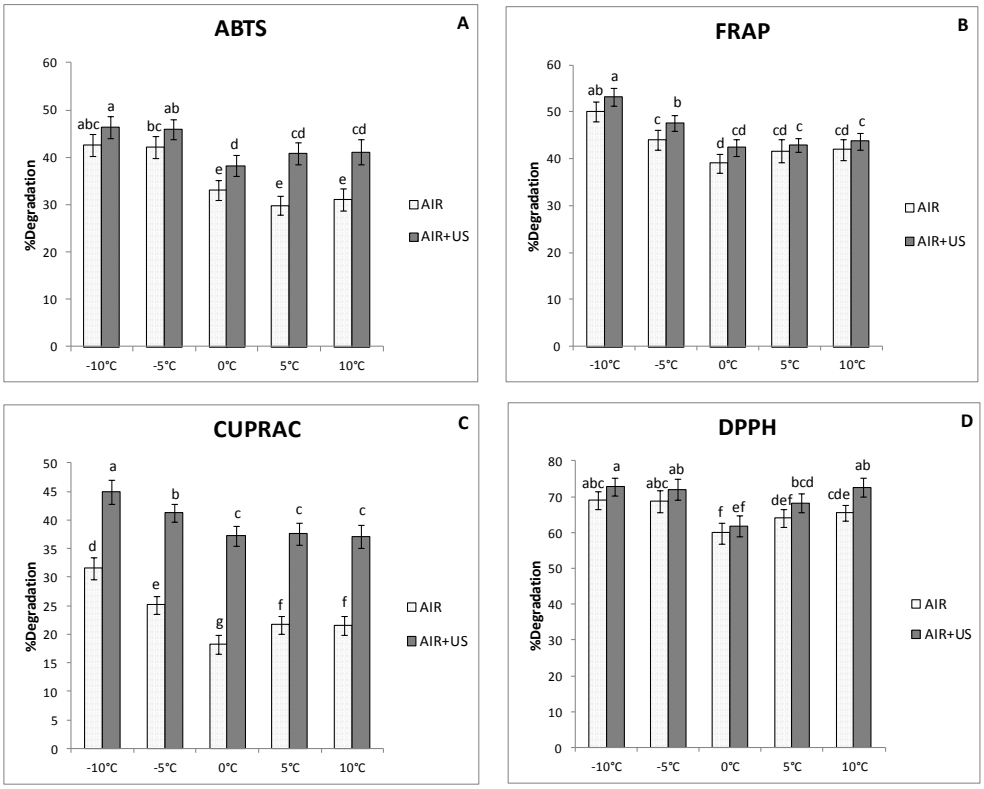

Figure 6. Degradation of the antioxidant capacity of apples during AIR and AIR+US drying. ABTS (A), FRAP(B), CUPRAC (C), DPPH (D). Different letters show significant differences according to LSD intervals ($p<0.05$).

In overall terms, it should be emphasized that under every experimental condition tested, the drying process caused degradation in the AC of the fresh apple, regardless of the method used (Figure 6), but PU application during drying induced

a greater AC degradation. Nevertheless, whether the differences between the AC degradation of the AIR and the AIR+US samples were significant or not depended on both the assay and the drying temperature used.

4. Conclusions

In this work, the feasibility of applying PU to increase the mass transfer rate during low-temperature drying has been demonstrated. Thus, a maximum drying time reduction of 76.5% was achieved by PU application. Water transport followed a clear diffusion pattern for cubic samples, except for experiments with PU application carried out at -5 and -10ºC, because the ultrasonic energy modified the mass transport controlling mechanisms, decreasing the internal mass transfer resistance more than the external. Thus, the effective diffusivity and the mass transfer coefficient were increased by up to 501 and 148%, respectively. As regards antioxidant potential, in overall terms, ultrasound application involved a greater degradation of polyphenol and flavonoid contents and a reduction of antioxidant capacity, which was linked to the cell disruption under acoustic stress. Therefore, PU can be used to speed-up the low-temperature drying processes and further works should focus on determining the energy budget for the scaling-up and elucidating if the time saving is linked to a less energy consumption. However, it should be taken into account that PU may negatively affect the biological components due to the mechanical stress caused by the acoustic waves.

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ULTRASONICALLY ASSISTED LOW-TEMPERATURE DRYING OF DESALTED CODFISH

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ULTRASONICALLY ASSISTED LOW-TEMPERATURE DRYING OF DESALTED CODFISH

Abstract

Low-temperature drying (LTD) constitutes an interesting means of dehydrating foodstuffs, thus preserving the quality of the product. Power ultrasound (US) generates several mechanical effects that could help to shorten the long drying times associated with LTD. In this work, the feasibility of using US in LTD of desalted cod was assessed.

For this purpose, desalted cod slices (50x30x5 mm) were dried (2 m/s) at different temperatures (10, 0 and -10ºC) without (AIR) and with (AIR+US, 20.5 kW/m^3) US application. Afterwards, the dried samples were rehydrated in distilled water (25°C). A diffusion model was used to describe both drying and rehydration kinetics. The color and hardness of both dried and rehydrated cod samples were also measured.

The application of US increased the drying rate at every temperature tested, shortening the drying time by 16% at 0ºC and up to 60% at -10ºC. The ultrasonically assisted dried samples presented a rehydration rate which was slightly lower than that of those that had been conventionally dried, but they were harder and whiter, which is more suited to consumer preferences. Therefore, power ultrasound could be considered an affordable technology with which to accelerate LTD of desalted cod, providing high quality dried products.

Keywords: Ultrasound; Dehydration; Rehydration; Texture; Color

1. Introduction

Dried and salt-cured cod (*Gadus morhua*) is a highly-appreciated product due to its high nutritional value (high protein and low fat content) and its particular sensory properties. It is mainly produced in Norway and Iceland and primarily consumed in the Southern European countries, such as Spain and Portugal (Martínez-Álvarez and Gómez-Guillén, 2013; Oliveira et al., 2012). The high salt concentration of this product (approximately 20% w/w) prevents its degradation but limits its direct consumption; for this reason salted cod must be desalted (Ozuna et al., 2014a), a process that takes approximately 24h. This slow salt diffusion constrains the consumption of salted cod for both domestic use and the catering industry. In addition, the desalting converts the cod into a highly perishable product (Fernández-Segovia et al., 2007) and, in fact, the fish must be either immediately consumed, chilled or frozen (Lauritzsen et al., 2004). Therefore, it could be interesting to explore alternative preservation methods, such as drying, that ensure both the desalted product's stability and the retention of the sensory attributes (Andrés et al., 2005). The desalted and dried cod may be used as an ingredient in prepared foods, such as instant meals or ready-to-use products, due to its low salt content and rehydration ability.

Convective drying constitutes a traditional dehydration method for foodstuffs (Garcia-Perez et al., 2011). The use of high air temperatures accelerates the drying kinetics, but causes chemical and physical changes that can affect the quality traits of the dried product (Soria et al., 2010). Consumer demand for high quality products has encouraged research into alternative techniques to minimize quality degradation during processing. In this sense, low temperature drying (LTD) could be an interesting method. However, the long drying times linked to LTD could limit its use on an industrial scale.

Power ultrasound (US) has been used to speed up the convective drying of several foodstuffs (Cárcel et al., 2011; Gallego-Juárez et al., 2007; Garcia-Perez et al., 2011), mainly by introducing mechanical energy. The ultrasonic waves generate alternating expansions and contractions when travelling across a medium, which have a similar effect to that found in a sponge when it is repeatedly squeezed and released (Gallego Juárez et al., 2007). This mechanical stress helps the water

move from the inner parts of the product to the surface and could create microscopic channels that reduce the internal resistance to mass transfer (Gallego-Juárez, 2010). Moreover, in solid/gas systems, the application of US also produces oscillating velocities, micro-streaming and pressure variation at the interfaces, which reduce the boundary layer and, as a consequence, improve water movement from the solid surface to air. Therefore, US could help to reduce both the external and the internal mass transfer resistance without introducing a significant amount of thermal energy during drying (Cárcel et al., 2011). In this sense, the feasibility of US application during the LTD process of different products, such as apple (Santacatalina et al., 2014, Garcia-Perez et al., 2012), salted cod (Ozuna et al., 2014b), green peas (Bantle and Eikevik, 2011), carrot or eggplant (Garcia-Pérez et al., 2012) has been proved. More research has been done on analyzing the effect of US on the drying kinetics than on the product quality (Pingret et al., 2013). Therefore, the aim of this work was to evaluate the feasibility of using US in LTD of desalted cod, analyzing not only drying and rehydration kinetics but also quality parameters, such as color and texture.

2. Materials and methods

2.1. Raw material and sample preparation

A homogeneous batch of salted cod (*Gadus morhua*) was provided by a local supplier (Carmen Cambra S. L., Spain). The pieces of salted cod averaged 1.5±0.25 kg. Parallelepiped-shaped samples (50x30x5 mm) were obtained from the central part of the cod loin using a sharp knife and, afterwards, were wrapped in plastic waterproof film and kept refrigerated at 2±1ºC (maximum storage time 120 h) until the desalting process took place. For that purpose, the slices of salted cod were immersed in water (70 g cod/L water) of low mineral content (Cortes S.A., Spain) at 4±1ºC for 24 h. After desalting, the surface water was removed with tissue paper. Then the samples were wrapped in plastic waterproof film and separated into three batches. Two of them were kept in refrigeration at 2±1ºC (maximum storage time 4 h) until the drying experiments were conducted (samples dried at 0 and 10ºC). The third (samples dried at -10ºC) was frozen by placing samples at -18±1ºC until processing (at least 72 h).

The moisture and the NaCl content of the cod samples were measured before and after desalting following standard methods 950.46 and 971.27, respectively (AOAC, 1997). Thus, the moisture content was obtained by the difference of weighting between salted or desalted cod samples and the same cod samples dried at 105ºC until they achieved constant weight (24 h approximately). For the NaCl measurement, approximately 0.5 g of ground sample was placed into 100 mL of distilled water and homogenised at 9500 r.p.m. for 5 min with an ultra-turrax mod. T25 provided with a dispersion tool mod. S25N-18G (IKA Labortechnik, Janke & Kunkel GMBH & Co, Staufen, Germany). The chloride content of the extract was determined in triplicate using a chloride meter (Ciba Corning, mod. 926. L; Halstead, Essex, United Kingdom). Thus, the average value of the moisture content of desalted cod was 4.42±0.02 kg water/kg dry matter of desalted cod (dmdc) and the NaCl content was 0.023±0.001 kg NaCl/kg dmdc.

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation (Figure 1), already described in the literature (Garcia-Perez et al., 2012). The system provides an automatic temperature and air velocity control. Moreover, an ultrasonically activated cylindrical radiator generates a high intensity ultrasonic field (155 dB) in the drying chamber. Drying experiments were conducted using a constant air velocity (2 m/s) at three different temperatures (10, 0 and -10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3) US application. Drying kinetics were obtained by weighing samples at preset times (interval of 15 min) and considering the initial moisture content. In every case, the initial mass load was of 138.7±6.9 g (10 cod slices) and the relative humidity of drying air was maintained below 10±3% during the whole drying process.

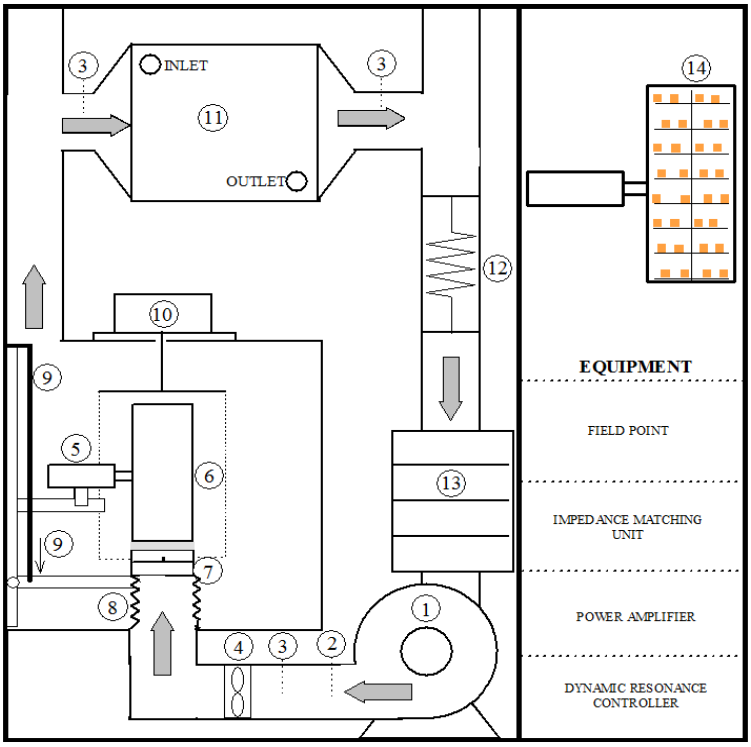

Figure 1. Diagram of the ultrasonically assisted convective dryer: 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer; 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe; 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13, desiccant tray chamber; 14, details of the sample load on the trays.

The drying experiments were replicated at least three times for each drying condition tested and extended until samples lost 65±3% of the initial weight. After drying, the moisture content of the samples was also measured following standard method 950.46 (AOAC, 1997). Finally, the dried samples were vacuum-sealed and stored in refrigeration (0±1ºC; maximum storage time 4 days) until the quality analyses (rehydration, color and texture) were carried out.

2.3. Modeling of drying kinetics

A diffusion model was used to describe the drying kinetics. The mass transport was considered to be one-dimensional due to the fact that sample thickness (5 mm)

was 1/6 (30 mm) and 1/10 (50 mm) shorter than the other dimensions. Thus, the approach of considering the samples as infinite slabs can be considered as appropriate (Garau et al., 2006). Assuming the effective moisture diffusivity as constant and the solid to be isotropic and homogeneous, the diffusion equation (equation 1) is written as follows:

$$\frac{\partial W_p(x,t)}{\partial t} = D_{ed}\left(\frac{\partial^2 W_p(x,t)}{\partial x^2}\right) \quad (1)$$

where W_p is the local moisture (kg water/kg dmdc), t is the time (s), D_{ed} is the effective moisture diffusivity (m^2/s) during drying and x represents the characteristic mass transport direction in the slab geometry (m).

In order to solve equation (1), the following assumptions were considered: solid symmetry, uniform initial moisture content and temperature, constant shape during drying and negligible external resistance to mass transfer. The analytical solution of the diffusion equation, expressed in terms of the average moisture content, is shown in equation (2) (Crank, 1975).

$$W(t) = W_e + (W_0 - W_e)\left[2\sum_{n=0}^{\infty}\frac{1}{\lambda_n^2 L^2}e^{-D_{ed}\lambda_n^2 t}\right] \quad (2)$$

where, λ_n are the eigenvalues calculated as $\lambda_n L = (2n+1)\frac{\pi}{2}$, W is the average moisture content (kg water/kg dmdc), L the half-thickness of the sample (m) and subscripts 0 and e represent the initial and equilibrium state, respectively.

The diffusion model was fitted to the experimental drying kinetics in order to identify the effective moisture diffusivity. The identification was carried out by minimizing the sum of the squared differences between the experimental and the calculated average moisture content. For that purpose, the Generalized Reduced Gradient (GRG) optimization method, available in Microsoft Excel™ spreadsheet (Microsoft Corporation, Seattle, WA, USA) was used. The goodness of the fit was determined by calculating the percentage of explained variance (VAR, equation 3).

$$VAR = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \quad (3)$$

where S_{xy} and S_y are the standard deviation of the estimation and the sample, respectively.

2.4. Rehydration experiments

The rehydration capacity was determined by immersing the dried cod samples in distilled water at 25±1ºC. In order to obtain the rehydration kinetics, the samples were taken out of the bath at preset times, blotted with tissue paper to remove the surface water and weighed. The rehydration tests were carried out in triplicate for each drying condition considered, using 10 samples (16.5±1.5 g) of dried cod in each run. The experiments were extended until the difference in sample weight between two consecutive measurements (60 min) was lower than 0.5 g, assuming that this point was close to the equilibrium weight. The rehydration kinetics were modeled using the same diffusion model described in section 2.3. for the drying kinetics. In this case, W_0 represents the moisture content of the dried samples and W_e the equilibrium moisture content of the rehydrated samples and the term D_{ed} was replaced by D_{er} to differentiate the effective moisture diffusivity (m^2/s) during drying and rehydration.

2.5. Color

The color of both dried and rehydrated cod samples was determined by measuring the CIE L*a*b* color coordinates (Bai et al., 2013) using a colorimeter (Minolta CM-2500d, Konica Minolta Optics, Inc., Japan), provided with a standard illuminant D65, an observation angle of 10° and calibrated using a standard white. In every case, the measurements were carried out directly on the sample surface, in triplicate and at room temperature (20±1ºC). Thus, for each type of dried sample, a minimum of 90 color measurements were carried out. The overall color difference (ΔE, equation 4) was computed as the difference between AIR+US (L*, a*, b*) and AIR (L_0*, a_0*, b_0*) samples. In the case of the rehydrated samples, ΔE indicates the

color difference between the rehydrated samples (L*, a*, b*) and the desalted cod before drying (L_0*, a_0*, b_0*).

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2} \quad (4)$$

2.6. Texture

The hardness of both dried and rehydrated cod samples was measured using a Texture Analyzer (TAX-T2, Stable Micro System, Godalming, United Kingdom) with a load cell of 25 kg. The penetration tests were conducted with a 2 mm flat cylinder probe (SMS P/2N), at a crosshead speed of 1 mm/s and a strain of 75% (penetration distance 3.5 mm). The hardness was characterized as the maximum penetration force achieved. In each sample, the penetration tests were carried out at 16 points following a preset pattern. For each drying run, at least three dried and three rehydrated samples were analyzed. Because each drying conditions was tested by triplicate, this means that nine dried and nine rehydrated samples was used to assess the hardness in each case.

2.7. Statistical analysis

Analyses of variance (ANOVA) ($p<0.05$) were carried out and LSD (Least Significant Difference) intervals were estimated using the statistical package, Statgraphics Centurion XVI (Statpoint Technologies Inc., Warrenton, VA, USA), in order to assess the significance of the influence of the different operating conditions (temperature and US application) on the identified D_{ed} and D_{er}, as well as on the color and hardness of both the dried and rehydrated samples.

3. Results and discussion

3.1. Drying experiments

The drying kinetics of desalted cod without (AIR) and with (AIR+US) ultrasound application are shown in Figure 2. In both AIR and AIR+US, the lower the drying temperature, the longer the drying time. Thus, in AIR experiments, 69% less time

was needed for drying at 10ºC (18.1±1.9 h) than at -10ºC (57.7±5.9 h). It should be noted that at 0 and 10ºC, the water was removed from the solid matrix by evaporation. On the contrary, at -10ºC, water removal took place by sublimation due to the fact that the water remains frozen during drying; therefore, under these conditions it could be considered as atmospheric freeze drying (AFD) (Claussen et al., 2007).

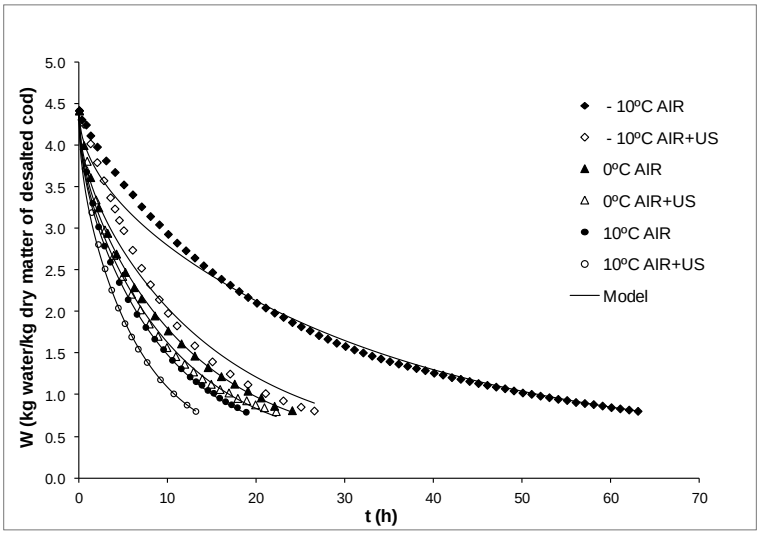

Figure 2. Experimental and calculated (diffusion model) drying kinetics (2 m/s) of desalted cod at different temperatures (-10, 0 and 10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application.

The application of US increased the drying rate at every temperature tested (Figure 2). The shortening of the drying time depended on the temperature being higher at -10ºC (60%) than at 0 and 10ºC (16 and 29%, respectively). As observed in Figure 2, the influence of temperature on AIR+US drying kinetics was less remarkable than in AIR experiments. Thus, the difference in drying time between the AIR experiments carried out at -10 and 10ºC was 39.6 h, while this difference was only 10.2 h in the case of AIR+US experiments. Using the same US device, Ozuna et al. (2014b) succeeded in shortening the drying time by between 35 and 54% when US was applied during the drying of salted cod (from -10 to 20ºC). In the case of apple drying, and under similar experimental conditions (from -10 to 10ºC), Santacatalina et al. (2014) found time savings of between 60 and 77%. Likewise,

Garcia-Perez et al. (2012) reported drying time reductions of around 70% in the drying of carrot and eggplant at -14°C. Bantle and Hanssler (2013) reduced the drying time by over 90% when drying salted codfish at 10ºC using a commercial ultrasonic plate-like emitter (20kHz; DN 20/200, Sonotronic, Karnsbald, Germany), but considering only the initial drying period (until samples reached a moisture content of 45%). Schössler et al. (2012) reported that, when freeze-drying red bell pepper cubes using a contact ultrasonic system, the drying time was shortened by 11.5%.

3.2. Modeling of drying kinetics

The proposed model was adequate for describing the drying kinetics of desalted cod slices at 0 and 10ºC, obtaining percentages of explained variance (VAR) of over 99% (Table 1). The goodness of the fit at 0 and 10ºC is illustrated in Figure 2, where the similar trend of the experimental and calculated moisture content can be observed. On the contrary, a lower VAR value (98.5%) was found in the experiments carried out at -10ºC, probably because the samples remain frozen during drying. Under these conditions, the water is removed by sublimation and two layers can be found in the product: a frozen inner core and a dry outer layer. Therefore, the product is not homogeneous, as is assumed in the diffusion model.

Table 1. Effective moisture diffusivity (D_{ed}) for the drying kinetics of desalted cod at different temperatures (10, 0 and -10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± standard deviation are shown. VAR (%) is the percentage of explained variance. ΔD_{ed} shows (in percentage) the increase in effective moisture diffusivity produced by ultrasonic application.

	AIR		**AIR+US**		
T (ºC)	D_{ed} (10^{-11} m^2/s)	VAR (%)	D_{ed} (10^{-11} m^2/s)	VAR (%)	ΔD_{ed} (%)
10	7.77±0.62^{e}	99.7	10.51±0.33^{f}	99.1	35.4
0	5.65±0.35^{c}	99.3	6.63±0.09^{d}	99.2	17.4
-10	2.17±0.20^{a}	98.5	4.84±0.60^{b}	94.4	123.5

Superscript letters (a, b, c, d, e, f) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p< 0.05$).

At the drying temperatures tested, the fit of the diffusion model was poorer when US was applied. This is probably due to the fact that US application partially

modifies the mechanisms of mass transport that could affect the relationship between internal and external mass transport resistance, meaning that diffusion was not the only mechanism controlling mass transfer, as assumed in the model.

In any case, in the proposed model, any effect on the drying rate was included in the D_{ed}. Therefore, this parameter can be used to compare and assess the overall effect of the different conditions tested (temperature and/or US application) on the drying rate. In the case of temperature, the higher the air drying temperature applied, the higher the identified D_{ed} (Table 1). The application of US during LTD of desalted cod also involved a significant ($p<0.05$) increase in the D_{ed} at the three temperatures studied (Table 1). This influence of US on the identified diffusivities were similar to those reported by Ozuna et al. (2014b) for US-assisted drying kinetics of salted cod at temperatures between 20 and -10ºC. The mechanical stress caused by the alternating compressions and expansions (sponge effect) produced by US could improve the internal diffusion of moisture (Gallego-Juárez et al., 2007). Moreover, this stress could create microscopic channels that help to make the movement of the water towards the product surface easier (Gallego-Juárez, 2010). At the solid-air interface, US produces alternating pressures and microstirring that could also help to speed-up the convective moisture transport.

As can be observed in Table 1, the increase in D_{ed} produced by US application was significantly ($p<0.05$) larger in the experiments conducted at -10ºC (123.5%) than in those carried out at 0 and 10ºC (17.4 and 35.4%, respectively). As stated before, while evaporation was responsible for the water removal at 0 and 10ºC, at -10ºC it took place through sublimation which can be assumed to be atmospheric freeze drying. This makes the outer porous dry layer developed during this kind of drying more prone to the ultrasonic effects than the more compact structure developed during drying by evaporation at 0 and 10ºC. In this sense, Ozuna et al. (2014c) observed that the product porosity influences the extension of the ultrasound effects during drying. Thus, highly porous materials present higher values of impedance, closer to the surrounding air, than materials with a hard and closed-compact structure. The fact that the coupling of the air-porous structure is better makes easier the ultrasound transmission and helps ultrasound effects to be more intense (Ozuna et al., 2014c).

3.3. Rehydration experiments

Since rehydration potential is an important quality attribute for products that need to be reconstituted before consumption, the influence of the drying method on the rehydration kinetics of dried samples (0.54±0.07 kg water/kg dmdc) was experimentally determined. The results obtained showed that the AIR samples dried at -10ºC rehydrated significantly ($p<0.05$) faster than those dried at 10 and 0ºC (Figure 3). Thereby, the average rehydration time for AIR samples dried at 0 and 10ºC was 22.0±0.9 h, while for AIR samples dried at -10ºC it was 8.7±0.3 h. The moisture content reached at the end of the rehydration process was also significantly ($p<0.05$) higher for samples dried at -10ºC (3.05±0.44 kg water/kg dmdc) than for those dried at 10 and 0ºC (2.61±0.24 and 2.41±0.10 kg water/kg dmdc, respectively). These results could be explained by the fact that drying at -10ºC leads to a minimum shrinkage and a highly porous structure (Stawczyk et al., 2007). So, the high porosity makes it easier for water to enter the dried matrix.

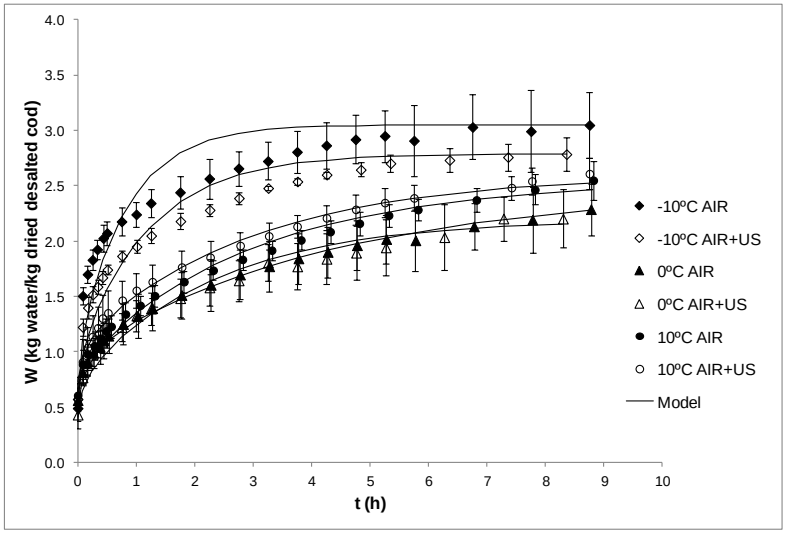

Figure 3. Experimental and calculated (diffusion model) rehydration kinetics of desalted and dried cod (2 m/s) at different temperatures (-10, 0 and 10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application.

The application of US during drying did not significantly ($p<0.05$) affect the moisture gain rate during the rehydration of samples dried at 0 and 10ºC (Figure 3). On the contrary, for samples dried at -10ºC, US application slightly reduced the

rehydration rate and the final moisture gain. US could affect the microstructure of cod samples, provoking ruptures in the cod fibers and causing the formation of wider spaces between myofibrils (Ozuna et al., 2014c). The extension of these effects were enough to modify the rehydration capacity of cod slices dried at -10ºC, but not for those dried at 0 and 10ºC. It is likely that this is due to the combined impact of freezing and US application on the structure of the samples dried at -10ºC, which results in a softer and more unstructured matrix where the water intake and its retention during the rehydration process is more difficult. In this sense, Nowacka et al. (2012) reported that a short ultrasonic pretreatment of apple cubes before drying reduced their moisture content after 60 minutes of rehydration due to changes in the product's microstructure. However, Schössler et al. (2012) reported no differences in the rehydration characteristics of the US assisted freeze-dried red bell pepper in comparison with those conventionally freeze-dried, probably due to the lower efficiency of the contact ultrasonic system used in this work.

The experimental rehydration kinetics were also modeled, taking Equation 2 into account. A satisfactory description (VAR>98%) (Table 2) of the rehydration kinetics was only obtained for AIR dried samples at 0 and 10ºC (Figure 3). In samples dried at -10ºC, mechanisms other than diffusion, and probably linked to the high porosity and bulk water input, could be involved.

Table 2. Effective moisture diffusivity (D_{er}) for the rehydration kinetics of desalted cod dried at different temperatures (10, 0 and -10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± standard deviation are shown. VAR (%) is the percentage of explained variance.

	AIR		**AIR+US**	
T (ºC)	D_{er} (10^{-10} m^2/s)	VAR (%)	D_{er} (10^{-10} m^2/s)	VAR (%)
10	$1.99\pm0.66^{a,b}$	99.1	$2.26\pm0.87^{a,b}$	97.5
0	1.89 ± 0.52^{a}	98.3	$2.34\pm0.58^{a,b}$	95.5
-10	9.93 ± 4.35^{c}	86.7	5.60 ± 2.17^{b}	94.3

Superscript letters (a, b, c) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p< 0.05$).

The D_{er} identified for samples dried at 0 and 10ºC was similar (Table 2). At these temperatures, US application during drying caused a slight but not significant ($p<0.05$) increase in the D_{er}. However, the D_{er} identified for AIR samples dried at -10ºC was five times greater than that identified for those dried at 0 and 10ºC. In this case, AIR+US samples dried at -10ºC showed a significantly ($p<0.05$) lower D_{er} than AIR samples.

3.4. Color

3.4.1. Dried samples

The average values of the color coordinates of desalted cod before drying were 63.7±1.9 for L*, -3.85±0.52 for a* and 0.95±0.78 for b*. In general terms, as can be observed in Table 3, the drying increased the value of the three coordinates. AIR dried samples at 0 and 10ºC showed higher a* and b* coordinates and lower L* than those dried at -10ºC. These results suggest that the moisture removal by evaporation (0 and 10ºC) caused a yellowing (higher b*) and a darkening (lower L*), while the removal by sublimation (-10ºC) leads to brighter and whiter samples. According to Asli and Morkore (2012), cod should preferably have a high lightness value (L*-value), as the color white is considered positive by consumers. Bjorkevoll et al., (2014) also associated high quality with a whiter and less yellow surface in the sensory evaluation of the heavy salted cod. However, Lauritzsen et al. (2004) reported that the reduction in the water content causes changes in the color of the fish. Brás and Costa (2010) reported an increase in both the lightness (L*) and yellowness (b*) of the cod caused by drying, which was more marked as drying progressed.

The application of US during drying only significantly ($p<0.05$) affected the L* coordinate for samples dried at -10ºC, reducing their lightness as compared with AIR samples. Moreover, the overall color difference (ΔE) between samples dried without (AIR) and with (AIR+US) (Table 3) showed negligible differences in the case of samples dried at 0 and 10ºC due to the fact that, as reported by Francis and Clydesdale (1975), ΔE values lower than 2 are not detected by the human eye. On the contrary, the ΔE obtained for the samples dried at -10ºC was significantly ($p<0.05$) higher; this indicated that, at this drying temperature, US application

caused a meaningful color difference. This was probably due to the slight thermal effect generated by US on the sample's surface, which could be more marked in this case and bring about a little darkening.

Table 3. CIELab (L*, a*, b*) color coordinates for desalted cod dried at different temperatures (10, 0 and -10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± standard deviation are shown. ΔE represents the overall color differences between AIR+US and AIR samples.

		-10ºC	**0ºC**	**10ºC**
L*	**AIR**	79.9±4.4^{a}	57.9±4.1^{c}	54.1±2.3^{c,d}
	AIR+US	67.0±4.3^{b}	55.3±4.2^{c,d}	55.9±5.0^{d}
a*	**AIR**	-1.2±0.4^{m}	-1.0±1.3^{m}	-0.1±1.2^{n}
	AIR+US	-0.9±0.5^{m}	-1.0±0.8^{m}	-1.0±1.0^{m}
b*	**AIR**	13.6±3.0^{x}	16.1±3.0^{y}	16.1±2.9^{y}
	AIR+US	12.6±2.6^{x}	15.8±2.6^{y}	15.6±3.0^{y}
ΔE	**AIR+US vs AIR**	12.9	2.6	2.1

Superscript letters (a, b, c, d), (m, n) and (x, y) show homogeneous groups, established from LSD (Least Significance Difference) intervals ($p<0.05$) for L*, a* and b*, respectively.

3.4.2. Rehydrated samples

The drying temperature did not affect the color of the rehydrated samples (Table 4) and no significant ($p<0.05$) differences were found for samples previously dried at 10, 0 or -10ºC. In a similar way, US application during drying did not cause noticeable changes in the color coordinates of the rehydrated samples (Table 4).

In this case, ΔE was calculated by considering the desalted cod prior to drying as reference. In general terms, the dried and rehydrated cod samples did not recover the color of the desalted samples, the ΔE ranging from 8.8 to 11.7 (Table 4).

Table 4. CIELab (L*, a*, b*) color coordinates for rehydrated cod, previously desalted and dried at different temperatures (10, 0 and -10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± standard deviation are shown. ΔE represents the overall color differences between rehydrated samples and desalted cod (DC) before drying.

		-10ºC	0ºC	10ºC
L*	**AIR**	71.1±2.2^{a}	71.9±2.7^{a}	71.3±3.6^{a}
	AIR+US	72.2±3.0^{a}	71.4±2.4^{a}	71.8±3.4^{a}
a*	**AIR**	-3.7±0.7^{m}	-3.5±0.8^{m}	-3.5±1.1^{m}
	AIR+US	-3.7±0.5^{m}	-3.5±0.7^{m}	-3.6±1.2^{m}
b*	**AIR**	5.5±3.1^{x}	9.2±5.1^{y}	6.8±4.7^{x,y}
	AIR+US	6.0±4.4^{x}	7.5±4.3^{x,y}	8.1±4.0^{x,y}
ΔE	**AIR vs DC**	8.8	11.7	9.6
	AIR+US vs DC	9.9	10.2	10.9

Superscript letters (a), (m) and (x, y) show homogeneous groups, established from LSD (Least Significance Difference) intervals ($p<0.05$) for L*, a* and b*, respectively.

3.5. Texture

3.4.1. Dried samples

The initial hardness of the desalted cod was 1.55±0.53 N. Therefore, the drying process provoked a hardening of the samples (Figure 4), regardless of the drying conditions used. For the AIR samples, the hardness was dependent on the drying temperature (Figure 4), so, the lower the air temperature, the harder the dried cod sample. No influence of the air drying temperature on the hardness was observed in the case of AIR+US samples. However, when comparing ultrasonically assisted dried samples with those conventionally dried, it was observed that the AIR+US samples dried at 0 and 10ºC were significantly ($p<0.05$) harder than the AIR ones (Figure 4). This fact could be attributed to the successive compression and expansion cycles of the material produced by US, which could affect cod proteins thus causing a hardening of the samples. At -10ºC, the hardening of AIR and AIR+US samples was similar. The previous freezing step and the fact that water removal occurred by sublimation could provoke changes in the sample's structure that may mask the structural US effect.

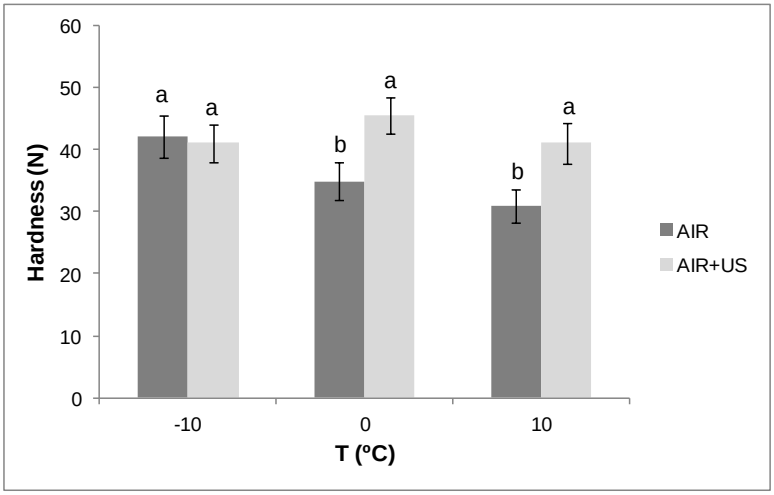

Figure 4. Hardness of desalted and dried cod at different temperatures (-10, 0 and 10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± LSD intervals ($p<0.05$) are plotted. Different letters show significant differences according to LSD intervals ($p<0.05$).

3.4.2. Rehydrated samples

In general, both the drying and the later rehydration process produced samples that were slightly harder than the initial desalted cod (1.55±0.53 N), but their final hardness depended on the drying temperature and US application. Thus, in the case of AIR samples, the effect of drying temperature on rehydrated samples was to the opposite of that found in dried samples; so, the higher the air temperature, the harder the rehydrated sample (Figure 5). As regards the application of US, the rehydrated AIR+US samples dried at 0 were significantly ($p<0.05$) harder than AIR samples (Figure 5). The textural changes caused by US application could be linked to the denaturation of proteins (Lee and Feng, 2011). In the case of samples dried at 10ºC, no significant ($p<0.05$) differences were observed between AIR and AIR+US, which could be explained by the fact that the shorter drying time at 10ºC prevented a lengthy action of US on the internal structure. In the case of -10ºC experiments, the effects of freezing on structure can mask the effects of ultrasound.

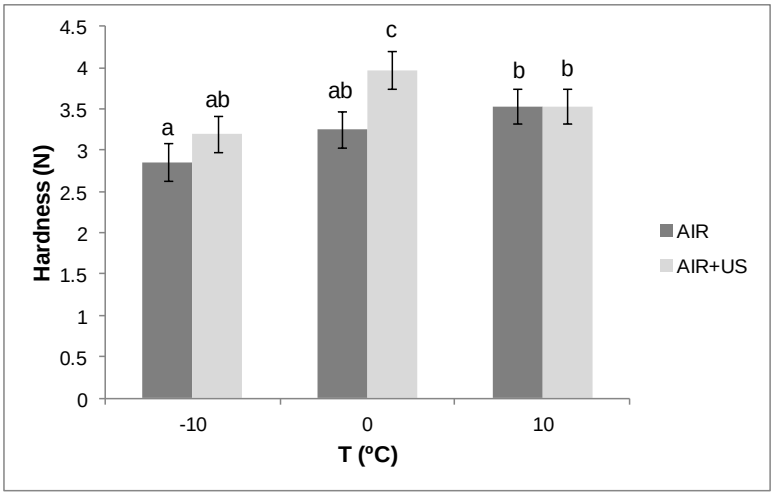

Figure 5. Hardness of rehydrated cod previously desalted and dried at different temperatures (-10, 0 and 10ºC), without (AIR) and with (AIR+US, 20.5 kW/m^3, 21 kHz) ultrasound application. Average values ± LSD intervals ($p<0.05$) are plotted. Different letters show significant differences according to LSD intervals ($p<0.05$).

4. Conclusions

The application of US during the low temperature drying of desalted cod improved the drying rate at every temperature tested, but it was particularly noticeable when drying took place at -10ºC, which is when water removal took place by sublimation. As far as quality attributes are concerned, the cod dried at -10ºC rehydrated faster and gained more water than that dried at higher temperatures. Moreover, these samples were brighter, whiter and slightly softer than those dried at 0 and 10ºC. US application slightly reduced the rehydration rate and increased the sample's hardness, but allowed whiter samples to be obtained, which are usually preferred by consumers. Therefore, power ultrasound could be considered an interesting technology to speed-up the low temperature drying of desalted cod without greatly affecting the quality of the obtained product.

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INFLUENCE OF AIR VELOCITY AND TEMPERATURE ON ULTRASONICALLY ASSISTED LOW TEMPERATURE DRYING OF EGGPLANT

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INFLUENCE OF AIR VELOCITY AND TEMPERATURE ON ULTRASONICALLY ASSISTED LOW TEMPERATURE DRYING OF EGGPLANT

Abstract

The aim of this work was to evaluate the feasibility of power ultrasound (US) application during the low temperature drying (LTD) of eggplant, analyzing the influence of the process variables linked to the air flow (velocity and temperature) on the drying kinetics and different quality aspects of the dehydrated product. For that purpose, eggplant (*Solanum melongena* var. Black Enorma) cubes (8.6 mm side) were dried at different air velocities (1, 2, 4 and 6 m/s) and temperatures (10, 0 and -10ºC) without (AIR) and with (AIR+US) US application. The rise in the air velocity and temperature led to an increase in the drying rate in AIR experiments. US application accelerated the drying process under every experimental condition tested, shortening the drying time by up to 87%. As for the quality parameters, no remarkable influence of the process variables (US application, air velocity and temperature) on the rehydration, reconstitution in olive oil or hardness of the rehydrated product was observed.

Keywords: Dehydration; temperature; air velocity; ultrasound; modeling; rehydration

1. Introduction

Eggplant is a relevant crop in North America, Asia and the Mediterranean area. Its limited shelf life, about 10 days after being harvested and stored at a temperature between 10 and 15ºC (Hu et al., 2010), is one of the main restrictions on the trade of eggplant as a fresh product. Several studies deal with the possibility of extending the shelf-life using several preservation techniques, such as drying (Arvanitoyannis et al., 2005; Hu et al., 2010; Jha and Matsuoka, 2002; Wu et al., 2008; 2009; Zhang and Chen, 2006). Dehydration provides stable dried eggplant products (Akpinar and Bicer 2005) that are, for example, common ingredients in the preparation of dry long-life vegetable mixtures (Brasiello et al., 2013). In most of the cases, dried eggplant must be rehydrated before consumption, as in the case of the preparation of soups (Doymaz, 2011). Convective drying is one of the most commonly-used dehydration techniques within the food industry, but it provokes a series of changes in materials, such as oxidation, browning, shrinkage, softening and loss of nutritional-functional properties (Russo et al., 2013; Vega-Gálvez et al., 2012). These changes largely depend on the drying conditions, with those parameters linked to the air flow, such as air velocity and temperature, being of particular relevance.

Nowadays, there is an increasing demand in the food market for high quality products that preserve the nutritional and sensorial properties of the fresh product. In this sense, low-temperature convective drying can represent an interesting alternative to both conventional hot air drying and freeze-drying and a low-cost means of obtaining high-quality dried products (Santacatalina et al., 2014). Low-temperature drying (LTD) is conducted at temperatures below standard room conditions (<20ºC), which includes figures above and below the products' freezing point. The low level of thermal energy available in LTD applications leads to very low drying rates. Therefore, there is a particular interest in the intensification of the LTD process, making its application in the food industry feasible.

Power ultrasound (US) application constitutes an interesting non-thermal intensification for LTD (Cárcel et al., 2011). The mechanical energy introduced into the drying medium by US could help to reduce both the external and the internal mass transfer resistance (Riera et al. 2011). US has recently been applied in the

LTD of different products, such as fish, fruits and vegetables, leading to shorter drying times. Thus, Ozuna et al. (2014a) reported a shortening of the drying time by between 35 and 54% when US was applied during the drying of salted cod (from -10 to 20ºC). Santacatalina et al. (2014) and Garcia-Perez et al. (2012) obtained similar drying time reductions by applying US (50 W) during apple drying at -10ºC (77%) and -14ºC (70%), respectively. Using a contact ultrasonic system for the freeze-drying of red bell pepper cubes, Schössler et al. (2012) found a drying time 11.5% shorter than in conventional experiments. Meanwhile, Bantle and Eikevik (2011) succeeded in reducing the drying time by around 10% when drying green peas at -3ºC using a commercial air-borne ultrasonic radiator. The variable ultrasonic performance of LTD applications found in the literature could be linked to the efficiency of the ultrasonic system used. The ultrasonic effects also depend on the magnitude of the process variables used, such as air velocity, temperature or ultrasonic power applied (Garcia-Perez et al., 2006). In this sense, during the atmospheric freeze drying of apple, Santacatalina et al. (2015) reported that the effect of US application on drying time was more marked than other factors, such as air temperature or velocity. As far as we are concerned, the influence of these aspects on the LTD of a high porosity product like eggplant have not been reported. This is especially relevant if it is borne in mind that the performance of US application is also product-dependent (Ozuna et al., 2014b). Therefore, the aim of this work was to evaluate the influence of the air velocity and temperature during the low-temperature drying of eggplant assisted by power ultrasound, analyzing the impact of these variables on both the drying kinetics and quality parameters of the dried product.

2. Materials and methods

2.1. Raw material

Eggplants (*Solanum melongena* var. Black Enorma) were purchased in a local market (Valencia, Spain). The pieces were selected to obtain a homogeneous batch in terms of ripeness, size and color, and held at 4±1ºC until processing. Cubic samples (8.6 mm side) were obtained from the flesh using a household tool. Samples to be dried at 10ºC and 0ºC were immediately processed, while those to

be dried at -10ºC were wrapped in plastic film and frozen by placing in a freezing room at -18±1ºC until processing (at least 24 h). The initial moisture content was measured by placing samples in a vacuum oven at 70ºC and 200 mmHg until constant weight according to the Association of Official Analytical Chemists standard method no. 934.06 (AOAC, 1997).

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation, already described in the literature (Garcia-Perez et al., 2012). The system is provided with an air velocity and temperature control and an ultrasonically activated drying chamber excited by an ultrasonic transducer. Air-borne ultrasound is transmitted from the walls of the drying chamber to the air, finally reaching the samples. The system is able to generate an acoustic field (21.9 kHz) of 157 dB inside the chamber with an electric power input of 90 W at stagnant air conditions, which is reduced to 154 dB at an air velocity of 6 m/s (Riera et al., 2011). Based on the results of Ozuna et al. (2014b), the ultrasonic transmission coefficient in the interface air/eggplant should be of 0.011.

The drying experiments were carried out at different air velocities (1, 2, 4 and 6 m/s) and temperatures (10, 0 and -10ºC) without (AIR, 0 W) and with (AIR+US, 50 W) US application. The relative humidity of air was maintained below 15±5% for the entire drying time and the initial mass load density was 5.3 kg/m^3, which corresponds with 40 cubes of fresh eggplant. The drying kinetics were determined from the initial moisture content of the eggplant and by automatically weighing the samples at preset times (every 300 s). Every condition was tested in triplicate at least and the drying experiments were extended until the samples lost 90% of the initial weight. Thus, the total number of experiments carried out was 72 (3 Temperaturesx4 Air velocitiesx2 US applicationx3 Replicates).

2.3. Modeling of the drying kinetics

The modeling of the drying kinetics focused only on quantifying the effect of the drying conditions tested on overall mass transport. For that purpose, a diffusion

model was used to describe the drying kinetics of eggplant cubes, considering the effective moisture diffusivity to be constant, the temperature uniform and the shrinkage negligible. Thus, the governing equation of diffusion (Equation 1) is written as follows:

$$\frac{\partial W_p(x,y,z,t)}{\partial t} = D_{ed}\left(\frac{\partial^2 W_p(x,y,z,t)}{\partial x^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial y^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial z^2}\right) \quad (1)$$

where W_p is the local moisture (kg water/kg dry matter, kg w/kg dm), t is the drying time (s), D_{ed} is the effective moisture diffusivity (m^2/s) and x, y and z represent the characteristic mass transport pathways in the cubic geometry (m).

In order to solve Equation 1, the initial moisture was assumed to be uniform and the symmetry was considered in directions x, y, z. The moisture transport was considered to be jointly controlled by diffusion and convection, the latter being included in the model by the boundary condition shown in Equation 2 for the x coordinate. Thus, the diffusion model permits the quantification of both the effective diffusivity and the external mass transfer coefficient (k, kg w/m^2s):

$$t > 0 \qquad x = L \qquad -D_{ed}\rho_{ds}\frac{\partial W_p(L,y,z,t)}{\partial x} = k(a_w(L,y,z,t) - \varphi_{air}) \quad (2)$$

where ρ_{ds} is the dry solid density (kg dm/m^3) and φ_{air} is the relative humidity of the drying air. The water activity on the surface of the material (a_w (L,y,z,t)) was estimated from sorption isotherm data at 20ºC reported in the literature (Moreira et al., 2010).

The fact of considering the samples as homogeneous and isotropic is only valid for drying experiments carried out at 0 and 10ºC. In drying experiments at -10ºC where samples were frozen before drying, it was possible to distinguish two main zones in the particle during drying: an inner frozen core and an outer dry layer. The vapor diffusion only occurs in this outer layer, which becomes thicker as the drying progresses. Then, in the experiments at -10ºC, the proposed diffusion model just becomes an empirical model. A more rigorous approach for modeling LTD at -10ºC was addressed by Santacatalina et al. (2015). However, the proposed diffusion model in this work allowed for the comparison and quantification of the effect of the

studied variables on the drying kinetics, which was, as mentioned above, the main goal of the modeling.

The model was numerically solved by applying an implicit finite difference method (Garcia-Perez et al., 2012), for which a computational algorithm was written in MATLAB 7.13.0.564 (The MathWorks, Inc., USA). An optimization problem was defined for the purposes of fitting the model to the experimental data. The objective function was the sum of the squared differences between the experimental and the calculated average moisture contents. The kinetic parameters, D_{ed} and k, were jointly identified by minimizing the objective function using the SIMPLEX method available in the fminsearch function (MATLAB). The model was fitted to each drying run and the kinetic parameters averaged. The percentage of explained variance (VAR, Equation 3) and the mean relative error (MRE, Equation 4) were calculated in order to determine the goodness of the fit.

$$VAR(\%) = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \tag{3}$$

$$MRE(\%) = \frac{100}{N}\left[\sum_{i=1}^{N} \frac{|W_{ei} - W_{ci}|}{W_{ei}}\right] \tag{4}$$

where S_{xy} and S_y are the standard deviation of the estimation and the sample, respectively, W_{ei} and W_{ci} are the experimental and calculated average moisture contents (kg w/kg dm) and N is the number of experimental data.

2.4. Rehydration experiments

The eggplant samples dried under the different conditions tested were rehydrated in distilled water at 30±1ºC using a thermostatic bath provided with an agitation system (Tectron 200, JP Selecta, Abrera, Spain). During rehydration, samples were taken out of the bath at preset times (0, 3, 10, 30, 60, 100, 200, 300, 400, 500 and 700 s), blotted with tissue paper to remove the surface water and weighed in order to estimate the rehydration kinetics. 10 cubes of dried eggplant (0.38±0.06 g) were used for each run and four replicates were performed for each drying condition tested.

2.5. Modeling of the rehydration kinetics

The rehydration kinetics were also modeled following the diffusion theory. However, in this case, the external resistance was considered negligible due to the high turbulence maintained in the liquid medium during experiments. Therefore, it is assumed that the particle surface moisture content suddenly reached equilibrium, as reflected in Equation 5 for the x coordinate. The model's analytical solution, in terms of the average moisture content, is given in Equation 6.

$$W_p(L,y,z,t>0) = W_e \tag{5}$$

$$W(t) = W_e + (W_0 - W_e)\left[\sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2}\exp\left(-\frac{D_{er}(2n+1)^2\pi^2 t}{4L^2}\right)\right]^3 \tag{6}$$

where W is the average moisture content (kg w/kg dm), L the half-length of the cube side (m) and subscripts 0 and e represent the initial and equilibrium states, respectively.

This model was fitted to the experimental rehydration kinetics in order to identify the effective moisture diffusivity (D_{er}) and the equilibrium moisture content (W_e). For that purpose, the objective function to be minimized was the sum of the squared differences between experimental and calculated average moisture contents. The optimization was conducted by applying the generalized reduced gradient method available in the Solver tool (Microsoft Excel 2014). In order to determine the goodness of the fit, the VAR (Equation 3) and the MRE (Equation 4) were calculated.

2.6. Hardness of the rehydrated samples

The textural properties of the fresh and rehydrated eggplant samples were measured using a TA-XT2 texturometer (SMS, Godalming, UK) provided with a load cell of 25 kg. Simple compression tests were carried out at constant temperature (16±1ºC) using a flat 75 mm diameter aluminum plunger (SMS P/75) and applying a compression ratio of 80%. Hardness was computed from the force/deformation profiles as the maximum force achieved. At least 40 cubes were analyzed for each set of samples.

2.7. Absorption capacity of olive oil

The absorption capacity (AC) of olive oil was evaluated in order to assess the interaction of dried eggplant with another liquid, which is frequently used for cooking in Mediterranean countries. Moreover, it is one of the most interesting parameters with which to determine the functional properties of dietary fiber (O'Shea et al., 2012) and could be used, for example, to estimate the needs of oil during a frying process. For that purpose, the eggplant samples dried under the different conditions tested were immersed in 300 mL of olive oil at 30±1ºC (stagnant conditions). The AC of olive oil was estimated as the weight increase (as a percentage with respect to the initial weight) after 60 s of immersion. 10 cubes (0.37±0.09 g) of dried eggplant were used for each run and four replicates were performed for each drying condition tested.

2.8. Statistical analysis

An analysis of variance (ANOVA) ($p<0.05$) was carried out and LSD (Least Significant Difference) intervals were assessed using the statistical package, Statgraphics Centurion XVI (Statpoint Technologies Inc., Warrenton, VA, USA), in order to determine whether the operating conditions studied (temperature, air velocity and US application) significantly ($p<0.05$) influenced the D_e and k parameters identified in the drying kinetics and D_e and W_e in the rehydration kinetics. Likewise, the influence of drying conditions on the hardness of the rehydrated samples and the absorption capacity of olive oil were also compared.

3. Results and discussion

3.1. Drying experiments

The vegetable tissue of eggplant is heterogeneous in structure (Ozuna et al., 2014b) which leads to a high degree of experimental variability in the drying kinetics (Figure 1). For this reason, in order to properly compare the influence of air velocity, temperature and US application on the drying kinetics, all the replicates performed under every drying condition tested were fitted to a polynomial function. Thereby, the polynomial equation obtained reflects the average behaviour for a

particular drying condition (Figure 1) and permits comparison with trials conducted under other conditions (Figures 2 and 3).

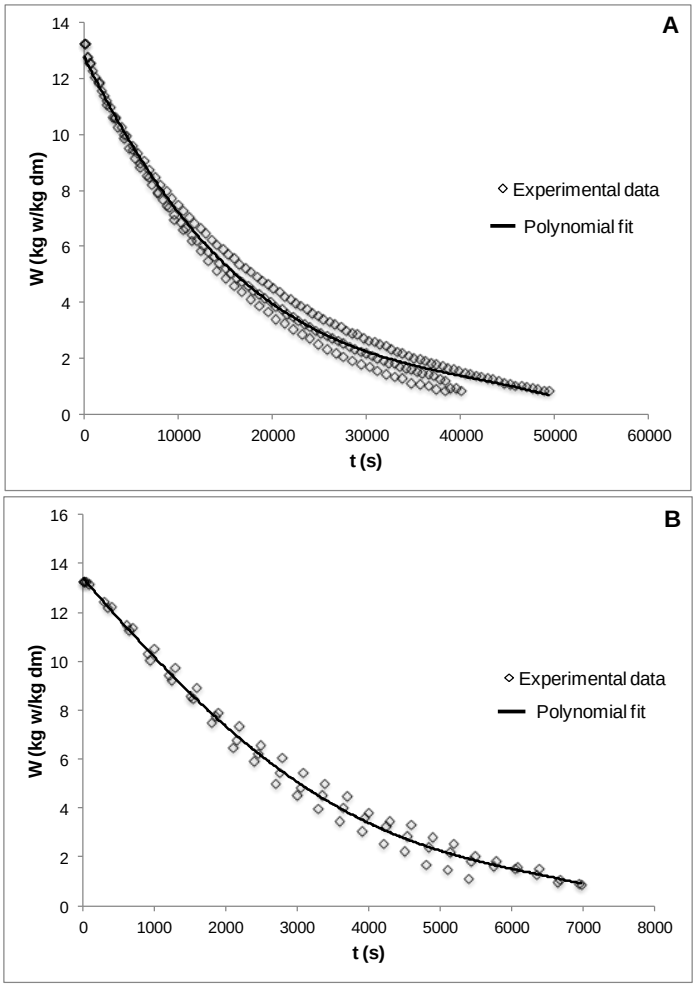

Figure 1. Examples of polynomial fit to experimental drying kinetics of eggplant cubes. A: 1 m/s, -10ºC, 0 W (AIR); B: 2 m/s, -10ºC, 50 W (AIR+US).

As for AIR kinetics, it can be observed that the higher the air velocity, the faster the drying kinetic at every temperature tested (Figure 2). Thus, for example, the drying times (loss of 90% of the initial weight) for the AIR experiments carried out at 0ºC and 1 and 6 m/s were 425±74 and 313±33 minutes, respectively. The increase in air velocity reduced the external resistance to mass transfer due to the reduction in the thickness of the boundary layer (Garcia-Perez et al., 2007). No air velocity threshold, above which external resistance is negligible compared to internal, was

found in the range of the air velocities studied. However, when US was applied during drying (AIR+US experiments), no clear trend in the air velocity effect was observed (Figure 2). This fact could be linked to the marked influence of US application on the drying kinetics, which could mask the air velocity effect (Garcia-Perez et al., 2007).

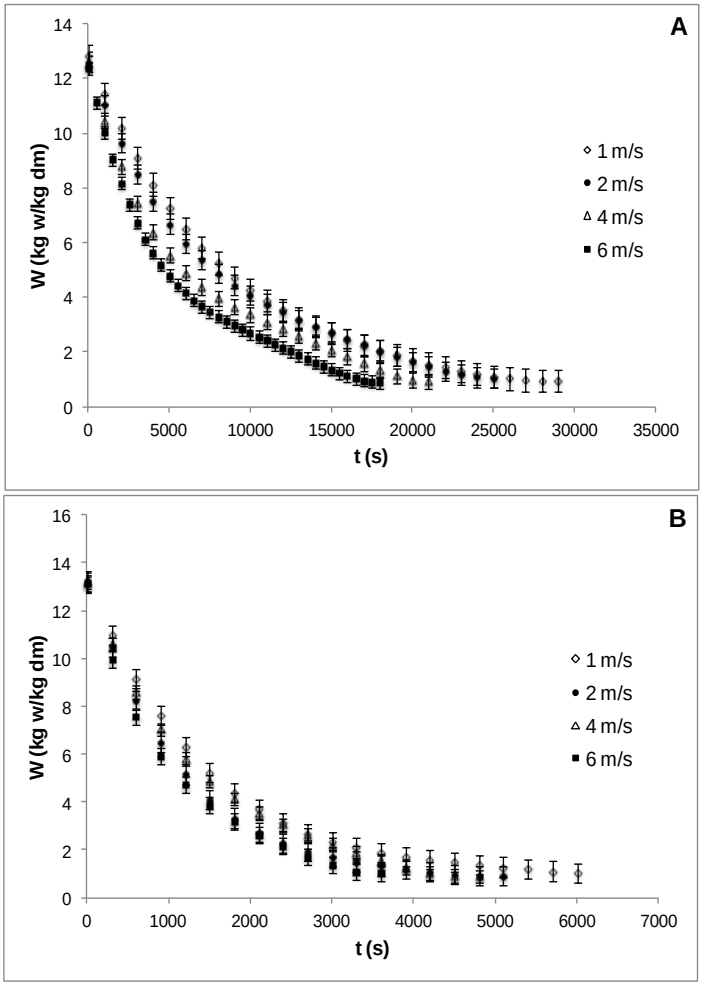

Figure 2. Drying kinetics of eggplant at different air velocities (1, 2, 4 and 6 m/s). A: 0ºC, 0 W (AIR); B: 10ºC, 50 W (AIR+US). Error bars show the differences between experimental data and the polynomial equation.

As regards the effect of temperature on the drying kinetics, the increase in the drying temperature in AIR experiments implied a shorter drying time at every air velocity used (Figure 3). The drying time was reduced by 73% (on average) when the drying temperature was increased from -10 to 10ºC. It should be noted that at 0 and 10ºC the water was removed from the solid matrix by evaporation, while at -10ºC, water removal occurred by sublimation, a process known as atmospheric freeze drying (Claussen et al., 2007). The temperature influence was less marked in AIR+US (Figure 3) than in AIR experiments. For example, in US experiments carried out at 4 m/s, the drying time was reduced by 47% when the drying temperature was increased from -10 to 10ºC. The kinetic effect of air temperature has been widely reported in the hot air drying of eggplant (Brasiello et al., 2013; Doymaz, 2011; Ertekin and Yaldiz, 2004; Russo et al., 2013) but, as far as we know, it has not been reported in the LTD of eggplant. The influence of temperature has been computed in the LTD of other products, such as apple (Santacatalina et al. 2014 and 2015) and salted cod (Ozuna et al., 2014a). Bantle and Eikevik (2011) also studied the influence of temperature on the drying of peas from -6ºC to 20ºC.

Under every drying condition tested, the application of power ultrasound increased the drying rate. The major difference in the drying time between AIR and AIR+US experiments (87%) was found in experiments at -10ºC and 4 m/s. The temperature influenced the magnitude of the ultrasound effects. Thus, the reduction in the drying time linked to US application was less significant at 10ºC than at -10ºC (Figure 4). However, the air velocity was found to exert no clear influence on US effects, so, the ultrasonic performance was similar at every air velocity tested. The kinetic intensification achieved in this study was greater than that reported by Santacatalina et al. (2014) and Garcia-Perez et al. (2012) using the same ultrasonically assisted drier during apple drying at -10ºC (77%) and -14ºC (70%), respectively. This could be explained by the greater porosity of eggplant, which favors the mechanical effects produced by US application (Puig et al., 2012).

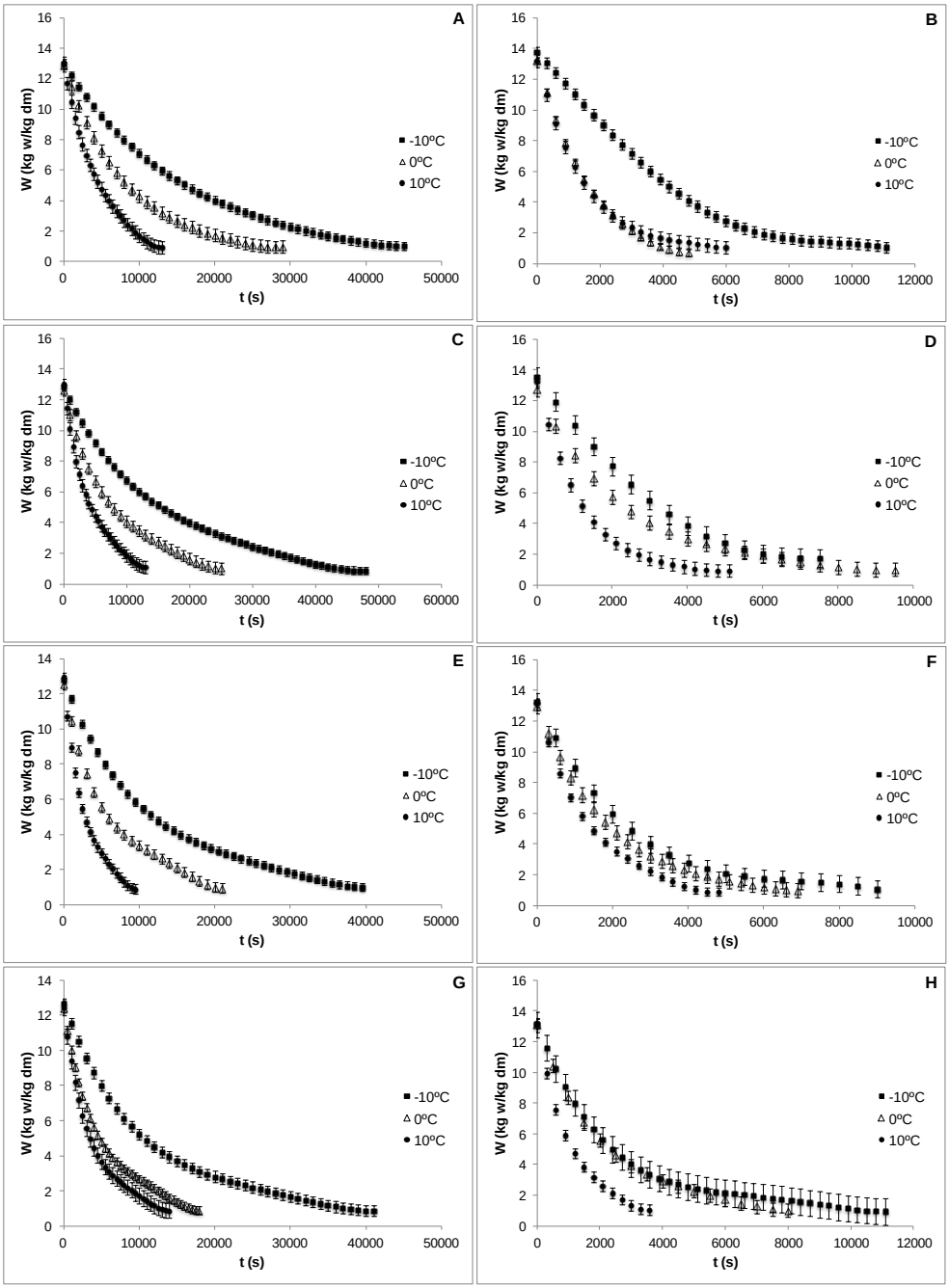

Figure 3. Drying kinetics of eggplant at different temperatures (-10, 0 and 10ºC). A: 1 m/s, 0 W (AIR); B: 1 m/s, 50 W (AIR+US); C: 2 m/s, 0 W (AIR); D: 2 m/s, 50 W (AIR+US); E: 4 m/s, 0 W (AIR); F: 4 m/s, 50 W (AIR+US); G: 6 m/s, 0 W (AIR); H: 6 m/s, 50 W (AIR+US). Error bars show the differences between experimental data and the polynomial equation.

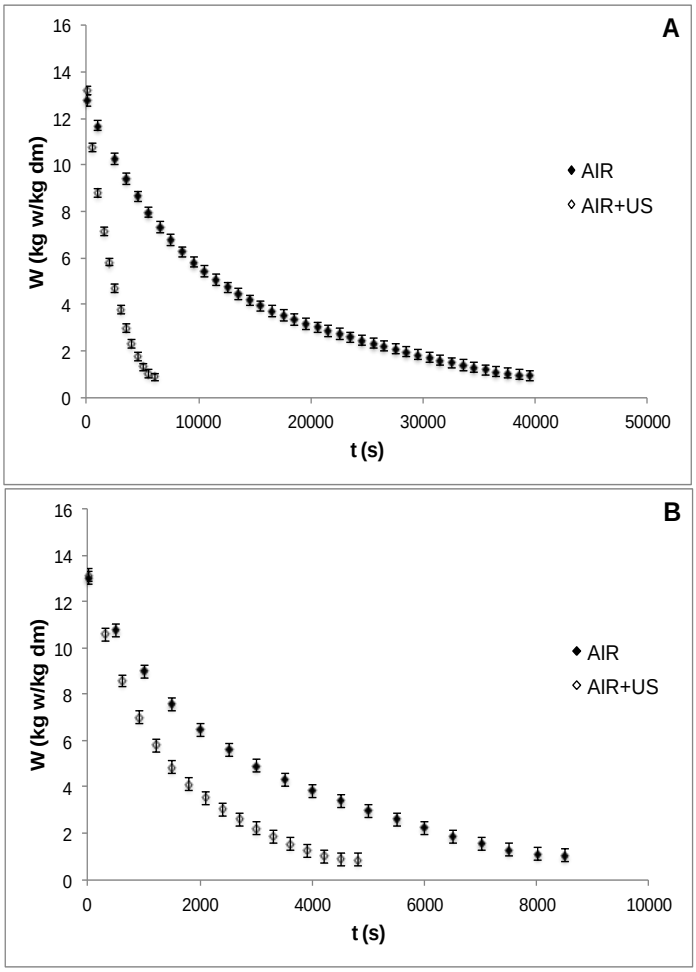

Figure 4. Drying kinetics of eggplant without (AIR, 0 W) and with (AIR+US, 50 W) US application. A: 4 m/s, -10ºC; B: 4 m/s, 10ºC. Error bars show the differences between experimental data and the polynomial equation.

3.2. Modeling of the drying kinetics

The diffusion model considered showed a good fit to the experimental data, with percentages of explained variance (VAR) of over 99% and mean relative errors (MRE) of under 9% in every case (Table 1). Moreover, this model allowed the identification of the effective moisture diffusivity (D_{ed}) and the external mass transfer coefficient (k), the drying parameters inversely linked to the internal and external resistances to water transfer, respectively. These parameters were

analyzed in order to compute the influence of the drying conditions (air velocity, temperature and US application) on the drying rate.

The D_{ed} identified for AIR experiments (Table 1) ranged between $1.2x10^{-10}$ m^2/s (-10ºC; 2 m/s) and $5.7x10^{-10}$ m^2/s (10ºC; 4 m/s). These values are higher than those reported by Santacatalina et al. (2014) when performing the LTD of apple, probably due to the greater porosity of eggplant (Ozuna et al., 2014b) that makes it easier for the water to flow out of the solid matrix. Despite the fact that the increase in air velocity shortened the drying process of eggplant, the ANOVA reflected that this influence was non-significant ($p<0.05$) as regards the D_{ed} parameter (Table 1), which points to the fact that internal water transfer is not dependent on the air flow rate. However, the air temperature significantly ($p<0.05$) influenced the D_{ed}; therefore, the higher the temperature, the higher the identified D_{ed} value (Table 1). These effects that the drying conditions had on D_{ed} were consistent with those reported by Santacatalina et al. (2015) in the case of the atmospheric freeze drying of apple at different air velocities and temperatures.

US application significantly ($p<0.05$) increased the D_e (Table 1), the average improvement ranging from 153 to 824% (Table 1). Previous studies have shown that the improvement in D_{ed} brought about by US application is linked to the mechanical effects provoked in the material (Garcia-Perez et al., 2009). Power ultrasound generates alternating expansions and contractions when travelling in a medium (Riera et al., 2011); this mechanical stress facilitates the water movement to the product surface. In addition, the thermal effect of air-borne ultrasonic application has also been documented (Garcia-Perez et al., 2013; Bantle and Hanssler, 2013), which would also contribute to the kinetic improvement linked to US application. Thus, Bantle and Hanssler (2013) reported an increase of approximately 5ºC in US drying of clipfish at 10, 20 and 30ºC. While, Garcia-Perez et al. (2013) found an increase of air temperature of up to 10ºC by US application in hot air drying of grape stalk. The temperature rise would contribute to increase the evaporation/sublimation rates and the inner water diffusion. Although, it should be mentioned that this thermal effect would be dependent on the product being dried and the US device used as well as the process variables involved (air temperature, velocity and ultrasonic power). Further studies should assess the importance of the thermal effect and its comparison with the mechanical stress.

Table 1. Modeling of drying kinetics of eggplant at different air velocities (1, 2, 4 and 6 m/s) and temperatures (10, 0 and -10ºC) without (AIR, 0 W) and with (AIR+US, 50 W) US application. Average values and standard deviation are shown for the effective moisture diffusivity (D_{ed}) and mass transfer coefficient (k). VAR (%) is the percentage of explained variance and MRE (%) the mean relative error. ΔD_{ed} and Δk report (as a percentage) the increase in a kinetic parameter as the result of ultrasound application.

			1 m/s	2 m/s	4 m/s	6 m/s
10ºC	AIR	D_{ed} (10^{-10} m^2/s)	4.5 ± 0.3^{a}	4.0 ± 0.4^{a}	5.7 ± 0.2^{a}	4.6 ± 0.6^{a}
		k (10^{-3} kg w/m^2s)	1.3 ± 0.2^{A}	1.6 ± 0.2^{A}	2.5 ± 0.4^{B}	2.5 ± 0.3^{B}
		VAR (%)	99.7	99.5	99.6	99.2
		MRE (%)	4.8	6.1	5.7	7.5
	AIR +US	D_{ed} (10^{-10} m^2/s)	16.5 ± 0.4^{b}	18.4 ± 0.5^{bc}	14.5 ± 0.4^{bc}	16.1 ± 0.5^{c}
		k (10^{-3} kg w/m^2s)	4.8 ± 0.4^{C}	5.2 ± 0.5^{CD}	5.2 ± 0.7^{DE}	6.1 ± 0.3^{E}
		VAR (%)	99.9	99.8	99.8	99.8
		MRE (%)	3.7	6.4	4.6	4.9
		ΔD_{ed} (%)	264	357	153	250
		Δk (%)	262	228	106	144
0ºC	AIR	D_{ed} (10^{-10} m^2/s)	2.2 ± 0.4^{a}	2.0 ± 0.4^{a}	2.3 ± 0.2^{a}	2.8 ± 0.4^{a}
		k (10^{-3} kg w/m^2s)	0.8 ± 0.1^{A}	1.0 ± 0.1^{AB}	1.4 ± 0.2^{BC}	1.8 ± 0.4^{C}
		VAR (%)	99.7	99.1	99.1	99.1
		MRE (%)	6.0	8.1	7.9	6.9
	AIR +US	D_{ed} (10^{-10} m^2/s)	10.8 ± 0.8^{ab}	10.7 ± 0.6^{b}	9.7 ± 0.2^{b}	7.2 ± 0.1^{b}
		k (10^{-3} kg w/m^2s)	3.7 ± 0.5^{D}	3.5 ± 0.6^{D}	3.6 ± 0.5^{D}	3.2 ± 0.3^{D}
		VAR (%)	99.6	99.3	99.6	99.5
		MRE (%)	3.7	7.9	10.8	8.2
		ΔD_{ed} (%)	389	435	324	157
		Δk (%)	383	251	153	79
-10ºC	AIR	D_{ed} (10^{-10} m^2/s)	1.4 ± 0.4^{a}	1.2 ± 0.1^{a}	1.3 ± 0.1^{a}	1.5 ± 0.2^{a}
		k (10^{-3} kg w/m^2s)	0.4 ± 0.1^{A}	0.5 ± 0.1^{A}	0.7 ± 0.2^{AB}	0.9 ± 0.2^{B}
		VAR (%)	99.8	99.5	99.6	99.7
		MRE (%)	4.1	6.4	7.6	4.1
	AIR +US	D_{ed} (10^{-10} m^2/s)	8.4 ± 0.8^{b}	11.1 ± 0.4^{b}	10.0 ± 0.3^{b}	10.9 ± 0.5^{b}
		k (10^{-3} kg w/m^2s)	1.5 ± 0.3^{C}	2.2 ± 0.3^{D}	3.1 ± 0.1^{E}	3.6 ± 0.8^{F}
		VAR (%)	98.7	99.5	99.9	99.7
		MRE (%)	7.6	4.6	3.8	4.3
		ΔD_{ed} (%)	485	824	645	631
		Δk (%)	227	322	313	271

Superscript letters (a, b, c) and (A, B, C, D, E, F) show homogeneous groups, established from LSD (Least Significance Difference) intervals ($p<0.05$) at every temperature, for D_{ed} and k, respectively.

As regards the external mass transfer coefficient, both air velocity and temperature were shown to have a significant ($p<0.05$) influence in the AIR experiments; thus, the higher the air velocity and temperature, the higher the k parameter (Table 1). Santacatalina et al. (2014) and Garcia-Perez et al. (2012) obtained similar values of k to those reported in this study when carrying out LTD drying of carrot, eggplant

and apple. In AIR+US experiments, the influence of air velocity and temperature was similar to that found in AIR experiments except for those carried out at 0ºC, where the effect of air velocity was negligible. The US application provoked a significant ($p<0.05$) increase in k (Table 1), which ranged between 79% (0ºC; 6 m/s) and 383% (0ºC; 1 m/s). This increase is linked to the decrease in the external resistance to water transfer due to the reduction of the boundary layer caused by the pressure variations, oscillating velocities and microstreaming that US generates on the solid-gas interfaces (Ozuna et al., 2014a). As for AIR+US experiments at 0ºC, it can be observed that the higher the air velocity, the lower the increase in k. This could be linked to the disruption of the ultrasonic field by the high air flow rates. Low air flow rates would not affect the ultrasonic field; thus, a greater amount of ultrasonic energy is available to increase the drying rate than at high air velocities (Garcia-Perez et al., 2006). Moreover, high air velocities reduced the external resistance because they increased the air turbulence and, therefore, the scope for improvement is narrower at these velocities.

It should be noted that US application led to a greater increase in D_{ed} than in k (Table 1) under every drying condition. This suggests that ultrasound effects had a greater influence on internal transport than on external. Therefore, ultrasound application reduced the relative importance of diffusion in mass transport and, as a consequence, increased the relative influence of convection in drying. The greatest differences between the degree to which D_{ed} and k improved were found at -10ºC because atmospheric freeze drying generates a very porous external layer that is more prone to the effects of ultrasound because more acoustic energy is absorbed into the particle (Ozuna et al., 2014b).

3.3. Rehydration

The rehydration ability of dried eggplant was assessed from the experimental determination of the rehydration kinetics. The fit of a diffusion model to experimental data permitted the identification of the effective moisture diffusivity (D_{er}) and the equilibrium moisture content (W_e), parameters which are directly linked to the water absorption rate and the rehydration capacity, respectively. Thus, the proposed diffusion model fitted the experimental rehydration kinetics

appropriately, providing VAR of over 95% and MRE of under 10% (Table 2). The agreement between the experimental and calculated data can also be observed in Figure 5.

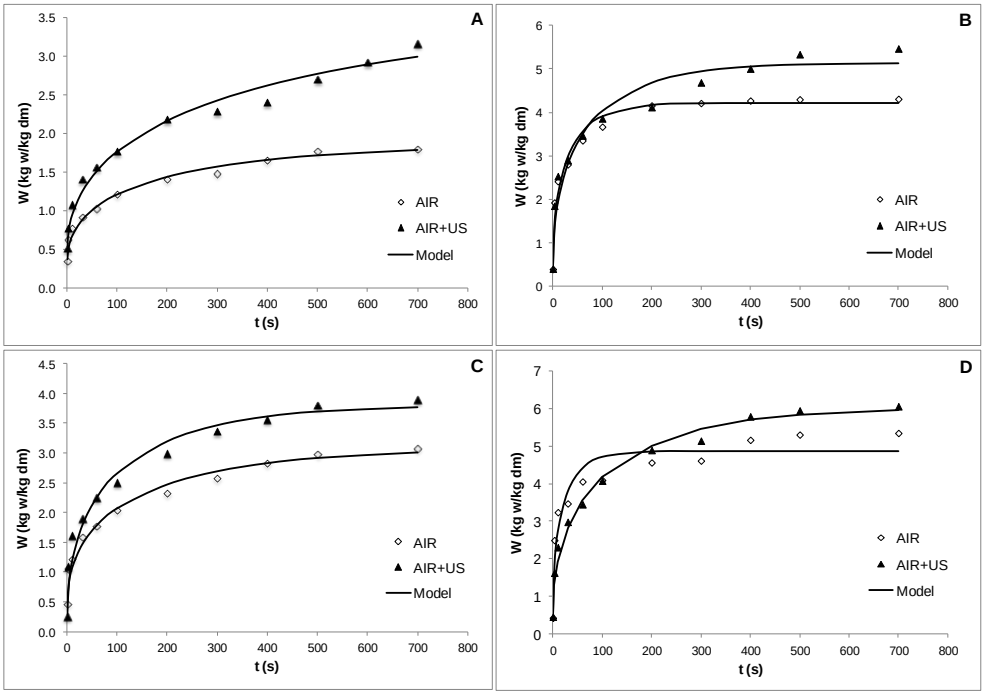

Figure 5. Rehydration kinetics of eggplant dried without (AIR, 0 W) and with (AIR+US, 50 W) US application and diffusion model. A: 1 m/s, 10ºC; B: 1 m/s, -10ºC; C: 6 m/s, 10ºC; B: 6 m/s, -10ºC.

Compared with the drying process, rehydration was a faster operation regardless of the drying condition used (Figure 5). Thus, the dried eggplant was totally rehydrated in less than 700 s (approximately 12 min). This was confirmed by the high identified D_{er} values, which were over 10^{-8} m^2/s (Table 2). The air velocity used in AIR experiments had no significant ($p<0.05$) effect on the D_{er} identified in the subsequent rehydration. Thus, the increase in air velocity gave rise to the D_{er} identified at -10ºC, whereas, at 10ºC, the opposite behavior was found. On the contrary, the influence of the drying temperature on D_{er} was significant ($p<0.05$). In this sense, the D_{er} identified for the experiments carried out at -10ºC was higher than those obtained at 0 and at 10ºC (Table 2). These results could be explained by the highly porous structure caused by the water sublimation at -10ºC, due to the

fact that the sample shrinkage is almost negligible (Stawczyk et al., 2007), which makes the water transfer faster. The effect of the temperature was also observed in the W_e; thus, in AIR samples, the lower the temperature, the higher the identified W_e (Table 2). Therefore, the samples dried at -10ºC rehydrated more and faster than those dried at 10ºC.

Table 2. Modeling of rehydration kinetics of eggplant dried at different air velocities (1, 2, 4 and 6 m/s) and temperatures (10, 0 and -10ºC) without (AIR, 0 W) and with (AIR+US, 50 W) US application. Average values and standard deviation are shown for the effective moisture diffusivity (D_{er}) and equilibrium moisture content (W_e). VAR (%) is the percentage of explained variance and MRE (%) the mean relative error.

			1 m/s	2 m/s	4 m/s	6 m/s
10ºC	AIR	D_{er} (10^{-8} m^2/s)	2.9 ± 0.9^{b}	1.2 ± 0.3^{b}	1.9 ± 0.2^{b}	1.2 ± 0.1^{ab}
		W_e (kg w/kg dm)	2.9 ± 0.4^{AB}	2.4 ± 0.4^{A}	4.5 ± 0.1^{C}	3.2 ± 0.2^{B}
		VAR (%)	98.3	97.9	97.3	97.9
		MRE (%)	4.3	6.6	8.1	6.0
	AIR+ US	D_{er} (10^{-8} m^2/s)	0.5 ± 0.2^{a}	1.2 ± 0.2^{ab}	1.9 ± 0.6^{ab}	1.5 ± 0.1^{ab}
		W_e (kg w/kg dm)	3.1 ± 0.6^{B}	1.9 ± 0.3^{A}	3.5 ± 0.1^{BC}	3.8 ± 0.1^{BC}
		VAR (%)	98.1	97.8	96.1	96.8
		MRE (%)	6.9	8.3	8.6	9.6
0ºC	AIR	D_{er} (10^{-8} m^2/s)	1.1 ± 0.5^{a}	1.2 ± 0.3^{a}	0.9 ± 0.4^{a}	1.3 ± 0.2^{a}
		W_e (kg w/kg dm)	3.1 ± 0.2^{B}	2.9 ± 0.3^{AB}	3.1 ± 0.4^{B}	2.5 ± 0.2^{AB}
		VAR (%)	98.1	98.3	98.0	97.7
		MRE (%)	7.0	6.2	5.7	8.1
	AIR+ US	D_{er} (10^{-8} m^2/s)	1.6 ± 0.5^{a}	1.4 ± 0.7^{a}	0.9 ± 0.3^{a}	1.4 ± 0.3^{a}
		W_e (kg w/kg dm)	2.5 ± 0.5^{A}	2.9 ± 0.3^{AB}	2.4 ± 0.4^{AB}	2.2 ± 0.4^{A}
		VAR (%)	94.8	97.6	96.4	97.3
		MRE (%)	7.9	6.0	7.8	5.6
-10ºC	AIR	D_{er} (10^{-8} m^2/s)	2.6 ± 0.2^{ab}	3.3 ± 0.9^{ab}	5.1 ± 0.5^{ab}	5.9 ± 0.9^{b}
		W_e (kg w/kg dm)	3.4 ± 0.2^{A}	3.3 ± 0.4^{A}	6.6 ± 0.4^{B}	4.7 ± 0.5^{A}
		VAR (%)	97.3	93.8	91.1	91.4
		MRE (%)	7.6	8.0	8.9	9.9
	AIR+ US	D_{er} (10^{-8} m^2/s)	3.2 ± 0.9^{ab}	2.9 ± 0.8^{ab}	4.7 ± 0.5^{ab}	1.3 ± 0.1^{a}
		W_e (kg w/kg dm)	3.9 ± 0.7^{A}	3.2 ± 0.6^{A}	3.4 ± 0.4^{A}	6.5 ± 0.7^{B}
		VAR (%)	95.0	93.6	95.4	96.9
		MRE (%)	9.7	9.2	7.5	9.7

Superscript letters (a, b) and (A, B, C) show homogeneous groups, established from LSD (Least Significance Difference) intervals ($p<0.05$) at every temperature, for D_{er} and W_e, respectively.

The application of US during drying increased the D_{er} in the rehydration, but this increase was not significant ($p<0.05$), probably due to the highly variable nature of eggplant (Table 2). The reason for this higher value of D_{er} could be linked to the generation of microchannels in the dried samples produced by US application that make it easier for the water to be absorbed during the subsequent rehydration

(Mulet et al., 2011). Moreover, US application was found to have no significant ($p<0.05$) influence on W_e (Table 2). Therefore, this indicates that although US application caused a faster water inlet (higher D_{er}) it did not lead to greater water absorption (no influence on W_e) during rehydration.

3.4. Hardness of rehydrated samples

The hardness of the fresh and rehydrated eggplant was measured by means of simple compression tests in order to quantify the influence of the drying conditions in the texture (Figure 6). In general terms, fresh eggplant samples were significantly ($p<0.05$) harder (15.7±2.6 N) than the rehydrated ones (8.7±1.2 N). The hardness of AIR samples ranged between 8.3 and 10.4 N and between 6.5 and 10.3 N for the AIR+US ones. The softening of the rehydrated samples could be due to the structural degradation caused by the drying process (Puig et al., 2012) that constrains the recovery of the initial texture.

The drying conditions tested did not affect the hardness of the rehydrated samples. Thus, no significant ($p<0.05$) influence of either air velocity, temperature or US application was found on the experimental values measured (Figure 6). Therefore, the possible changes produced by the drying temperature or US application in the internal structure of the samples, which, as shown before, affected the rehydration capacity, were not enough to influence the final hardness of the rehydrated eggplant.

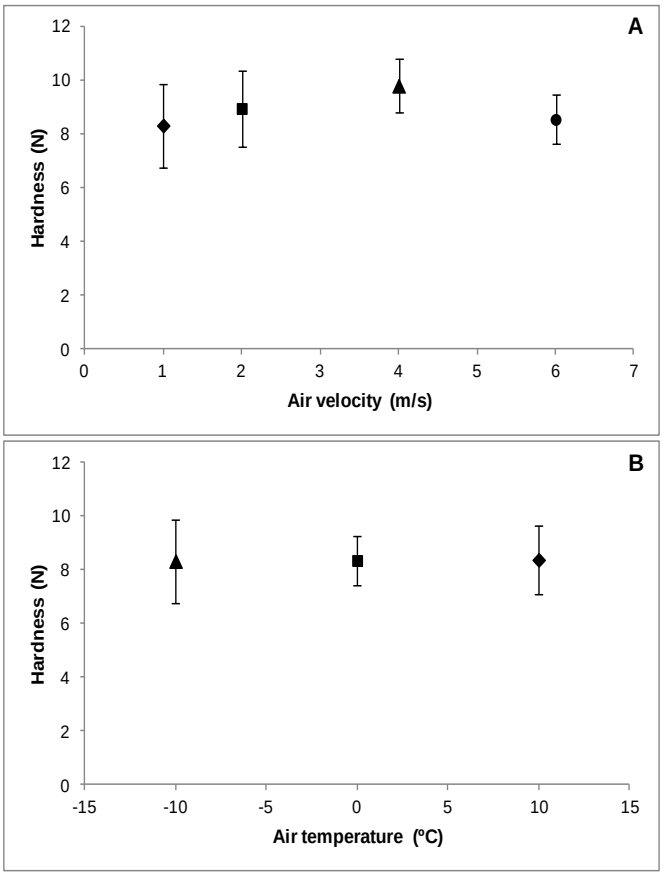

Figure 6. Hardness of rehydrated eggplant dried at -10ºC and different air velocities (A) and at 1 m/s and different temperatures (B) without US application (AIR samples).

3.5. Absorption capacity of olive oil

The absorption of olive oil in dried eggplant was so fast that it was completed in a few seconds. This made the experimental determination of the absorption kinetics non-feasible. Therefore, the absorption capacity (AC) of olive oil was estimated as the weight increase (as a percentage with respect to the initial weight) after 60 s of immersion.

In general terms, the air velocity and temperature used during drying did not cause significant ($p<0.05$) differences in the AC of eggplant (Figure 7). The application of US increased the AC, especially in eggplant samples dried at -10ºC; however, these differences were not significant ($p<0.05$), probably due to the highly variable

nature of the experimental data, as already stated for other aspects in this paper. As an example, the AC of eggplant samples dried at -10ºC and 1 m/s without and with US application was 263.5±16.2% and 292.7±16.8%, respectively. At -10ºC, the high porosity generated by the formation of ice crystals and the subsequent sublimation (Voda et al., 2012) could also increase the AC of olive oil of these samples. Therefore, as occurred in the case of hardness, the structural changes produced by the different drying conditions tested, particularly the effect of the air drying temperature and US application, were not enough to produce significant changes in the AC of the olive oil in the dried samples. In any case, further research will be necessary to determine the influence of the drying conditions on the microstructure of dried eggplant.

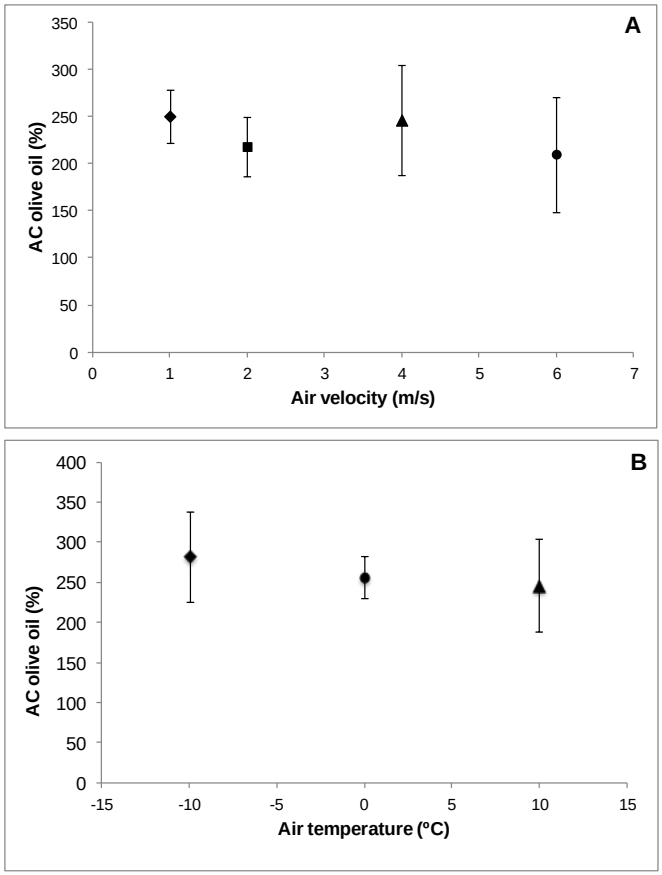

Figure 7. Absorption capacity (AC) of olive oil in eggplant dried at 10ºC and different air velocities (A) and at 4 m/s and different temperatures (B) without US application (AIR samples).

4. Conclusions

In this study, the influence of different processing variables (air velocity, temperature and US application) on the kinetics of the LTD of eggplant was assessed, as were some quality aspects. The application of US increased the drying rate, shortening the drying time by as much as 87%. In addition, ultrasound decreased the influence of both air velocity and temperature on the LTD kinetics. As far as the quality aspects are concerned, the processing variables did not show a significant ($p<0.05$) influence either on the hardness of the rehydrated samples or on the absorption capacity of olive oil. The rehydration capacity was only significantly ($p<0.05$) influenced by the drying temperature. Therefore, US could be considered a feasible technology with which to intensify the low temperature drying of high quality foodstuffs. Further studies should elucidate if the kinetic improvement linked to the ultrasonic application is accompanied by an energy saving.

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IMPACT OF APPLIED ULTRASONIC POWER ON THE LOW TEMPERATURE DRYING OF APPLE

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IMPACT OF APPLIED ULTRASONIC POWER ON THE LOW TEMPERATURE DRYING OF APPLE

Abstract

Low temperature drying (LTD) allows high-quality dried products to be obtained, preserving the nutritional properties of fresh foods better than conventional drying, but it is a time-consuming operation. Power ultrasound (US) could be used to intensify LTD, but it should be taken into account that process variables, such as the level of applied power, have an influence on the magnitude and extension of the ultrasonic effects. Therefore, the aim of this work was to assess the influence of the level of applied ultrasonic power on the LTD of apple, analyzing the drying kinetics and the quality of the dried product. For that purpose, apple (*Malus domestica* cv. Granny Smith) cubes (8.8 mm side) were dried (2 m/s) at two different temperatures (10 and -10ºC), without and with (25, 50 and 75 W) US application. In the dried apple, the rehydration kinetics, hardness, total phenolic content, antioxidant capacity and microstructure were analyzed to evaluate the impact of the level of applied ultrasonic power.

At both temperatures, 10 and -10ºC, the higher the ultrasonic power level, the shorter the drying time; the maximum shortening of the drying time achieved was 80.3% (at -10ºC and 75 W). The ultrasonic power level did not significantly ($p<0.05$) affect the quality parameters analyzed. Therefore, US could be considered a non-thermal method of intensifying the LTD of fruits, like apple, with only a mild impact on the quality of the dried product.

Keywords: Drying kinetics; Dehydration; Power ultrasound; Modeling; Quality

1. Introduction

Apple is one of the most widely-produced fruits in the world and is consumed not only as a fresh fruit but also in processed forms, such as juice and jam. In this sense, numerous prepared foods, such as snacks, whole grain breakfast cereals, functional foods or instant baby food (Doymaz, 2009), contain dried apple portions. Apple has been identified as one of the main dietary sources of fiber and phenolic compounds (Khanizadeh et al., 2008), which have very interesting antioxidant properties (Van der Sluis et al., 2002; Vrhovsek et al., 2004). However, apple processing can have a great impact on the antioxidant potential (Van der Sluis et al., 2002), as well as on other quality traits. In particular, drying provokes a series of changes in materials, such as oxidation, browning, shrinkage, softening and the loss of nutritional-functional properties (Beck et al., 2014; Vega-Gálvez et al., 2009). Microstructure is also modified by water removal (Rodríguez et al, 2014) which could reduce the rehydration capacity of dried products and affect the extractability of target compounds. Therefore, the search for alternative means of dehydration is a relevant subject for research; for example, exploring the use of the so-called non-thermal technologies to reduce the loss of heat sensitive bioactive compounds (Chantaro et al., 2008; Romero and Yépez, 2015).

Low temperature drying (LTD) was defined as a convective drying process carried out at temperatures below standard room conditions (20ºC) (Santacatalina et al., 2014). Thereby, the temperature range covered by LTD covers figures both above and below the product's freezing point (Ozuna et al., 2014a). In this last case, the process is also known as atmospheric freeze drying (AFD) (Claussen et al., 2007) because water removal occurs by sublimation at atmospheric pressure. The cold air used in LTD reduces the negative impact of hot air drying on the nutritional properties of fresh foods. However, LTD is a time-consuming operation, which is the reason for the great interest in its intensification. Power ultrasound (US) has been applied during the hot air drying of different products, such as fruits or vegetables, and proved to be highly effective at shortening the drying time (Gallego-Juárez et al., 2007; Garcia-Perez et al., 2007). The effects of US on mass transfer are mainly mechanical, with a mild thermal effect (Gallego-Juárez et al., 2010; Riera et al., 2011). For this reason, US application represents an interesting method of non-thermal intensification for LTD (Cárcel et al., 2011). In this sense,

during the AFD of apple, Santacatalina et al. (2015) observed that the effect of US application on the drying time was more marked than other factors, such as air temperature or velocity. During the AFD (-6ºC) of peas, Bantle and Eikevik (2011) reported an increase of 14.6% in the diffusion coefficient linked to US application. Meanwhile, Garcia-Perez et al. (2012) achieved an increase in effective diffusivity of around 400% during the drying of apples, carrot and eggplants at -14ºC. The ultrasonic performance variable found in the literature for LTD applications could be linked to the efficiency of the transducer used, and so to the different ultrasonic power applied. As far as we are concerned, unlike other US applications in food processing (Awad et al., 2012; Chemat et al., 2011; Ozuna et al., 2014b), neither the influence which the level of applied ultrasonic power has on LTD kinetics nor its effect on product quality have been reported. Therefore, the aim of this work was to evaluate the impact of the level of applied ultrasonic power on the low temperature drying of apple, focusing particularly on both the kinetics and quality parameters of the dried product.

2. Materials and methods

2.1. Raw material

Apples (*Malus domestica* cv. Granny Smith) were purchased in a local market (Valencia, Spain). Fruit pieces were selected to obtain a homogeneous batch in terms of ripeness, size and color, and held at 4±1ºC until processing. Cubic samples (8.8 mm side) were obtained from the flesh using a household tool. Samples to be dried at 10ºC were immediately processed, while those dried at -10ºC were wrapped with plastic film and frozen by placing in a freezing room at -18±1ºC until processing (24 h). The initial moisture content was measured by placing samples in a vacuum oven at 70ºC and 200 mmHg until constant weight, following standard method no. 934.06 (AOAC, 1997).

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation (Figure 1), already described in the literature (Garcia-Perez et al., 2012). The

system provides automatic air velocity and temperature control and a drying chamber excited by an ultrasonic transducer. Air-borne ultrasound is transmitted from the walls of the drying chamber to the air, finally reaching the samples. The system is able to generate an acoustic field (21.9 kHz) of 155 db inside the chamber with an electric power input of 90 W.

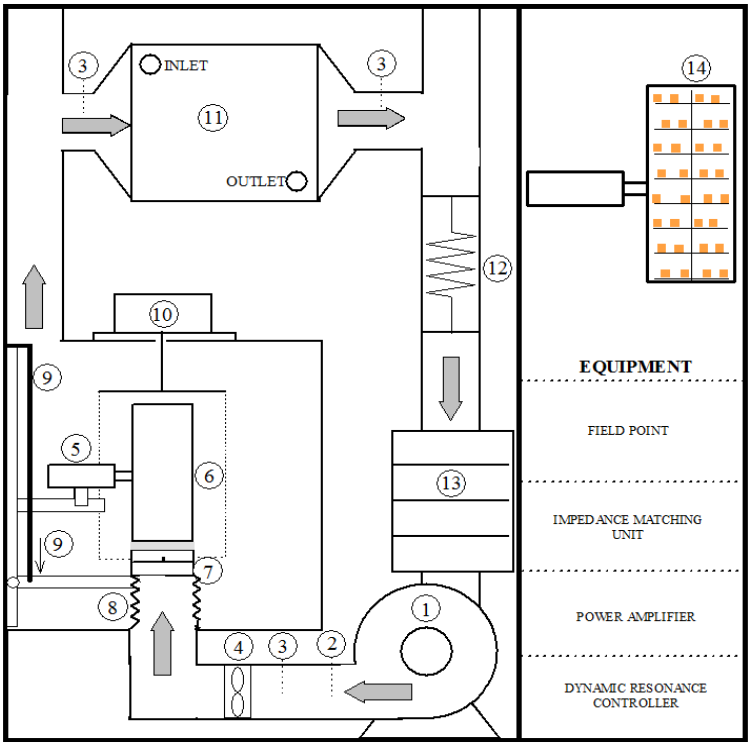

Figure 1. Diagram of the ultrasonically assisted convective drier: 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer; 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe; 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13, desiccant tray chamber; 14, details of the sample load on the trays.

The drying experiments were carried out at constant air velocity (2 m/s). The relative humidity of air was maintained below 15±5% and the initial mass load density was 9.5 kg/m^3. The experiments were conducted at two different temperatures (10 and -10ºC), without (0 W) and with US application at three different power levels, which was modulated by supplying different electric powers (25, 50 and 75 W) to the ultrasonic transducer. Drying kinetics were determined

from the initial moisture content of the apple and by automatically weighing samples at preset times. Every drying condition was tested, at least three times and the drying experiments were extended until the samples lost 80% of the initial weight.

2.3. Modeling of drying kinetics

The modeling of the drying kinetics only focused on quantifying the effect of the drying conditions tested on the overall mass transport. For that purpose, a diffusion model was used to describe the drying kinetics of apple cubes, considering the effective moisture diffusivity to be constant, the temperature uniform and the shrinkage negligible. Thus, the governing equation of diffusion (Equation 1) is written as follows:

$$\frac{\partial W_p(x,y,z,t)}{\partial t} = D_e\left(\frac{\partial^2 W_p(x,y,z,t)}{\partial x^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial y^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial z^2}\right) \quad (1)$$

where W_p is the local moisture (kg water/kg dry matter, dm), t is the drying time (s), D_e is the effective moisture diffusivity (m^2/s) and x, y and z represent the characteristic mass transport pathways in the cubic geometry (m).

In order to solve Equation 1, the initial moisture was assumed to be uniform and the symmetry was considered in x, y, z. directions. The moisture transport was assumed to be jointly controlled by diffusion and convection; the latter is included in the model by the boundary condition shown in Equation 2 for the x coordinate. Thus, the diffusion model permits the quantification of both the effective diffusivity and the external mass transfer coefficient (k, kg water/m^2s):

$$t > 0 \qquad x = L \qquad -D_e\rho_{ds}\frac{\partial W_p(L,y,z,t)}{\partial x} = k(a_w(L,y,z,t) - \varphi_{air}) \quad (2)$$

where ρ_{ds} is the dry solid density (kg dm/m^3) and φ_{air} is the relative humidity of the drying air. The water activity on the surface of the material (a_w (L,y,z,t)) was estimated from the sorption isotherm data at 10ºC reported in the literature (Veltchev and Menko, 2000).

The fact of considering the samples as homogeneous and isotropic is valid for drying experiments carried out at 10ºC. However in the drying experiments at -10ºC, where samples were frozen before drying, two main zones could be distinguished in the particle: an inner frozen core and an outer dry layer. Sublimation occurs at the interface and vapor only diffuses in the outer layer, which becomes thicker as drying progresses. Then, in the experiments at -10ºC, the proposed diffusion model just becomes an empirical approach. A more mechanistic approach for modeling AFD experiments was addressed by Santacatalina et al. (2015). However, the proposed diffusion model allowed the effect of the studied variables in the drying kinetics to be compared and quantified, which was, in the present work, the main goal of the modeling.

The diffusion model was numerically solved by applying an implicit finite difference method (Garcia-Perez et al., 2012), for which a computational algorithm was written in MATLAB 7.13.0.564 (The MathWorks, Inc., Natick, MA, USA). An optimization problem was defined for the purpose of fitting the model to the experimental data,. The objective function was the sum of the squared differences between the experimental (W_{exp}) and the calculated (W_{calc}) average moisture contents. The kinetic parameters, D_e and k, were jointly identified by minimizing the objective function using the SIMPLEX method. The model was fitted to each drying run and the kinetic parameters averaged. The percentage of explained variance (VAR, Equation 3) and the mean relative error (MRE, Equation 4) were calculated in order to determine the goodness of the fit.

$$VAR(\%) = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \tag{3}$$

$$MRE(\%) = \frac{100}{N}\left[\sum_{i=1}^{N} \frac{|W_{ei} - W_{ci}|}{W_{ei}}\right] \tag{4}$$

where S_{xy} and S_y are the standard deviation of the estimation and the sample, respectively, W_{ei} and W_{ci} are the experimental and calculated average moisture contents (kg water/kg dm) and N is the number of experimental data.

2.4. Rehydration experiments

The dried apple samples were rehydrated in distilled water at 25±1ºC using a thermostatic bath. During rehydration, samples were taken out of the bath at preset times (0, 20, 100, 360, 600, 900, 1200, 1800, 2400, 3600 and 4800 s), blotted with tissue paper to remove the surface water and weighed so as to estimate the net weight increase (ΔW). 20 cubes of dried apple (2.16±0.24 g) were used for each run and three replicates were carried out for each drying condition tested.

2.5. Hardness

The textural properties of fresh and rehydrated apple samples were measured using a texturometer (TA-XT2, SMS, Godalming, UK) provided with a load cell of 25 kg. Simple compression tests were carried out at constant temperature (16±1ºC) using a flat 75 mm diameter aluminum plunger (SMS P/75) and a compression ratio of 80%. The hardness was computed from the force/deformation profiles as the maximum force achieved. At least 30 cubes were analyzed for each set of samples (fresh apple and each drying condition tested).

2.6. Antioxidant potential

The antioxidant potential of fresh and dried apple samples was estimated from the measurement of the total phenolic content and the antioxidant capacity. The pre-treatment consisted of placing the samples (1 g for fresh apple and of 0.5 g for dried samples) in flasks with 10 mL of an ethanol-water solution (80:20, v/v). The mixture was homogenized using a blender (T25 Digital, IKA, Staufen, Germany) at 13,000 rpm for 1 min. Then, the solution was filtered (nylon, 0.45 µm) and the obtained extract was placed in opaque vials at 4ºC until the measurement of phenolic content and antioxidant capacity was carried out.

2.6.1. Total phenolic content measurement (TPC)

The phenolic content was determined by means of the Folin-Ciocalteu method (Singleton et al., 1999). For that purpose, 100 µL of extract were mixed with 200 µL

of Folin-Ciocalteu's phenol reagent (Sigma-Aldrich, Madrid, Spain) and 2 mL of distilled water. After 3 min at 25ºC, 1 mL of Na_2CO_3 (Panreac, Barcelona, Spain) solution (Na_2CO_3-water 20:80, p/v) was added to the mixture. The reaction was kept in the dark at room temperature for 1 h. Finally, the absorbance was read at 765 nm using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK). The measurements were carried out in triplicate. The standard curve was previously prepared using solutions of known concentrations of gallic acid hydrate (Sigma-Aldrich, Madrid, Spain) in ethanol-water (80:20, v/v). Results were expressed as mg of gallic acid (GAE) per g of dried matter (dm) of apple.

2.6.2. Antioxidant capacity measurement (AC)

The antioxidant capacity of apple extracts was determined by using the Ferric-reducing ability power (FRAP) method based on the procedure described by Benzie and Strain (1996) with some modifications. For that purpose, 900 µL of freshly prepared FRAP reagent were mixed with 30 µL of distilled water and 30 µL of sample extract or water as reagent blank and kept at 37°C for 30 min. The FRAP reagent contained 2.5 mL of a 10 mM TPTZ (Fluka, Steinheim, Germany) solution in 40 mM HCl (Panreac, Barcelona, Spain) plus 2.5 mL of 20 mM $FeCl_3 \bullet 6H_2O$ (Panreac, Barcelona, Spain) and 2.5 mL of 0.3 M acetate buffer (Panreac, Barcelona, Spain), pH 3.6 (Pulido et al., 2000). Readings were taken at the maximum absorption level (595 nm) using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK). Three replicates were carried out for each measurement. The antioxidant capacity was evaluated through a calibration curve, which was previously determined using solutions of ethanol-water (80:20, v/v) of known Trolox (Sigma-Aldrich, Madrid, Spain) concentration and expressed as mg Trolox per g of dried matter (dm) of apple.

2.6.3. Degradation of TPC and AC

The relative degradation (%Degradation, Equation 5) was computed in order to quantify the influence of both the temperature and the level of applied ultrasonic power during drying on TPC and AC:

$$\%\text{Degradation} = \frac{(C_0 - C_f)}{C_0} \cdot 100 \quad (5)$$

where C_0 and C_f are the initial (fresh product) and the final (dried product) TPC or AC.

2.7. Cryo-scanning electron microscopy (Cryo-SEM)

The microstructure of the dried apple was studied using Cryo-SEM (Salvador et al., 2008). The analysis was carried out in a section of the sample. The experimental setup involves a cryostage (CT-15000 C, Oxford Instruments, Witney, UK) coupled to a scanning electron microscope (JSM-5410, Jeol, Tokyo, Japan). Samples were immersed in slush N_2 (at -210°C) and then quickly transferred to the cryostage at 1 kPa, where sample fracture took place at -180ºC. The sublimation was carried out at -95°C and finally, the sample was gold-coated using an ionization current of 2 mA and applying vacuum (0.2 kPa) for 3 min, in order to allow the cross-section visualization. The microscopic observations in the scanning electron microscope were carried out at 10 kV, -130ºC and at a working distance of 15 mm.

2.8. Statistical analysis

An analysis of variance (ANOVA) ($p<0.05$) was carried out and LSD (Least Significant Difference) intervals were assessed using the statistical package Statgraphics Centurion XVI (Statpoint Technologies Inc., Warrenton, VA, USA) in order to determine if the operating conditions studied (temperature and ultrasonic power applied) significantly ($p<0.05$) influenced the D_e and k parameters. Likewise, the influence of the drying conditions on the rehydration capacity, hardness, TPC and AC of the samples dried under different conditions was also analyzed. In addition, a principal component analysis (PCA) was carried out in order to identify significant relationships among the different variables measured: drying time, weight increase during rehydration, hardness, TPC and AC. The PCA was also performed using the Statgraphics Centurion XVI software.

3. Results and discussion

3.1. Drying experiments

The US application during LTD of apple increased the drying rate at both temperatures tested, 10 and -10ºC (Figure 2). Thus, applying a power level of 75 W at -10ºC, the drying time was shortened by 80.3% compared to experiments without US application (0 W) (Table 1). In previous works carried out with the same experimental set-up, Santacatalina et al. (2014) and Garcia-Perez et al. (2012) obtained similar drying time reductions by applying US (50 W) during apple drying at -10ºC (77%) and -14ºC (70%), respectively. Using a contact ultrasonic system, Schössler et al. (2012) reported that the drying time in the freeze-drying of red bell pepper cubes was shortened by 11.5%. Bantle and Eikevik (2011) achieved a drying time shortening of around 10% when drying green peas at -3ºC using a commercial air-borne ultrasonic radiator (20kHz; DN 20/2000, Sonotronic). These remarkable differences between the ultrasonic performances in the different works reported in the literature could be linked to the efficiency of the transducers used and, therefore, the actual ultrasonic power applied in every case.

In the present work, it was observed that the shortening of the drying time was dependent on the ultrasonic power applied. Thus, the higher the power level applied, the shorter the drying time (Table 1). It should be highlighted that when applying the lowest ultrasonic power tested (25 W), a time shortening of 70.7% was achieved for experiments at -10ºC. This fact reveals that mass transport in LTD is very sensitive to US application and a very low level of ultrasonic energy brings about meaningful effects on the drying rate. From an energy point of view, this is an interesting result because with only a limited input of acoustic energy the drying time could be greatly reduced and so, the amount of energy needed.

The ultrasonic performance was better at -10ºC than at 10ºC for every ultrasonic power tested (Table 1). Thus, the shortening of the drying time for the experiments at -10ºC ranged between 70.7 and 80.3%, while for those conducted at 10ºC it was between 49.9 and 75.0%.

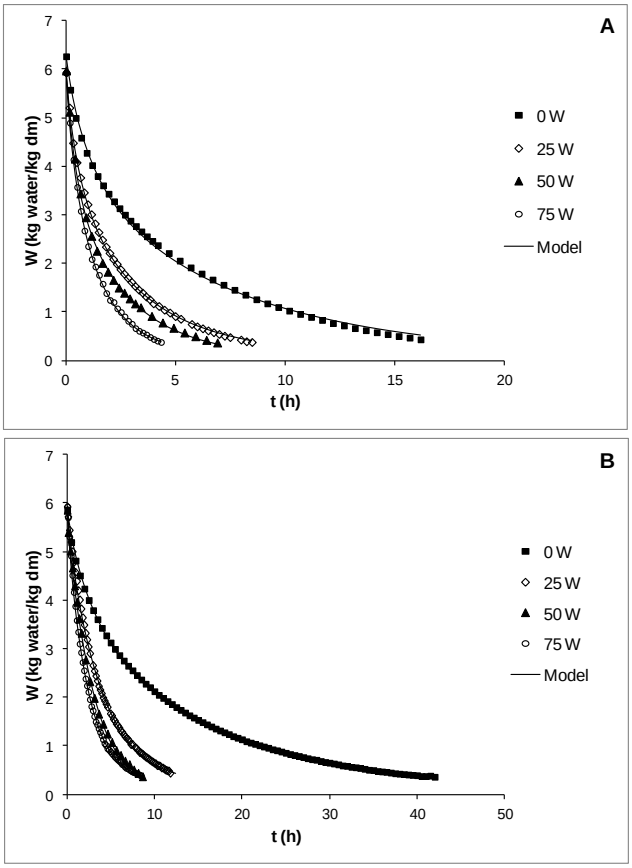

Figure 2. Experimental and modeled drying kinetics of apple at 10ºC (A), -10ºC (B) and different ultrasonic power levels (0, 25, 50 and 75 W).

Table 1. Drying time (t, h) needed to achieve 80% initial weight loss during drying of apple at 10, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W). Average values and standard deviation are shown**.** Δt is the reduction (in percentage) of the drying time caused by ultrasound application.

	10ºC		**-10ºC**	
	t (h)	Δt (%)	t (h)	Δt (%)
0 W	17.1±1.2		41.7±2.7	
25 W	8.6±0.2	49.9	12.2±1.3	70.7
50 W	6.7±0.3	61.0	9.7±1.1	76.6
75 W	4.3±1.1	75.0	8.2±0.3	80.3

3.2. Modeling of drying kinetics

The diffusion model was an accurate means of describing the LTD kinetics of apple cubes under the different conditions tested, providing percentages of explained variance higher than 99.8% and mean relative errors lower than 5% (Table 2). The accuracy of the model proposed for describing the drying kinetics is shown in Figure 2 where experimental and calculated curves are compared.

Table 2. Modeling of drying kinetics of apple at 10, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W). Average values and standard deviation are shown for the effective moisture diffusivity (D_e) and mass transfer coefficient (k). VAR (%) is the percentage of explained variance and MRE (%) the mean relative error. ΔD_e and Δk report (in percentage) the increase in a kinetic parameter as a result of ultrasound application.

		0 W	25 W	50 W	75 W
10ºC	D_e (10^{-11} m^2/s)	7.8 ± 0.3^{a}	18.1 ± 0.2^{ab}	22.9 ± 1.2^{b}	42.0 ± 1.3^{c}
	k (10^{-4} kg water/m^2s)	4.3 ± 0.6^{A}	7.5 ± 0.3^{B}	8.3 ± 0.2^{B}	10.0 ± 0.9^{C}
	VAR (%)	99.8	99.9	99.8	99.9
	MRE (%)	4.5	1.9	4.8	2.9
	ΔD_e (%)		132	193	437
	Δk (%)		75	94	132
-10ºC	D_e (10^{-11} m^2/s)	3.6 ± 0.3^{x}	17.3 ± 0.7^{y}	22.1 ± 1.0^{y}	26.9 ± 2.2^{y}
	k (10^{-4} kg water/m^2s)	1.7 ± 0.1^{X}	3.0 ± 0.1^{Y}	3.9 ± 0.2^{Y}	6.1 ± 1.0^{Z}
	VAR (%)	99.9	99.9	99.9	99.8
	MRE (%)	2.1	2.4	3.6	3.0
	ΔD_e (%)		375	507	639
	Δk (%)		79	133	261

Superscript letters (a, b, c) and (x, y) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of drying experiments at 10 and -10ºC, respectively.
Superscript letters (A, B, C) and (X, Y, Z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the k of drying experiments at 10 and -10ºC, respectively.

The identified effective moisture diffusivity (D_e) and mass transfer coefficient (k) were used to analyze the effect of US application on both the external and internal mass transport. The application of US during LTD involved a significant ($p<0.05$) increase in the D_e and k (Table 2). The higher the level of applied ultrasonic power, the greater the increase in the kinetic parameters. Thus, the biggest improvement in D_e and k was achieved for the experiments carried out at -10ºC and 75 W (ΔD_e=639% and Δk=261%). It should be noted that, for both drying temperatures tested and in the range of ultrasonic power levels used in this work (0-75 W), the

relationship between the ultrasonic power applied and the identified values of D_e and k was linear (Figure 3). In this sense, Garcia-Perez et al. (2009) and Ozuna et al. (2011) have also found linear relationships between D_e and k and the ultrasonic power applied during the hot air drying of different products.

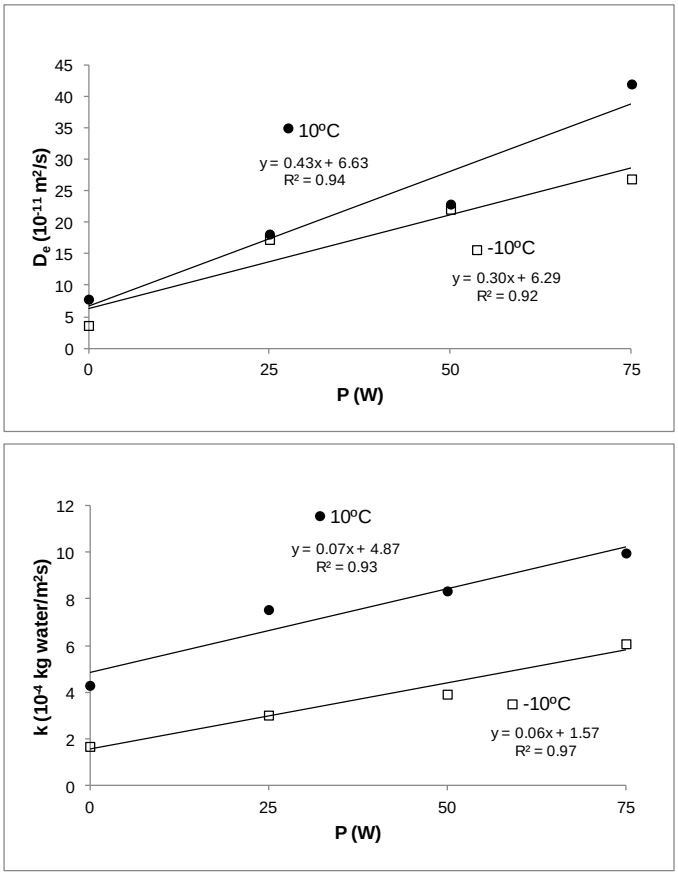

Figure 3. Kinetic parameters (D_e and k) identified by fitting the diffusion model to the experimental drying kinetics of apple at 10ºC, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W).

The effect of US on the kinetic parameters was greater in the experiments carried out at -10ºC than at 10ºC. This could be linked to the fact that water sublimation at -10ºC generates porous products with open structures. Ozuna et al. (2014b) observed that these porous structures have lower acoustic impedance than hard and dense products, and so present a better acoustic coupling with the air. This fact makes for a more efficient transmission of acoustic energy in the sample-air

interface and increases the energy introduced into the particle and therefore the energy which is available to induce effects on the mass transport (Ozuna et al. 2014b).

The increase in D_e produced by the application of US was greater than the increase observed in k under every drying condition tested (Table 2), indicating a greater impact of US on the internal than on the external mass transport resistance. As an example, the increase in D_e and k for drying experiments at 10ºC and 75 W was of 437 and 132%, respectively. This fact is relevant because the freeze-drying operation, vacuum or AFD, is mostly limited by the water vapor diffusion in the particle, which puts forward the application of US as a reliable, non-thermal strategy for the process intensification.

3.3. Rehydration experiments

The samples dried at -10ºC showed a faster rehydration than those dried at 10ºC (Figure 4A). Moreover, the final weight increase achieved (at 4800 s) was also significantly ($p<0.05$) higher for samples dried at -10ºC (5.8±0.4 g versus 4.9±0.2 g). These results could be explained by the highly porous structure caused by the water sublimation at -10ºC, due to the fact that the sample shrinkage is almost negligible (Stawczyk et al., 2007).

The US application during drying did not significantly ($p<0.05$) affect the water gain during rehydration (Figure 4B). These results agree with those obtained by Schössler et al. (2012), who reported no differences in the rehydration characteristics of the ultrasonically-assisted dried red bell pepper samples in comparison to those vacuum freeze-dried.

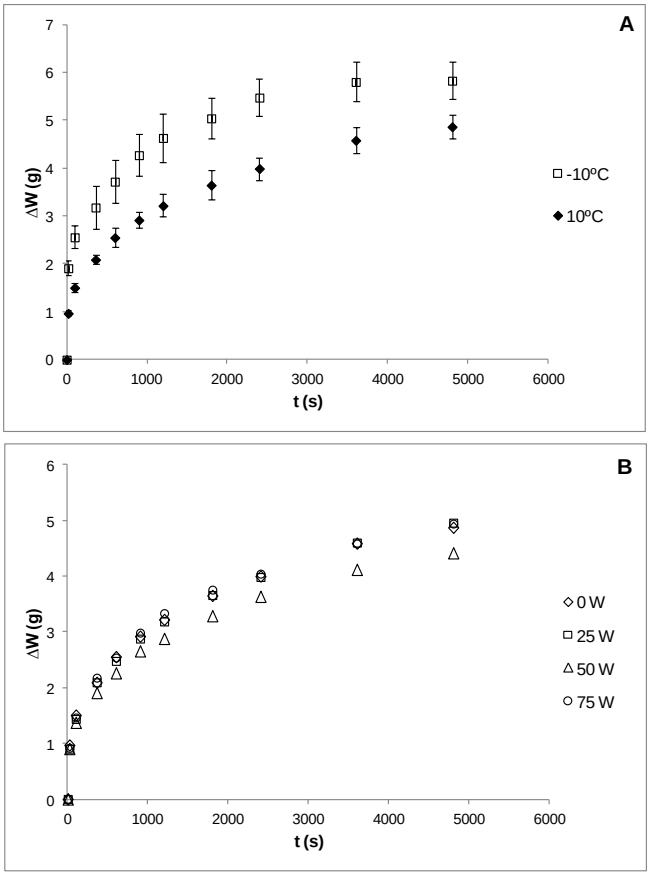

Figure 4. Rehydration kinetics (weight increase, ΔW) of apple dried at 10ºC and -10ºC without ultrasound application (0 W) (A) and at 10ºC by applying different ultrasonic power levels (0, 25, 50 and 75 W) (B). In B, error bars are not included because they are completely overlapped.

3.4. Hardness

The hardness of both the fresh and the rehydrated apple was measured by means of simple compression tests in order to quantify the influence of the drying conditions on the texture (Figure 5). In general terms, fresh apple samples were significantly ($p<0.05$) harder (37.8±3.1 N) than rehydrated ones (26.4±4.2 N on average). The softening was dependent on the drying temperature. Thus, samples dried at 10ºC without US application (0 W) were 35% harder than those dried at -10ºC (average hardness of 30.7±4.6 N and 22.8±3.5 N, respectively). This fact

could be linked to the growth of ice crystals during sample freezing, which damages the solid matrix structure. However, the ANOVA and the LSD intervals showed that these differences were not significant ($p<0.05$), probably due to the high experimental variability.

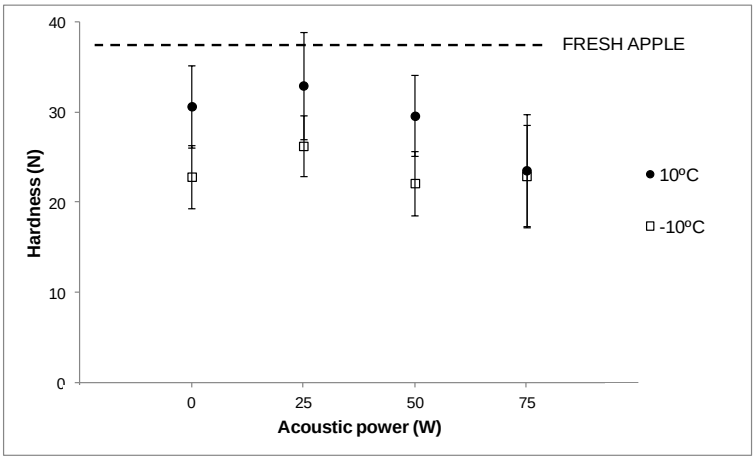

Figure 5. Hardness of dried-rehydrated apple at 10ºC, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W). The dotted line indicates the hardness of fresh apple.

As for the experiments at 10ºC, the increase in the level of applied ultrasonic power involved a slight, but non-significant ($p<0.05$), reduction in sample hardness. The reduction in hardness could be ascribed to the structural collapse caused by the high degree of acoustic stress (Puig et al., 2012). This fact was not observed for samples dried at -10ºC, probably because the freezing of the samples produced a greater degradation of sample structure that could mask the ultrasonic effects.

3.5. Antioxidant potential

The TPC of the fresh apple (6.7±1.3 mg GAE/g dm) was significantly ($p<0.05$) higher than the average computed for the dried samples (2.3±0.7 mg GAE/g dm). The reduction in the TPC caused by LTD ranged between 56.8±5.9% and 77.4±3.1% (Figure 6). The degradation of polyphenols could be linked to the structural collapse of the cells brought about by LTD which makes the release of the oxidative enzymes easier. In LTD, no thermal damage could be expected in the antioxidant compounds due to the fact that dehydration occurs at very low

temperatures. In this sense, Stawczyk et al. (2007) found an average reduction in the polyphenol content of 20% in the convective drying of apple cubes, pre-treated in a 3% citric acid solution (1 cm side) at -8 and -12ºC.

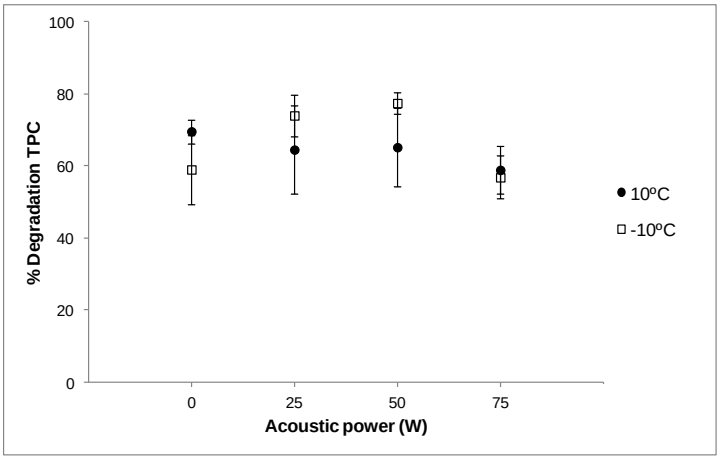

Figure 6. Degradation of total phenolic content (TPC) in apple dried at 10ºC, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W).

As far as the degradation of TPC is concerned, there were no significant ($p<0.05$) differences between the samples dried under the different conditions tested. As regards US application, slightly less TPC degradation was observed at the highest US power tested (75 W), but the differences were not significant ($p<0.05$). These results were not consistent with those previously published by Santacatalina et al. (2014), who found greater TPC degradation at temperatures below freezing point, and even greater when US was applied. The different results could be ascribed to the solvent used for extracting the polyphenols closed in the solid matrix, methanol in the case of Santacatalina et al. (2014) and a solution of ethanol-water (80:20, v/v) in this study. Martínez-Las Heras et al. (2014) reported that extraction conditions affect the extractability of the antioxidant compounds.

As occurred for TPC, the AC of apple samples was also reduced by the drying process (Figure 7) the AC degradation ranging between 76.0±4.7% and 46.1±9.8%. At intermediate ultrasonic power levels (25 and 50 W), the AC degradation was significantly ($p<0.05$) higher at -10ºC than at 10ºC. However, at 0 and 75 W, samples dried at 10ºC showed higher AC degradation than those dried at -10ºC, although the differences were not significant ($p>0.05$).

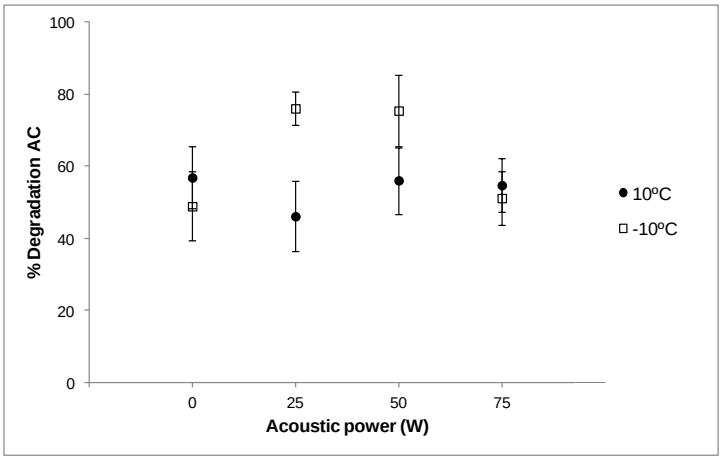

Figure 7. Degradation of antioxidant capacity (AC) in apple dried at 10ºC, -10ºC and different ultrasonic power levels (0, 25, 50 and 75 W).

3.7. Influence of US application on microstructure

The characterization of the microstructural changes caused by the application of US in LTD could help to explain the effects observed on the mass transport and quality properties. Thus, the samples dried without US (0W) at -10ºC (Figure 8C) exhibited a more porous structure than those dried at 10ºC (Figure 8A), probably due to the damage caused by the growth of ice crystals during the sample's freezing. Thus, a more compact tissue, where the cells cannot be easily identified, is observed in Figure 8A than in Figure 8C. This fact could explain the higher weight increase and the softer structure of the samples dried at -10ºC than those dried at 10ºC. Meanwhile, the US application seems to induce a greater degradation of apple structure at both temperatures, 10ºC (Figure 8B) and -10ºC (Figure 8D), causing an increase in product porosity and pore diameter that make the water movement in the matrix easier during drying. However, these changes were not enough to affect the rehydration and the water retention of the dried tissue, as shown in section 3.3.

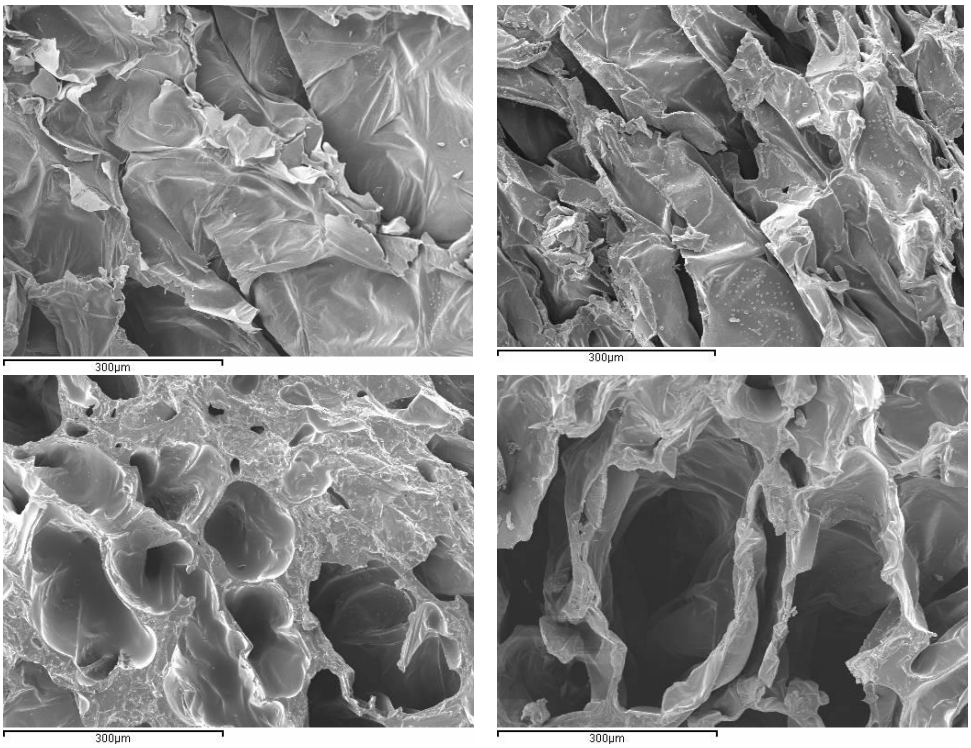

Figure 8. Cross-section observed by Cryo-SEM (200x) of apple dried at different conditions: 10ºC 0 W (A); 10ºC 75 W (B); -10ºC 0 W (C); -10ºC 75 W (D).

3.8. Principal component analysis

Two principal components (PC) were extracted from the statistical analysis (with eigenvalues>1), which together explained 65.8% of the total variance. In Figure 9, the close relationship found for the variables of "drying time" and "weight increase" may be observed, which suggests that the shortening of the drying time leads to dried samples with a lower rehydration capacity. In addition, the PCA also reveals the well-known relationship between TPC and AC.

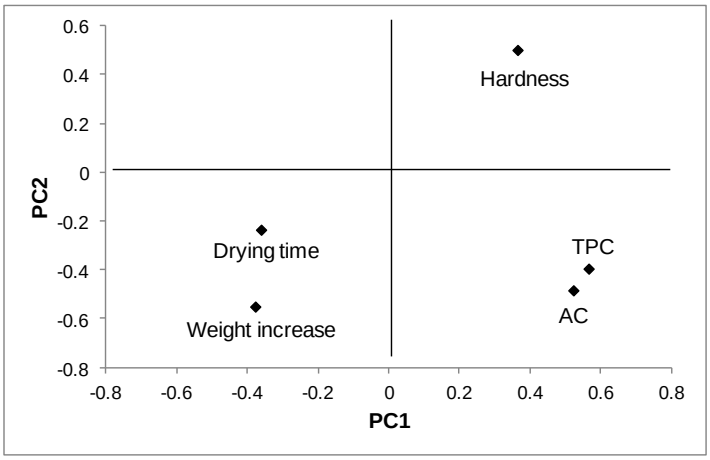

Figure 9. Principal component analysis. Correlation scatterplot of the variables with principal component 1 (PC1) and principal component 2 (PC2). AC: antioxidant capacity; TPC: total phenolic content.

For PC1, which explains 36.9% of the experimental variability, negative correlations were only found for "drying time" and "weight increase", which could explain the aforementioned influence of drying time on rehydration capacity. PC2 (explained variance 28.9%) could mainly be related to the hardness of the rehydrated samples since all the variables presented negative coefficients, except the hardness. The two-dimensional plot of the principal components (Figure 10) showed that PC2 separates samples dried at 10 and -10ºC. Therefore, regardless of the level of applied ultrasonic power, the drying temperature had direct implications on the hardness of the samples. Finally, from Figure 10, it should be remarked that the US application, at the power levels tested, had a limited influence on the TPC, AC, weight increase and hardness of the dried sample. Therefore, the application of US greatly contributed to the increased drying rate but did not substantially affect the measured quality parameters.

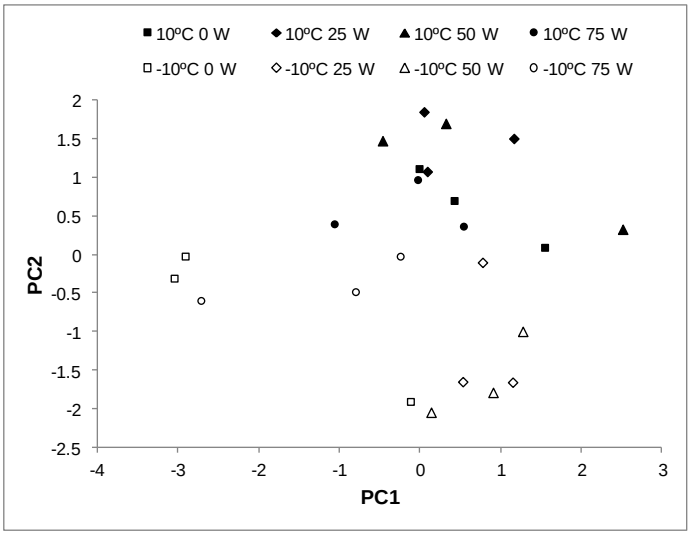

Figure 10. Representation of the different dried apple sets on the plane defined by the first and second principal components, PC1 (36.9%) and PC2 (28.9%).

4. Conclusions

This work illustrates the influence of the level of ultrasonic power applied during the low temperature drying of apple on both mass transport and some quality aspects. At both temperatures tested (-10ºC and 10ºC), the higher the power level applied, the shorter the drying time. The ultrasonic effect on drying kinetics was greater at -10ºC than at 10ºC, achieving a shortening of the drying time by as much as 80.3%. The application of US, regardless of the power level applied, only had a mild impact on the quality attributes analyzed in this work (rehydration capacity, hardness, total phenolic content, antioxidant capacity and microstructure). Therefore, US could be considered a feasible, non-thermal means of intensifying the low temperature drying of high quality foodstuffs.

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Chapter 2

Modeling of atmospheric freeze drying

Journal of Food Engineering (2015), 151, 7-15

MODEL-BASED INVESTIGATION INTO ATMOSPHERIC FREEZE DRYING ASSISTED BY POWER ULTRASOUND

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MODEL-BASED INVESTIGATION INTO ATMOSPHERIC FREEZE DRYING ASSISTED BY POWER ULTRASOUND

Abstract

Atmospheric freeze drying consists of a convective drying process using air at a temperature below the freezing point of the processed product, and with a very low relative humidity content. This paper focuses on the use of a simple one-dimensional model considering moving boundary vapor diffusion to describe the ultrasonic assisted atmospheric freeze-drying of foodstuffs. The case study is the drying of apple cubes (8.8 mm) at different air velocities (1, 2, 4 and 6 m/s), temperatures (-5, -10 and -15ºC), without and with (25, 50 and 75 W) power ultrasound application. By fitting the proposed diffusion model to the experimental drying kinetics, the effective diffusivity of water vapor in the dried product was estimated. The model was successfully validated by drying apple samples of different size and geometry (cubes and cylinders). Finally, a 2^3 factorial design of experiments revealed that the most relevant operating parameter affecting the drying time was the applied ultrasound power level.

Keywords: Atmospheric freeze-drying; ultrasound; modeling; optimization

1. Introduction

Atmospheric freeze drying (AFD) consists of a convective drying process where the temperature of the air has to be kept below the freezing point of the processed material, and the relative humidity has to be, in general, very low. Since the air is not saturated with water vapor, a vapor partial pressure gradient is created between the product and the air, forcing the ice to sublimate and the water vapor to diffuse to the air (Meryman, 1959; Bantle and Eikevik, 2011). AFD is generally carried out at temperatures of between -10ºC and the initial freezing point of the product, as this appears to be a good compromise between costs and final product quality (Wolff and Gibert, 1990a, 1990b; Claussen et al., 2007a, 2007b). The advantages of AFD are its lower cost compared to vacuum freeze drying and the possibility of its being carried out as a continuous process, thus also allowing energy recovery (Bantle et al., 2011)

In cold regions, the AFD process has a long history of use as a means of food preservation (Rhamann and Mujumdar, 2008a), although Meryman (1959) was the first to report the potential of AFD. Stawczyk et al. (2007) investigated the freeze-drying kinetics and the product quality of apple cubes in a fully automated heat pump-assisted drying system. Their results showed that the rehydration kinetics and the hygroscopic properties of the product were similar to those obtained by vacuum freeze drying. These findings agreed with the work of Claussen et al. (2007c), which was carried out using heat pump fluidized bed and tunnel dryers. However, despite the promises of low energy consumption and a better quality product, certain problems still exist in the atmospheric freeze-drying process, limiting its practical implementation. Furthermore, due to the low vapor diffusivity at atmospheric pressure, AFD is controlled by the internal resistance to heat and mass transfer, making it a long drying process (Rhamann and Mujumdar, 2008b).

Since the main drawback of the AFD process is the low sublimation rate, improving mass transfer would be beneficial. In the last few years, new power transducers with extensive surface radiators have been developed for applications in gas media (Gallego-Juárez et al., 2001), such as de-foaming and air drying. Thus, high-intensity airborne ultrasound application brings about mechanical effects when the sound wave is directed into the product (Bhaskaracharya et al., 2009), which

intensify the drying of foodstuffs (Gallego-Juarez et al., 2007; Gallego-Juarez, 2010; Riera et al., 2011). Therefore, high-intensity airborne ultrasound was suggested as a potential technology for improving mass transfer in AFD by Cárcel et al. (2011). Ozuna et al. (2014) and García-Perez et al. (2012) have also shown the feasibility of employing power ultrasound to accelerate the drying kinetics of fruits, vegetables and fish at low temperatures. The latter have achieved a maximum drying time reduction of 77% by applying power ultrasound during the drying of apple at -10ºC.

Mathematical modeling represents an important tool in the analysis of the drying process and the operation of the dryer (Mulet et al., 2010). Several empirical, semi-empirical, and analytical equations have been reported for predicting the drying curves for different products and operating conditions. However, there are few first principle models which have been reported to thoroughly describe the AFD process and even less effort has been made to assess its adequacy. One of these models is based on the Lewis equation and its accuracy depends greatly on the accurate evaluation of the thermal properties in the structure of the dried product (Claussen et al., 2007b). Rahman et al. (2009) also suggested a method based on the thermal properties of the product and used the analogy between Nusselt and Sherwood numbers to predict the drying rate in AFD. A similar approach was taken by Li et al. (2007), where a CFD model for an AFD process of apple was developed. When also working on the AFD of apple cubes, Stawczyk et al. (2007) observed that no first drying stage or constant drying rate occurred, and the complete dehydration process was controlled by internal water diffusivity. A similar conclusion was also drawn by Di Matteo et al. (2003). An analytical solution for AFD is presented by Wolff and Gibert (1990a, 1990b) where the ‘‘Uniformly Retreating Ice Front’’ (URIF) approach is coupled to the laws of heat and mass transfer. In the URIF model, the product is divided into two layers; a frozen (or wet) inner core and an outer dry layer. It is assumed that the drying occurs as a consequence of the frozen core gradually shrinking down to zero. Heat is transported from the surface of the product, causing sublimation at the ice front. The resulting water vapor is transported back to the surface and to the gas medium.

In this context, the main goals of this work were to evaluate the feasibility of a simple one-dimensional model to describe the ultrasonic assisted AFD process of apple cubes, as well as to validate such a model in different operating conditions. Finally, a suitable design of experiments coupled with the analysis of the effects was used to point out the key parameter for the atmospheric freeze drying process, which would positively contribute to further optimization stages.

2. Materials and methods

2.1. Raw material

Apples (*Malus domestica* cv. Granny Smith) were purchased in a local market (Valencia, Spain). Fruits were selected to obtain a homogeneous batch in terms of ripeness, size and color, and held at 4ºC until processing. Cubic samples (8.8 mm and 17.5 mm side) were obtained from the flesh using a household tool. Cylindrical samples (height 40 mm and diameter 15 mm) were also prepared using a 15 mm hole puncher. All the samples were wrapped in plastic film and frozen at -18±1ºC until processing (at least 24 h). The initial moisture content was measured by placing the samples in a vacuum oven at 70ºC and 200 mmHg until constant weight was reached, following the standard method 934.06 (AOAC, 1997).

2.2. Drying experiments

Drying experiments were carried out in a convective drier with air recirculation (Figure 1), already described in the literature (Garcia-Perez et al., 2012). The drier provides an automatic temperature and air velocity control. A cylindrical radiator (internal diameter 100 mm, height 310 mm, thickness 10 mm) driven by a power ultrasonic transducer (frequency 22 kHz, power capacity 90 W) was used as the drying chamber. The transducer generates an ultrasonic field inside the cylinder, which interacts with the samples and the surrounding air during drying. Air goes through the cylindrical radiator where samples were randomly placed in a holder for assuring a uniform treatment of them for both air flow and ultrasound application. A set of experiments was carried out to determine the drying kinetics of apple cubes (8.8 mm) at different air velocities (1, 2, 4 and 6 m/s), temperatures (-5, -10 and

-15ºC), without and with (25, 50 and 75 W) power ultrasound (US) application. Another set of experiments was carried out with larger apple cubes (17.5 mm). In this case, the drying conditions used were -10ºC, 2 m/s and without US application.

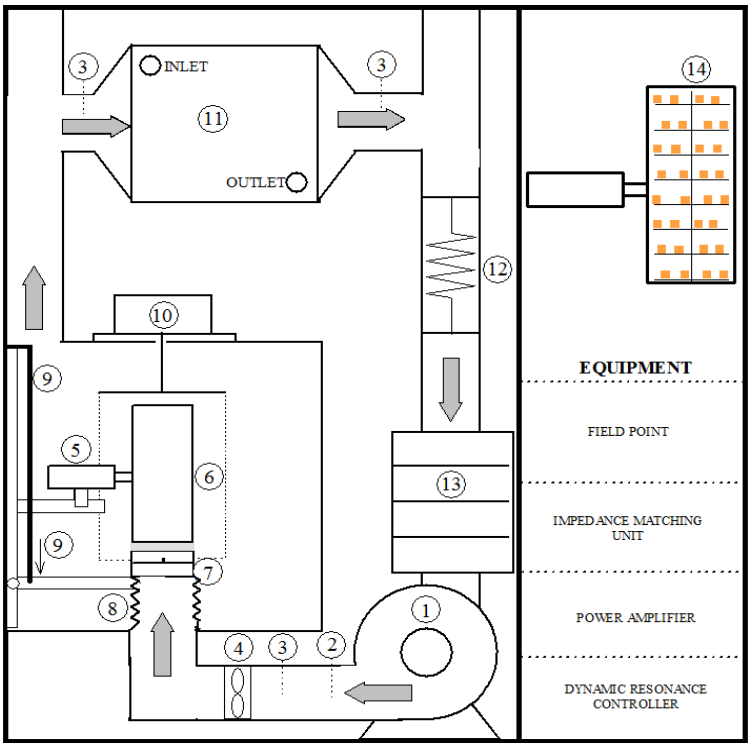

Figure 1. Scheme of the ultrasonically assisted convective drier: 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer; 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe; 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13, desiccant tray chamber; 14, details of the sample load on the trays.

In every experiment, the samples were weighed at preset times and the relative air humidity was kept at under 15±5%. For each run, the initial mass load density was 9.5 kg/m^3. The drying experiments were extended until the samples lost 80% of the initial weight. Every condition was tested in triplicate, at least.

Finally, a third drying test was carried out using apple cylinders, whose surface was kept isolated with a plastic film, with the exception of one of the flat surfaces. So, the water vapor outlet took place in only one direction. The samples were dried at -15°C, 2 m/s and without US application. In order to determine the moisture profile

for different percentages of weight loss (10, 20, 30 and 40%), the cylinder was split into 5 equal sections and the individual moisture content of each section was determined following the standard method 934.06 (AOAC, 1997).

2.3. Mathematical modeling

As previously mentioned, the Uniformly Retreating Ice Front (URIF) model has been used to model the atmospheric freeze-drying of foodstuffs. Assuming cubic samples behave as spherical bodies (Figure 2A) during AFD, the mass balance for the water vapor in the dried product is given, in steady-state conditions, by the following equation:

$$\frac{d}{dr}\left(r^2 J_w\left(r\right)\right)=0 \tag{1}$$

where the water flux is given by the well- known Fourier equation:

$$J_w\left(r\right)=-\frac{D_e M_w}{RT}\frac{dp_w\left(r\right)}{dr} \tag{2}$$

The integration of equation (1), using equation (2) and the following boundary conditions:

$$\begin{aligned} r &= L_0 - L_{dried} \qquad p_w = p_{w,i} \\ r &= L_0 \qquad\qquad\quad p_w = p_w^* \end{aligned} \tag{3}$$

gives:

$$p_w\left(r\right)=\frac{1}{r}\left(\frac{p_{w,i}-p_w^*}{L_{dried}}\right)L_0\left(L_0-L_{dried}\right)+\left[p_w^*-\frac{1}{L_0}\left(\frac{p_{w,i}-p_w^*}{L_{dried}}\right)L_0\left(L_0-L_{dried}\right)\right] \tag{4}$$

From equation (4), it is possible to calculate the sublimation flux (using equation (2)), thus obtaining:

$$J_w\left(r\right)=\frac{D_e M_w}{RT}\frac{1}{r^2}\left(\frac{p_{w,i}-p_w^*}{L_{dried}}\right)L_0\left(L_0-L_{dried}\right) \tag{5}$$

and, finally, the sublimation flow rate:

$$G = 4\pi r^2 J_w(r) = \frac{D_e M_w}{RT} 4\pi \frac{L_0 (L_0 - L_{dried})}{L_{dried}} \left(p_{w,i} - p_w^*\right) \quad (6)$$

The mass flow rate from the surface of the sample to the drying chamber is also given by the following equation: G

$$G = S\alpha \frac{M_w}{RT} \left(p_w^* - p_{w,c}\right) \quad (7)$$

Using eqs. (6) and (7) it is possible to calculate the sublimation flow rate in the following way:

$$G = \frac{M_w}{RT} \frac{1}{\frac{1}{S\alpha} + \frac{L_{dried}}{4\pi D_e L_0 (L_0 - L_{dried})}} \left(p_{w,i} - p_{w,c}\right) \quad (8)$$

where $p_{w,i}$, the partial pressure of water at the interface of sublimation is a well-known function of the temperature.

Following exactly the same approach, it is possible to calculate the heat flow rate in the dried layer by means of the following equation:

$$Q = \frac{1}{\frac{1}{S\beta} + \frac{L_{dried}}{4\pi\lambda_{dried} L_0 (L_0 - L_{dried})}} \left(T_{air} - T_i\right) \quad (9)$$

All the energy transferred into the product is used for ice sublimation and, thus:

$$Q = G\Delta H_s \quad (10)$$

Equation (10) can be used to calculate the interface temperature, given the values of the operating conditions, of the heat and mass transfer coefficients, of product parameters D_e and λ_{dried}, and of the dried layer thickness. Then, it is possible to calculate the sublimation flow rate (using equation (8)) and the evolution of the dried volume:

$$\frac{dV_{dried}}{dt} = \frac{G}{\rho_{dried} \left(W_0 - W_f\right)} \quad (11)$$

and, finally, of the residual amount of ice in the sample:

$$-\frac{dW}{dt} = \rho_{dried}\left(W_0 - W_f\right)\frac{dV_{dried}}{dt} \tag{12}$$

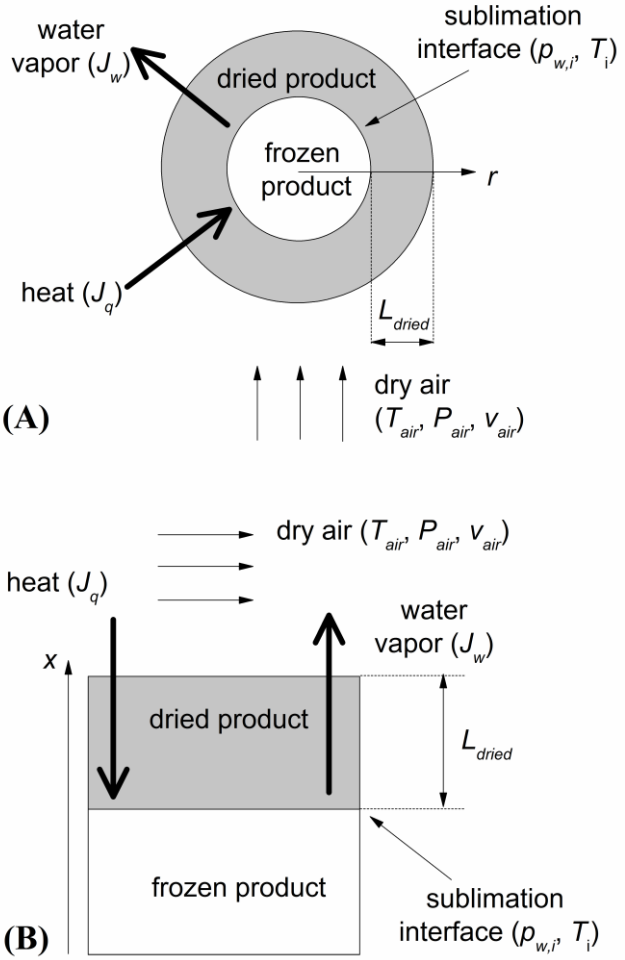

Figure 2. Sketch of a partially freeze-dried product with spherical (A) and planar (B) geometry.

In the case of planar geometry, as shown in Figure 2, graph B, exactly the same approach can be followed. Thus, the mass balance for the water vapor in the dried product is given, in steady-state conditions, by the following equation:

$$\frac{d}{dx}\left(J_w\left(x\right)\right) = 0 \tag{13}$$

with the following boundary conditions:

$$\begin{aligned} x &= L_0 - L_{dried} \qquad p_w = p_{w,i} \\ x &= L_0 \qquad\qquad\quad p_w = p_w^* \end{aligned} \tag{14}$$

and the water flux is given by the Fourier equation:

$$J_w(x) = -\frac{D_e M_w}{RT}\frac{dp_w(x)}{dx} \tag{15}$$

After some calculations, it is possible to obtain the following equation to calculate the sublimation flow rate:

$$G = \frac{M_w}{RT}\frac{1}{\frac{1}{\alpha} + \frac{L_{dried}}{D_e}}\left(p_{w,i} - p_{w,c}\right) \tag{16}$$

and the heat flow rate in the dried layer is given by the following equation:

$$Q = \frac{1}{\frac{1}{\beta} + \frac{L_{dried}}{\lambda_{dried}}}\left(T_{air} - T_i\right) \tag{17}$$

In this case, it is also possible to assume that all the energy transferred into the product is used for ice sublimation, i.e. equation (10) and, thus calculating the interface temperature from the values of the operating conditions, heat and mass transfer coefficients, product parameters D_e and λ_{dried}, and dried layer thickness. Then, the sublimation flow rate (using equation (16)) and the evolution of the dried layer thickness can be estimated:

$$\frac{dL_{dried}}{dt} = \frac{G}{\rho_{dried} S (W_0 - W_f)} \tag{18}$$

and, finally, of the residual amount of ice in the sample:

$$-\frac{dW}{dt} = S\rho_{dried}(W_0 - W_f)\frac{dL_{dried}}{dt} \tag{19}$$

As regards the estimation of heat and mass transfer coefficients, α and β, several equations can be found in the literature. Among others, Krokida et al. (2002)

reported various empirical equations with which to calculate the coefficient β, given as a function of the air Reynolds number:

$$j_h = aRe^n \tag{20}$$

while the Lewis equation is used to calculate the coefficient α:

$$\alpha = \frac{\beta}{\rho_{air} c_{p,air}} \tag{21}$$

In any case, the atmospheric freeze-drying process appears to be controlled by the internal resistance to water vapor transfer in most cases, as is also reported by Bantle et al. (2011) for the AFD process of peas, and as also pointed out in this study for apple drying; thus, the correlations used to calculate α and β do not significantly affect the accuracy of the results. The constant parameters used in the AFD modeling of apple cubes and cylinders are included in Table 1.

Table 1. Constant parameters used for the modeling of the atmospheric freeze drying kinetics of apple.

Parameter		Value
L_0, initial characteristic dimension (m)	Spherical geometry	0.0044
	Planar geometry	0.04
W_0, water content in the product at the beginning of the drying process ($kg_{water}/kg_{dry\ matter}$)		5.928
W_f, water content in the product at the end of the drying process ($kg_{water}/kg_{dry\ matter}$)		0.382
ρ_{dried}, density of the dried product (kg/m^3)		124.5
$\lambda_{dried,}$ thermal conductivity of the dried product (W/m K)		0.1
R, ideal gas constant (J/kmol K)		8.314
M_w, water molecular weight (kg/kmol)		18
$c_{p,air}$, air specific heat (J/kg K)		1005
a, parameter used to calculate the heat transfer coefficient		0.59
n, parameter used to calculate the heat transfer coefficient		-0.38

2.4. Design of experiments

In order to assess the effect of the various operating parameters, namely air temperature, air velocity and ultrasound application, on drying time, a standard Design of Experiments (DoE) technique was used. This aims to investigate the reciprocal interactions among the variables, and to find those which play the major role in the drying kinetics (Montgomery, 2005). In particular, a 2^3 factorial design of experiments was used to evaluate how air temperature (factor A), air velocity (factor B), and acoustic power (factor C) affect the drying time. High (+) and low (-) values of these parameters (factor A: -10 and -5°C, factor B: 2 and 6 m/s and factor C: 0 and 50 W) were considered, as is graphically illustrated in Figure 3, where these eight combinations are represented by lowercase letters of the alphabet. Lowercase letters indicate that the parameter is at the high level, for the sake of clarity: a identifies the combination of A at the high level (-5°C) and B and C at the low level (2 m/s and 0 W), ab identifies the combination of A and B at the high level (-5°C and 6 m/s) and C at the low level (0 W), abc identifies the combination of A, B and C at the high level (-5°C, 6 m/s, 50 W) while (1) identifies the combination of A, B and C at the low level (-10°C, 2 m/s and 0 W). Then, the single effects of various parameters can be calculated. For example, the effects of A are:

- $[a-(1)]/n$ when the values of B and C are both low;
- $[ab-b]/n$ when the value of B is high and the value of C low;
- $[ac-c]/n$ when the value of C is high and the value of B low and
- $[abc-bc]/n$ when the values of B and C are both high,

where n is the number of repetitions of the test. By averaging the previously calculated single effects, the total effect of A, also known as the contrast parameter, on the drying time is obtained:

$$A=\frac{1}{4n}\left[a-(1)+ab-b+ac-c+abc-bc\right]=\frac{Contrast_A}{4n} \tag{22}$$

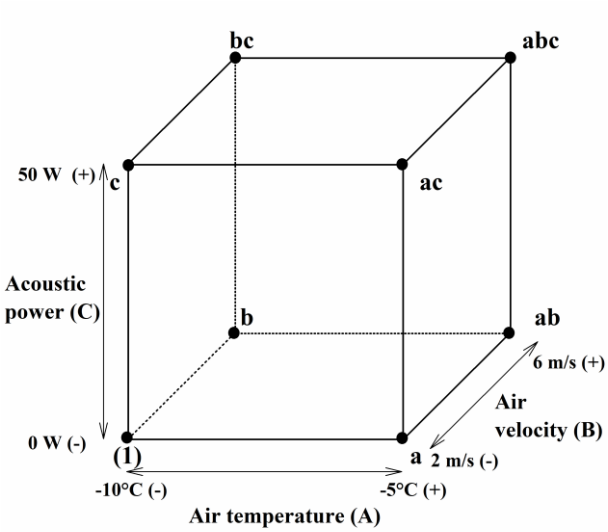

Figure 3. Graphical representation of the 2^3 factorial design used to investigate the effect of air temperature (A), of air velocity (B), and of ultrasonic application (C) on the drying time.

Similarly, the effects of parameters B and C can be calculated, as well as the interactions between these factors. The effect can be positive or negative: if the value is positive, when the parameter increases (from the minimum to the maximum) the observed variable (the drying time) also increases, and vice versa when the value is negative. Finally, the percentage contribution of each factor to the drying time can be determined. The analysis of variance "ANOVA" was carried out using the Fisher test to verify the significance of the differences between the arithmetic means of the various groups.

3. Results and discussion

3.1. Assessment of model adequacy and water diffusivity estimation

The drying kinetics of apple cubes (8.8 mm side) processed at different velocities (1, 2, 4 and 6 m/s), temperatures (-15, -10 and -5°C), and without and with (25, 50 and 75 W) power ultrasound application were modeled using the equations described in the previous sections. For modeling purposes, a spherical geometry has been assumed for the food samples, and the sphere diameter has been

determined in such a way that the product volume is the same as that of the cubic samples. The value of water effective diffusivity in the dried product (D_e) has been determined by looking for the best fit between the calculated and measured values of the residual moisture in the product vs time.

For every combination of the operating conditions under investigation, the model was observed to fit the experimental data very well, as can be observed in Figure 4. Claussen et al. (2007b) also used the URIF model to simulate the AFD of apple, turnip, cabbage and cod pieces, exhibiting a good agreement with the experimental data (not shown), whereas Li et al. (2007) found some differences between the experimental values and those calculated by means of the URIF model at the beginning of the AFD of apple cubes. Using the same approach, Reyes et al. (2010) reported a 10% deviation of the model for the AFD of berries.

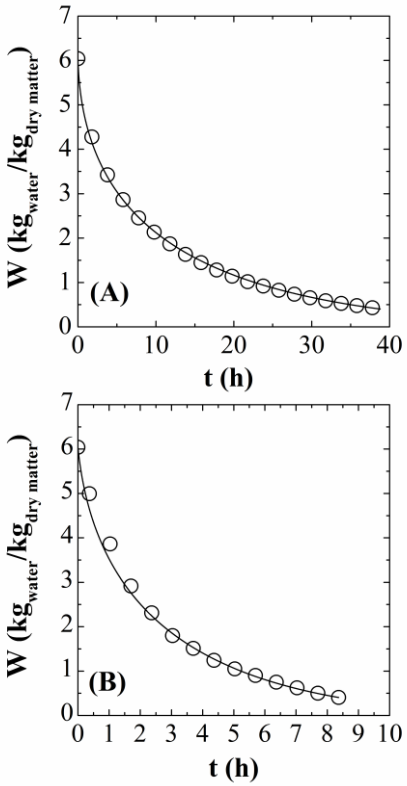

Figure 4. Comparison between the evolution of the residual amount of water in the product measured experimentally (symbols) and calculated using the mathematical model of the process (lines) during atmospheric freeze-drying of apple samples (air temperature: -10°C, air velocity: 2 m/s) without ultrasound (A) and with ultrasound application (50 W, B).

As regards the values of the water vapor effective diffusivity in the dried product, this study permitted the effect of the different operating parameters (temperature, air velocity and applied acoustic power) on D_e and, thus, on drying kinetics to be demonstrated. Air temperature was observed to have a significant ($p<0.05$) effect on the identified D_e (Table 2): the higher the temperature used, the higher the D_e value. This influence of temperature was also observed in the US-assisted experiments. As for the effect of air velocity, as expected, it has no effect on the estimated value of D_e (Table 3) when US is not applied. Otherwise, for drying experiments conducted with US application, a slightly lower D_e was identified for the experiments carried out at the highest air velocities tested (4 and 6 m/s); however, no significant ($p<0.05$) differences were observed. This fact could be due to some disruption of the ultrasonic field caused by the turbulences produced by high air flow velocities, reducing the acoustic intensity that reaches the sample, as reported by Garcia-Perez et al. (2006). Low air flow rates should not affect the ultrasonic field, thus a major fraction of ultrasonic energy would be available to increase water vapor diffusivity into the sample. In every case, the obtained D_e values were much higher (6 orders of magnitude) than those computed by Santacatalina et al. (2014) and Li et al. (2008) for AFD apple kinetics when using a strict diffusion model and identifying the liquid water diffusivity.

Table 2. Effective diffusivities (D_e) identified from the modeling of apple drying kinetics at 2 m/s with (50 W) and without (0 W) power ultrasound application. Mean values ± standard deviation.

	D_e (10^{-5} m^2/s)	
	0 W	**50 W**
-5°C	1.61 ± 0.12^{a}	6.95 ± 1.22^{c}
-10°C	1.50 ± 0.23^{a}	6.70 ± 1.03^{c}
-15°C	1.08 ± 0.09^{b}	3.60 ± 0.97^{d}

Superscript letters (a, b) and (c, d) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$).

Table 3. Effective diffusivities (D_e) identified from the modeling of apple drying kinetics at -10ºC with (50 W) and without (0 W) power ultrasound application. Mean values ± standard deviation.

	D_e (10^{-5} m^2/s)	
	0 W	**50 W**
1 m/s	1.38±0.10[a]	6.48±1.05[b]
2 m/s	1.50±0.23[a]	6.70±1.03[b]
4 m/s	1.34±0.62[a]	6.37±0.33[b]
6 m/s	1.50±0.16[a]	6.04±0.34[b]

Superscript letters (a, b) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$).

As regards the US application, the increase in the level of applied acoustic power led to a rise in the effective diffusivity (Table 4). It should also be remarked that the lowest power tested (25 W) allowed a huge increase (370%) in the D_e value to be obtained (Table 4). Therefore, it is illustrated that US application is very effective at accelerating the AFD experiments, even when using a low acoustic power. Several effects of ultrasonic waves to improve mass diffusion in solid matrix have been reported (Gallego-Juárez, 1998). In this sense, US produce series of cyclical and rapid (>20 kHz) compressions and expansions, a mechanism known as sponge effect; this alternating stress creates microscopic channels that help to make the movement of water vapor from the ice front towards the product surface easier. In addition, ultrasound may also contribute to the water sublimation since, to a certain extent, the attenuation of the acoustic wave may provide the energy needed for the water to change state (Gallego-Juárez, 2010).

Table 4. Effective diffusivities (D_e) identified from the modeling of apple drying kinetics at 2 m/s, -10ºC and different acoustic powers. Mean values ± standard deviation.

	D_e (10^{-5} m^2/s)
0 W	1.50±0.23[a]
25 W	5.54±0.33[b]
50 W	6.70±1.03[b]
75 W	12.24±1.05[c]

Superscript letters (a, b, c) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$).

The obtained results are interesting because, just by using a low acoustic power, the amount of energy consumed by an AFD experiment could be reduced (due to the shorter drying time) and the degradation of the structure of the sample could be minimal. In this sense, Puig et al. (2012) have analyzed the microstructure of eggplant and how it is affected by the application of US during its drying at 40ºC and have reported that the lowest acoustic power tested (45 W) provoked less degradation than when US was applied at its maximum power capacity (90 W).

3.2. Model validation

A first attempt to validate the model consisted of using the diffusivities identified for each one of the drying conditions tested to predict the drying times and compare them to the experimental times. Since the air velocity did not have a significant effect on the value of the diffusivity for the experiments conducted without US application, an average D_e value was used to simulate the drying kinetics at the four air velocities tested so it could be further compared to the experimental results (Figure 5). It may be observed that the experimental and calculated times were very similar for every condition tested.

Moreover, a more rigorous model validation was addressed by carrying out additional experiments to those used to identify the diffusivity values. Thus, the diffusivity value obtained in the experiments performed on apple cubes of 8.8 mm side (at -10°C, 2 m/s and without US application) to model a drying experiment carried out under the same drying conditions, but on different-sized samples: cubes of 17.6 mm side. As can be observed in Figure 6, experimental data were quite similar to those simulated.

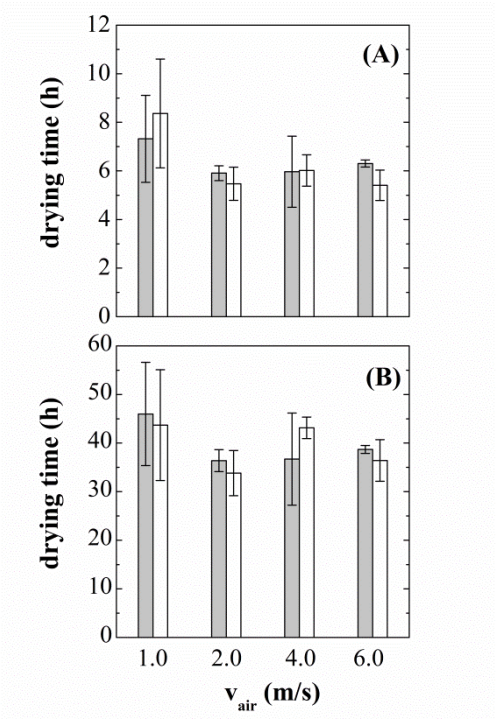

Figure 5. Comparison between the experimentally measured (empty bars) and the calculated (grey bars) values of the time required to reduce the amount of water in the sample by 50% (A) and by 90% (B) during atmospheric freeze-drying of apple samples as a function of air velocity (air temperature: -10°C), without ultrasound application.

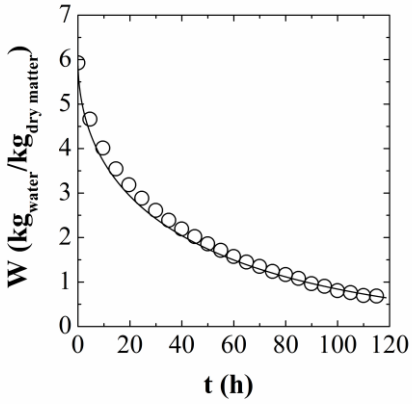

Figure 6. Comparison between the evolution of the residual amount of water in the product measured experimentally (symbols) and calculated using the mathematical model of the process (lines) during atmospheric freeze-drying of apple samples (17.6 mm side, air temperature: -10°C, air velocity: 2 m/s) without ultrasound application.

Model validation was also performed with a third set of experiments under completely different experimental conditions. In this case, atmospheric freeze drying experiments were carried out on apple cylinders, 40 mm in height and 15 mm in diameter, which were water-proof isolated to behave as infinite slabs of 40 mm, as already mentioned in section 2.2. The D_e obtained from the experiments performed on apple cubes (8.8 mm side) under the same experimental conditions (2 m/s, -15°C, without US application) was used to model apple cylinder experiments. The evolution of the moisture profile was calculated using the model, taking into account the position of the sublimation front at every time in order to estimate the moisture of each one of the five sections of apple cylinders. Figure 7 depicts the reasonably good match between the experimental moisture of the sections and the computed value. Therefore, the moisture profile in the samples confirmed the assumptions considered in the model, as well as the results obtained. In Figure 7, it may be seen how the sublimation front moves from the surface of the sample in contact with the air, leaving a dry layer through which water vapor diffuses onto the surface. Meanwhile, the frozen area maintained the initial moisture content ($W/W_0 = 1$) and shrank as drying progressed. These retreating ice fronts have also been observed by Crespi et al. (2008) when analyzing paper samples that had previously been soaked in distilled water and freeze-dried for different times by immersing the partially dried sample in a dye that colored the ice (wet zone). However, as far as we are concerned, the experimental validation of the URIF model showing the location of the ice front has not been reported for foodstuffs.

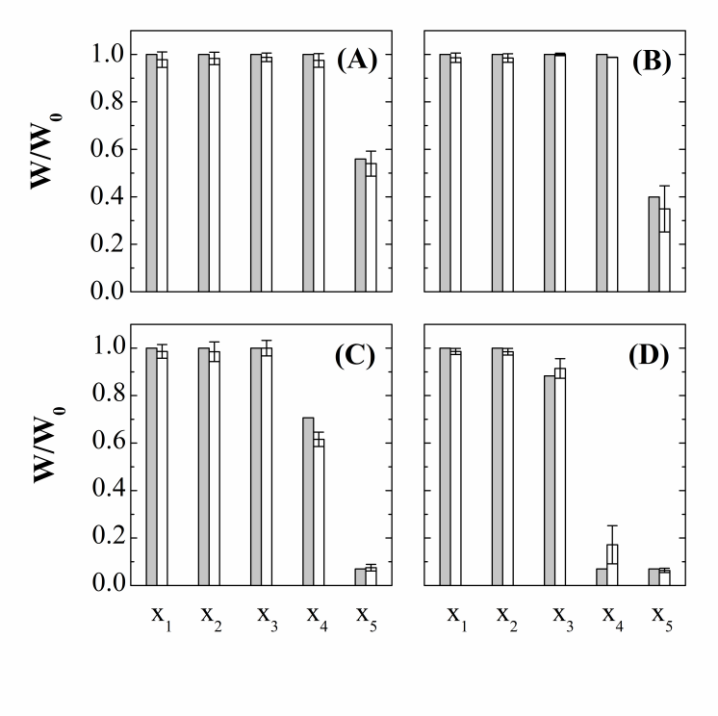

Figure 7. Comparison between the experimentally measured (empty bars) and the calculated (grey bars) values of the residual amount of water in the product at different axial positions (given as distance from the isolated flat surface; x_1 = 0.036 m, x_2 = 0.028 m, x_3 = 0.02 m, x_4 = 0.012 m, x_5 = 0.004 m) during atmospheric freeze-drying of apple samples (air temperature: -10°C, air velocity: 2 m/s, without ultrasound application), for different total weight loss (graph A: 10%, graph B: 20%, graph C: 30%, graph D: 40%).

3.3. Analysis of the effects

The process variables considered in this study were temperature, air velocity and ultrasound application. In order to quantify the effect of these operating variables on the AFD times, a set of experiments was performed. Two levels (high and low) of each variable were selected to make a two-level factorial design (2^3), with three replicates from each run. The contribution percentages of each factor to the drying time and their interactions are shown in Figure 8. It can be observed that the variable with the most relevant effect on the drying time was US application, followed by temperature and the interaction between them. The effect of air velocity appears to be negligible under these drying conditions, as has previously been

mentioned. Therefore, for the drying conditions studied in this design, the key parameter is US application. Consequently, this parameter should be conveniently modified to optimize the drying process.

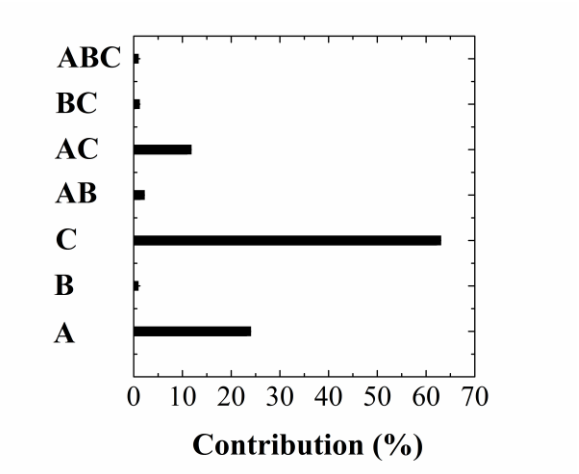

Figure 8. Contribution percentages of the process variables to the duration of the atmospheric freeze-drying of apple samples (A: temperature; B: air velocity; C: acoustic power).

4. Conclusions

In this study, a simple one-dimensional model has been successfully applied to assess the effect of the US application on the AFD kinetics of apple. US severely shortened the drying time under every condition tested. On the other hand, the model has been validated under different drying conditions (different size and geometry of the sample) obtaining a good fit to the experimental data and showing the retreat of the ice front during AFD. From a 2^3 factorial design of experiments, it has been proven that US application is the parameter with the greatest influence on the AFD time and, consequently, is the key factor for the further optimization of the process.

Acknowledgements

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List of symbols

S	surface of the product, m^2
a	parameter used to calculate the heat transfer coefficient
$c_{p,air}$	air specific heat, J/kg K
D_e	effective diffusivity of water vapor in the dried product, m^2/s
G	sublimation flow rate, kg/s
ΔH_s	heat of sublimation, J/kg
J_w	sublimation flux, kg/s m^2
j_h	*j-factor* for the heat transfer
L_0	initial characteristic dimension of the product, m
L_{dried}	characteristic dimension of the dried product, m
M_w	water molecular weight, kg/kmol
n	parameter used to calculate the heat transfer coefficient
p_w	water vapor partial pressure, Pa
$p_{w,c}$	water vapor partial pressure in the drying chamber, Pa
$p_{w,i}$	water vapor partial pressure at the sublimation interface, Pa
p_w^*	water vapor partial pressure at the product's external surface, Pa
Q	heat flow rate, W
R	ideal gas constant, J/kmol K
Re	Reynolds number
r	radial coordinate

T	temperature, K
T_{air}	air temperature, K
T_i	temperature of the sublimation interface, K
t	time, s
V_{dried}	volume of the dried product, m^3
W	water content in the product, $kg_{water}/kg_{dry\ matter}$
W_0	water content in the product at the beginning of the drying process, $kg_{water}/kg_{dry\ matter}$
W_f	water content in the product at the end of the drying process, $kg_{water}/kg_{dry\ matter}$
x	axial coordinate, m

Greek letters

α	mass transfer coefficient, m/s
β	heat transfer coefficient, W/m^2 K
λ_{dried}	thermal conductivity of the dried product, W/m K
ρ_{air}	density of the air, kg/m^3
ρ_{dried}	density of the dried product, kg/m^3

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Chapter 3

Prospective application

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USE OF NOVEL DRYING TECHNOLOGIES TO IMPROVE THE RETENTION OF INFUSED OLIVE LEAF POLYPHENOLS

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ABSTRACT

The infusion of phenolic extracts in dried fruits constitutes an interesting means of improving their nutritional content. However, drying can affect the further process of impregnation. In this work, different drying treatments (air temperature and ultrasound application) were applied to apple samples and impregnated with olive leaf extract. The application of ultrasound during drying did not significantly ($p<0.05$) affect the infusion capacity of samples but the ultrasonically assisted dried samples showed a greater antioxidant capacity than those conventionally dried. The highest content of oleuropein and verbascoside was found in samples dried at low temperature using ultrasound.

Keywords: drying; infusion; extract; antioxidant potential; HPLC-DAD/MS-MS

1. Introduction

Apple is one of the most widely-consumed fruits, not only raw but also in the form of juice or as a dried product included in snack preparations or whole grain breakfast cereals (Biedrzycka and Amarowicz, 2008). Apple is also characterized by a high concentration of phenolic compounds, with an important portion of free phenolics compared with other fruits (Boyer and Liu, 2004). The Granny Smith variety is one of the apple cultivars that is richest in polyphenols (66.2-211.9 mg/100 g fresh weight). Processing could provoke changes in the apple, affecting not only the matrix structure but also the bioactive components (Tiwari and Cummins, 2004).

Nowadays, consumers demand high quality products with an extended shelf life, which not only preserve the fresh-like characteristics of flavor, texture or color well but also enjoy an improved nutritional content (Rodríguez et al., 2014). Thus, the infusion of interesting compounds into vegetable solid matrices, compounds such as antioxidants (Fernandes et al., 2011), has gained importance in recent years. The internal structure of apple is composed of parenchyma cells interspersed with air spaces (Khan and Vincent, 1990) that makes the infusion of solutions easier than in more closed and compact structures. The process of infusion is made particularly easy if the water content has previously been reduced, e.g. by drying. In this sense, apple has been used as a matrix for the infusion of ascorbic acid solutions (Blanda et al., 2008) and grape phenolic compounds (Ferrando et al., 2011; Rózek et al., 2010). Olive leaf extracts could be an interesting alternative means of impregnating food products, since they are rich in phenolic compounds, such as oleuropein, verbascoside and luteolin glucoside (Ahmad-Qasem et al., 2013a,b) with proven bioactive properties (Karakaya, 2009). The infusion of olive leaf polyphenols in the dried apple matrix could greatly improve their bioactive content and, therefore, their benefits for human health.

Infusion can be addressed as a particular rehydration-impregnation operation. The structural damage caused by removing the water during the drying of the fresh product could greatly affect not only the infusion capacity and rate (Cunningham et al., 2008) but also the interaction force between the infused compounds and the solid matrix. Due to its simplicity and its relatively low cost, one of the most

frequently used dehydration methods in the food industry is that of conventional hot air drying. The high temperature used can help to inactivate some enzymatic reactions (Sanjuan et al., 2001), some of which can degrade antioxidant compounds. However, it can produce changes in the nutritional value, physical properties and microstructure of the products.

Recently, the feasibility of employing new drying technologies to improve drying has been evaluated. In this sense, the use of low temperature drying can represent an interesting alternative with which to reduce the changes produced by drying (Garcia-Perez et al., 2012). On the other hand, the application of power ultrasound has been proven to be an interesting means of increasing the drying rate, not only in conventional high-temperature drying (Cárcel et al., 2011) but also in low-temperature drying processes (Garcia-Perez et al., 2012).

All these different drying methods can affect the samples' structure and composition in different ways, thus influencing the further infusion of the antioxidant compounds. Therefore, the main objective of this work was to evaluate how the drying method used on the fresh apple affects the further infusion of the olive leaf extract. The retention of the polyphenols in the apple matrix and the antioxidant capacity of the obtained samples will also be addressed.

2. Materials and methods

To achieve this main goal, porous matrixes of apple were obtained by drying fresh samples by means of different methods. Then the dried samples were infused with olive leaf extract and, afterwards, dried again to obtain a final, stable product. The antioxidant capacity and phenolic content of the final product was assessed to determine the influence of the first drying process on the obtained product. Subsequently, a more detailed description of the different parts of the working plan is shown.

2.1. Obtaining of olive leaf extracts

Olive leaves (*Olea europaea*, var. Serrana) were collected on a farm located in Segorbe (Castellón, Spain), packaged and stored at 4°C (for less than 48 h). The

initial moisture content was determined following AOAC method nº 934.06 (AOAC, 1997). The olive leaves were separated in different sets and dried at 120°C (1±0.1% relative humidity) for 12 min in a forced air laboratory drier (FD, Binder, Tuttlingen, Germany) using an air flow of 0.094 m^3/s and an air velocity of 0.683 m/s following the experimental procedure reported by Ahmad-Qasem et al. (2013a). For each set, an initial mass load of 150 g was used. The dehydration process was extended until the samples lost 40±1% of the initial weight. After drying, the olive leaves of the different sets were mixed and packaged in plastic bags and stored at 4°C until the extraction operation.

The dried leaves were milled (Blixer 2, Robot Coupe USA, Inc., Jackson, MS, USA) and the obtained powder was sieved (Metallic mesh size 0.05 mm, Filtra Vibración, Barcelona, Spain) selecting particles with a diameter of under 0.05 mm. The extraction experiments were carried out in sealed containers, protected from light and immersed in a thermostatic (22±1°C) shaking (170 rpm) water bath (SBS40, Stuart, Staffordshire, UK) for 24 h. The ratio between olive leaf powder and solvent (water) was 10 g/150 mL. Afterwards, the extracts were centrifuged for 10 min at 5000 rpm (Medifriger BL-S, J.P. Selecta, Barcelona, Spain), filtered (nylon filters of 0.45 Tm), characterized (phenolic content and antioxidant capacity) and stored in opaque vials at 4°C until their use for apple infusion.

2.2. Apple drying experiments

Cubes of 10 mm side were obtained from apples (*Malus domestica* cv. Granny Smith) by using a cutting machine (CL50 Ultra, Robot Coupe USA, Inc., Jackson, MS, USA) and immediately processed. The initial moisture content was measured by placing the samples at 70ºC and 200 mmHg until constant weight was reached, following AOAC method nº 934.06 (AOAC, 1997).

Drying experiments were carried out with and without ultrasound application at 60ºC, a commonly high temperature used in the dying of fruits and vegetables, and at -1ºC, a low temperature that can contribute to preserve the natural components of apple. Therefore, four different methods were used to dry the apple cubes: hot air drying at 60ºC (relative humidity of 8±1%), without (HAD) and with ultrasound (USHAD) application and low temperature drying at -1ºC (relative humidity of

15±2%), without (LTD) and with ultrasound (USLTD) application. The drying experiments at 60ºC and -1ºC were carried out in convective driers showed in Figure 1A and Figure 1B respectively, already described in detail in previous studies (Garcia-Perez et al., 2012; Riera et al., 2011). The ultrasonically assisted experiments (USHAD and USLTD) were conducted using an acoustic power of 20.5 kW/m^3, which is defined as the electric power supplied to the ultrasonic transducer divided by the volume of the drying chamber. Ultrasound was applied in continuous way during drying. For each run, 110 apple cubic samples, that mean an initial mass load of 80±3 g, were placed in a sample holder such as that shown in Figure 2. The position of samples in the 9 trays of the holder assured a uniform treatment of them for both air flowing and ultrasound application (Garcia-Perez et al., 2012). Experiments were carried out at least in triplicate, using an air velocity of 2 m/s and extended until the samples lost 83±1% of the initial weight.

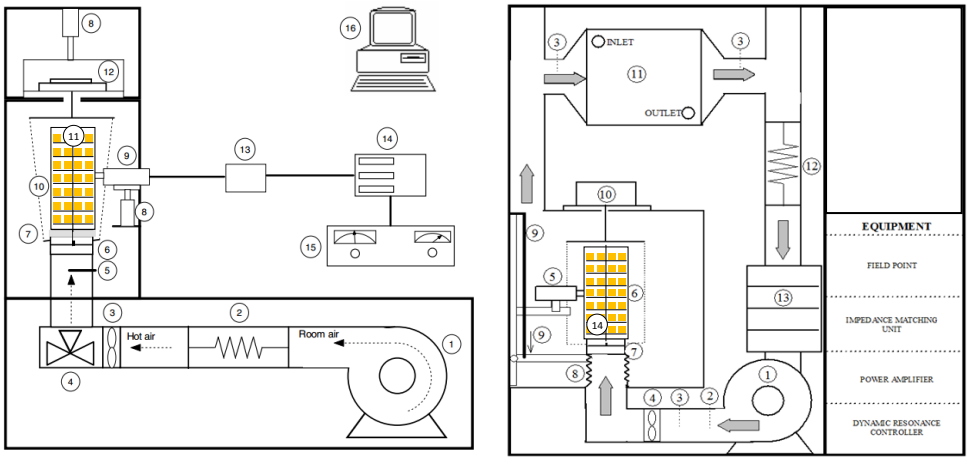

Figure 1. Scheme of ultrasonically assisted convective driers.

A; high temperature drier: 1, fan; 2, heating unit; 3, anemometer; 4, three-way valve; 5, thermo-couple; 6, sample loading chamber; 7, coupling material; 8, pneumatic moving arms; 9, ultrasonic transducer; 10, vibrating cylinder; 11, sample holder; 12, balance; 13, impedance matching unit; 14, wattmeter; 15, high-power ultrasonic generator; 16, PC.

B; low temperature drier: 1, fan; 2, Pt-100; 3, temperature and relative humidity sensor; 4, anemometer; 5, ultrasonic transducer; 6, vibrating cylinder; 7, sample load device; 8, retreating pipe; 9, slide actuator; 10, weighing module; 11, heat exchanger; 12, heating elements; 13, desiccant tray chamber; 14, sample holder.

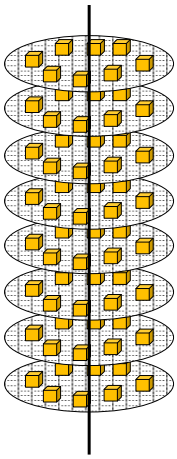

Figure 2. Scheme of distribution of apple cubes in the sample holder.

The dried samples were infused with the olive leaf extract and further dried for the final stabilization. Ahmad-Qasem et al. (2015) found that the influence the final drying step had on the antioxidant capacity and phenolic content of infused apples was negligible. For this reason, every sample was dried at 60ºC and 2 m/s using an initial mass load of 14±1 g until the samples achieved a constant weight.

2.3. Drying kinetics modeling

A diffusion model was used to describe the drying kinetics (HAD, USHAD, LTD and USLTD) of fresh apple cubes. The differential equation of diffusion was obtained combining Fick's first law and the microscopic mass balance. For cubic geometry, the diffusion model considering constant the effective moisture diffusivity and isotropic solid is shown in equation (1).

$$\frac{\partial W_p(x,y,z,t)}{\partial t} = D_e\left(\frac{\partial^2 W_p(x,y,z,t)}{\partial x^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial y^2} + \frac{\partial^2 W_p(x,y,z,t)}{\partial z^2}\right) \quad (1)$$

where W_p is the local moisture (kg water/kg dry matter, d.m.), t is the time (s), D_e is the effective moisture diffusivity (m^2/s) and x, y and z represent the characteristic coordinates in cubic geometry (m).

In order to solve equation (1), the following assumptions were considered: solid symmetry, uniform initial moisture content and temperature, constant shape during drying and a negligible external resistance to moisture transport. Taking these assumptions into account, the analytical solution of the diffusion equation, expressed in terms of the average moisture content, is shown in equation (2) (Crank, 1975).

$$W(t) = W_e + (W_0 - W_e)\left[\sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D_e (2n+1)^2 \pi^2 t}{4L^2}\right)\right]^3 \quad (2)$$

where W is the average moisture content (kg water/kg d.m.), L the half-length of the cube side (m) and subscripts 0 and e represent the initial and equilibrium state, respectively.

The diffusion model was fitted to the experimental drying kinetics in order to identify the effective moisture diffusivity. The identification was carried out by minimizing the sum of the squared differences between the experimental and the calculated average moisture content. For that purpose, the Generalized Reduced Gradient (GRG) optimization method, available in Microsoft Excel™ spreadsheet (Microsoft Corporation, Seattle, WA, USA) was used. The goodness of the fit was determined by calculating the percentage of explained variance (%VAR, equation (3)).

$$\%VAR = \left[1 - \frac{S_{xy}^2}{S_y^2}\right] \cdot 100 \quad (3)$$

where S_{xy} and S_y are the standard deviation of the estimation and the sample, respectively.

2.4. Infusion experiments

The infusion of the olive leaf extract into the dried apple samples was carried out in flasks protected from the light at 25ºC. In each experiment, 4 g of dried apple cubes were immersed in 250 mL of olive leaf extract. The infusion kinetics were determined by weighing the samples at preset times. For that purpose, apple cubes were extracted from the solution, blotted with tissue paper to remove the excess of superficial extract and jointly weighed. It was considered that the

equilibrium state was reached when the difference between two consecutive sample weights (at least, 1200 s of delay) was less than 0.02 g. The experiments were conducted in triplicate for each drying condition tested (HAD, USHAD, LTD and USLTD).

The infusion capacity (IC) was calculated from equation (4).

$$IC = \frac{(M_t - M_0)}{M_0} \quad (4)$$

where M_t is the weight (g) of the infused samples at time t and M_0 the initial weight of the dried samples (before the infusion).

2.5. Phenolic content and antioxidant capacity

The total phenolic content and the antioxidant capacity of both the olive leaf extracts and of the dried, infused and re-dried apple samples was assessed. The measurements were carried out directly in the olive leaf extract but the apple samples had to be pre-conditioned in order to extract the polyphenols. To that end, 10 g of the apple sample were placed in sealed containers protected from the light with 150 mL of distilled water at 22±1°C and agitated at 170 rpm for 24 h. Afterwards, the extracts were centrifuged (10 min at 5000 rpm) and filtered (nylon filters of 0.45 µm); the phenolic content and antioxidant capacity in the permeate solution were analyzed as is subsequently described (Ahmad-Qasem et al., 2013a).

2.5.1. Total phenolic content measurement (TPC)

The phenolic content was determined by means of the Folin-Ciocalteu method (Singleton et al., 1999). Briefly, 100 µL of sample were mixed with 200 µL of Folin-Ciocalteu's phenol reagent (Sigma-Aldrich, Madrid, Spain) and 2 mL of distilled water. After 3 min at 25ºC, 1 mL of Na_2CO_3 (Panreac, Barcelona, Spain) solution (Na_2CO_3-water 20:80, p/v) was added to the mixture. The reaction was kept in the dark at room temperature for 1 h. Finally, the absorbance was read at 765 nm using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK).

The measurements were carried out in triplicate. The standard curve was previously prepared using solutions of a known concentration of gallic acid hydrate (Sigma-Aldrich, Madrid, Spain) in distilled water. Results were expressed as mg of gallic acid (GAE) per g of dried matter (d.m.) of apple samples or mg GAE per mL of olive leaf extract.

2.5.2. Antioxidant capacity measurement (AC)

The antioxidant capacity of extracts was determined by using the Ferric-reducing ability power (FRAP) method, which is a simple method used to estimate the reduction of a ferric-tripyridyltriazine complex method. It was applied following the procedure described by Benzie and Strain (1996) with some modifications. Briefly, 900 µL of freshly prepared FRAP reagent were mixed with 30 µL of distilled water and 30 µL of test sample or water as appropriate reagent blank and kept at 37°C for 30 min. The FRAP reagent contained 2.5 mL of a 10 mM TPTZ (Fluka, Steinheim, Germany) solution in 40 mM HCl (Panreac, Barcelona, Spain) plus 2.5 mL of 20 mM $FeCl_3 \bullet 6H_2O$ (Panreac, Barcelona, Spain) and 2.5 mL of 0.3 M acetate buffer (Panreac, Barcelona, Spain), pH 3.6 (Pulido et al., 2000). Readings were taken at the maximum absorption level (595 nm) using a spectrophotometer (Helios Gamma, Thermo Spectronic, Cambridge, UK). Four replicates were made for each measurement. The antioxidant capacity was evaluated through a calibration curve, which was previously determined using water solutions of known Trolox (Sigma-Aldrich, Madrid, Spain) concentrations and expressed as mg Trolox per g of dried matter (d.m.) of apple sample or mg Trolox per mL of olive leaf extract.

2.5.3. Identification and quantification of polyphenols by HPLC-DAD/MS-MS

In order to identify and quantify the main polyphenols present in the olive leaf extracts and apple samples, these were analyzed using an HPLC instrument (Agilent LC 1100 series; Agilent Technologies, Inc., Palo Alto, CA, USA) controlled by the Chemstation software. The HPLC instrument was coupled to an Esquire 3000+ (Bruker Daltonics, GmbH, Germany) mass spectrometer equipped with an

ESI source and ion-trap mass analyzer, and controlled by Esquire control and data analysis software. A Merck Lichrospher 100RP-18 (5 µm, 250 x 4 mm) column was used for analytical purposes.

Separation was carried out through a linear gradient method using 2.5% acetic acid (A) and acetonitrile (B), starting the sequence with 10% B and programming the gradient to obtain 20% B at 10 min, 40% B at 35 min, 100% B at 40 min, 100% B at 45 min, 10% B at 46 min and 10% B at 50 min. For the LC-MS pump to perform accurately, 10% of organic solvent was pre-mixed in the water phase. The flow-rate was 1 mL/min and the chromatograms monitored at 240, 280 and 330 nm. Mass spectrometry operating conditions were optimized in order to achieve maximum sensitivity values. The ESI source was operated in negative mode to generate $[M–H]^-$ ions under the following conditions: desolvation temperature at 365°C and vaporizer temperature at 400°C; dry gas (nitrogen) and nebulizer were set at 12 L/min and 4.83 bar, respectively. The MS data were acquired as full scan mass spectra at 50–1100 m/z by using 200 ms for the collection of the ions in the trap.

The main compounds were identified by HPLC-DAD analysis, comparing the retention time, UV spectra and MS/MS data of the peaks in the samples with those of authentic standards or data reported in the literature. Only the main olive leaf polyphenols were quantified using commercial standards: oleuropein (Extrasynthese, Genay Cedex, France), luteolin-7-O-glucoside (Phytolab, Vestenbergsgreuth, Germany) and apigenin (Nutrafur, Murcia, Spain). A purified extract (96.85%) provided by Universidad Miguel Hernández (Elche, Spain) was used to quantify verbascoside. The quantitative evaluation of the compounds was performed with a calibration curve for each polyphenol, using ethanol (oleuropein), methanol (verbascoside and luteolin) or dimethyl sulfoxide (apigenin) solutions of known concentration. The polyphenol concentrations were expressed as mg polyphenol per g of dried matter (d.m.) of apple sample or mg polyphenol per mL of olive leaf extract.

3. Results and discussion

3.1. Characterization of olive leaf extract

The antioxidant potential of the olive leaf extracts was assessed from the determination of TPC and AC. As can be observed in Table 1, the average TPC and AC values were 1.7±0.3 mg GAE/mL and 5.1±0.7 mg Trolox/mL, respectively. These figures are slightly lower than others published in previous studies (Ahmad-Qasem et al., 2013a,b), which can be ascribed to the use of a different solvent, water in this study, while Ahmad-Qasem et al. (2013a,b) used an ethanol-water solution at 80:20 (v/v). As regards the profile of the identified phenolic compounds, it was similar to the ones previously found by Ahmad-Qasem et al. (2013a,b), the main polyphenols identified being oleuropein, verbascoside and luteolin and apigenin derivates.

Table 1. Characterization of Olive leaf extracts.

Olive leaf extract characterization	
TPC (mg GAE/mL)	1.7 ± 0.3
AC (mg Trolox/mL)	5.1 ± 0.7
Oleuropein (mg/mL)	3.3 ± 0.2
Verbascoside (mg/mL)	0.18 ± 0.04
Luteolin glucoside (mg/mL)	0.31 ± 0.04
Apigenin-6,8-diglucoside*	0.013 ± 0.002

TPC: total phenolic content
AC: antioxidant capacity
*Content expressed as equivalents of apigenin (mg/mL)

3.2. Apple drying

Four different methods were used to dry the fresh apple cubes: HAD, USHAD, LTD and USLTD. The experimental drying kinetics are shown in Figure 3A for HAD and USHAD and in Figure 3B for LTD and USLTD. LTD was the longest drying process; under these conditions, apple cubes needed an average of 76 h to lose 83% of the initial weight. The application of US (USLTD) shortened the drying to 28 h, which implies a 63% reduction of the drying time. This kinetic improvement was similar to the ones reported for the ultrasonically assisted low temperature drying of different vegetables or fruits. Thus, when US was applied to the drying of eggplant,

carrot and apple at -14ºC, Garcia-Perez et al. (2012) found that, on average, the drying time was between 65 and 70% shorter. Santacatalina et al. (2014) applied US during the drying of apple cubes at 0ºC and obtained a drying time reduction of around 60%.

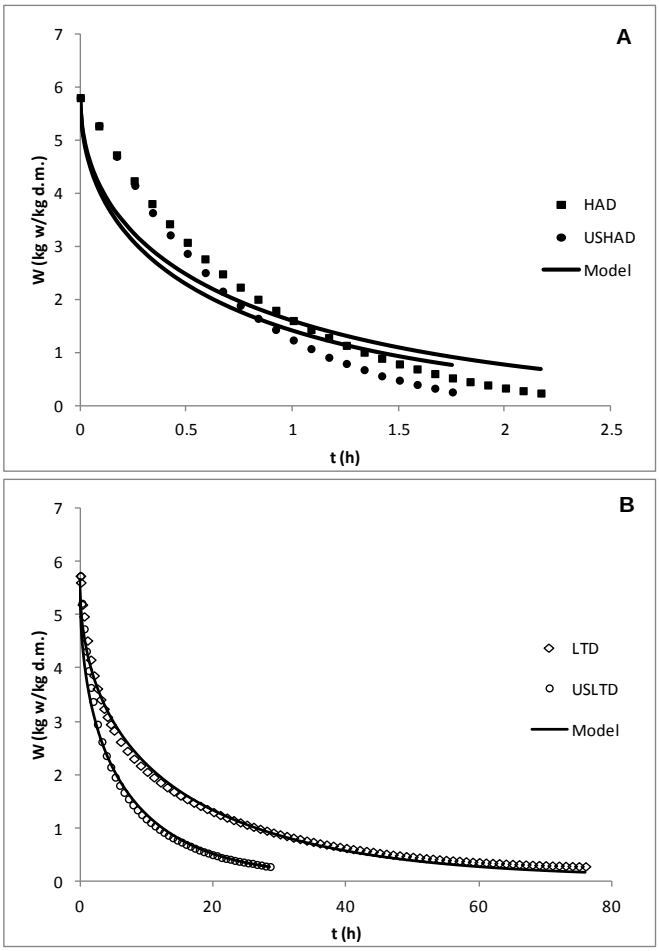

Figure 3. Experimental drying kinetics of fresh apple cubes (side 10 mm) and diffusion model. **A**: hot air drying without (HAD, 60ºC, 2m/s) and with power ultrasound application (USHAD, 60ºC, 2m/s, 20.5 kW/m^3) and **B**: low temperature drying without (LTD, -1ºC, 2m/s) and with power ultrasound application (USLTD, -1ºC, 2m/s, 20.5 kW/m^3).

The experiments carried out at 60ºC (HAD and USHAD) were much faster than those conducted at low temperature (-1ºC, LTD and USLTD); the difference in drying time between HAD and LTD was greater than one order of magnitude (approximately 2 hours as opposed to 80 hours, Figures 3A and 3B). The

application of power ultrasound (USHAD) under these conditions also shortened the drying time (by 15%), but to a lower extent than in USLTD experiments. During high temperature drying, ultrasound application has been observed to exert only a mild influence. Rodríguez et al. (2014) found a drying time reduction of 17.4% when US was applied (30.8 kW/m^3) during the drying of apple at 70ºC. Ultrasound provides additional energy to the thermal energy available in the drying air. When low temperatures are used, there is only a little energy available in the drying medium, which greatly increases the importance of the energy introduced by ultrasound. At high temperatures, the amount of energy in the medium is high and the acoustic energy provided by ultrasound is less relevant to the drying rate. This issue explains why the influence which power ultrasound exerts on drying performance is more marked at low temperatures than at high (Garcia-Perez et al., 2006).

The drying kinetics of fresh apples cubes were modeled in order to identify the effective moisture diffusivity (D_e) and to assess the differences between the drying techniques tested (Table 2). The model fitted the experimental drying kinetics of LTD and USLTD adequately, as suggested by the %VAR figures obtained, over 98%. This fact shows that, at low temperatures, the drying kinetics can be explained by considering a controlling diffusional mechanism; the assumptions considered should be close to the actual drying conditions. In the case of HAD and USHAD, the %VAR obtained drastically dropped to under 91%. The poor fit of the diffusion model in HAD can also be observed in Figure 3A, where the model deviated from the experimental curves, indicating that it is not only diffusion that acts on the mass transfer control, but other factors as well. Garcia-Perez et al. (2006) found similar results when applying this model to experimental drying kinetics of carrot drying obtained at 1m/s and temperatures ranging between 30 and 70ºC. They also used other model including external resistance that described better the experimental data providing percentages of explained variance above 99.9%. The high air temperature used in HAD and USHAD experiments reduced the internal resistance compared to the one found in the LTD and USLTD experiments, while the same air velocity makes that the external resistance remains similar. Therefore, the external resistance to water transfer plays a major

role in controlling the drying rate, which could explain the poorer fit of the diffusion model proposed, that neglects the external resistance, in HAD and USHAD.

Table 2. Effective moisture diffusivity (D_e) and percentage of explained variance (%VAR) from the modeling of fresh apple drying. Average values and standard deviation are shown for D_e.

Drying method	D_e (x10^{-11} m^2/s)	%VAR
LTD	4.50 ± 0.41^{a}	99.4
USLTD	9.30 ± 0.42^{b}	98.8
HAD	65.81 ± 2.22^{x}	90.3
USHAD	82.98 ± 5.40^{y}	90.1

Superscript letters (a, b) and (x, y) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the D_e of -1 (LTD and USLTD) and 60ºC (HAD and USHAD) drying experiments, respectively.

More mechanistic approaches for the drying modelling have been proposed in the literature including heat and mass transfer coupling, variable diffusivity or shrinkage of samples (Garcia-Perez et al., 2011; Mihoubi et al., 2004; Perré and May, 2001, 2007) fitting better drying kinetics than the model used in this work. However, the effective diffusivity identified in this case allowed evaluating the influence of the different drying methods tested on drying rate. On the one hand, the D_e values identified (Table 2) for USLTD experiments were significantly ($p<0.05$) higher (107%) than for LTD. At 60ºC, the influence of ultrasound on the D_e identified was lower compared to experiments carried out at -1ºC (26% higher in USHAD than in HAD). From preliminary tests, it was observed that the ultrasonically dried samples showed an increase of temperature at the end of drying lower than 3ºC. Similar increase of temperature has been observed by Kowalski (2014) drying apple slices at 30ºC and an ultrasonic power of 50 W. This fact can indicate that the effect of ultrasound in drying kinetics was not only associated to the thermal effect. Thus, Garcia-Perez et al. (2006), for drying carrots, found D_e values higher at 50ºC with ultrasound application than at 60ºC without ultrasound application. According to the literature, the improvement of D_e brought about by ultrasonic application can be mainly linked to the mechanical effects provoked in the material (Garcia-Perez et al., 2009). The alternating expansions and contractions produced by acoustic waves when travelling through a medium (Gallego-Juárez et al., 1999) generate a mechanical stress that facilitates the movement of water through the product. In

any case, it will be interesting to carry out a deep study to differentiate thermal and mechanical effects of ultrasound during drying.

3.3. Infusion of the olive leaf extract into the dried apple

Apple cubes dried by means of the four different techniques were impregnated with the olive leaf extract and the infusion kinetics were experimentally determined by weighing the samples at preset times. The results showed that the method employed to dry fresh apples had a significant ($p<0.05$) influence on the final infusion capacity (IC) (Figure 4). Thus, the IC after 3.5 h of HAD (3.26±0.03) and USHAD (3.17±0.15) samples infusion was significantly ($p<0.05$) greater than that observed in LTD (2.90±0.05) and USLTD (2.75±0.15) samples. These differences could be linked to the fact that LTD experiments were carried out at a temperature (-1ºC) close to the freezing point of the apple. Previously, it has been reported that freezing could introduce changes in the rehydration pattern of vegetables (Eshtiaghi et al., 1994). The application of power ultrasound did not lead to significant ($p<0.05$) differences in the IC. Therefore, it could be stated that ultrasonic assisted drying at low or high temperatures did not affect the solvent gain during the impregnation of the olive leaf extract into the dried apple. It is known that the mechanical stress produced by ultrasound can affect the internal structure of materials (Puig et al., 2012) and, therefore, the later infusion capacity. But this influence depends of process variables (temperature, ultrasonic power applied and product) and the final structure of ultrasonically assisted dried product can be less degraded than conventionally dried one (Puig et al., 2012). For the process studied in this work, it seems that the effects of ultrasound were enough to improve drying but not so high to significantly affect the infusion capacity.

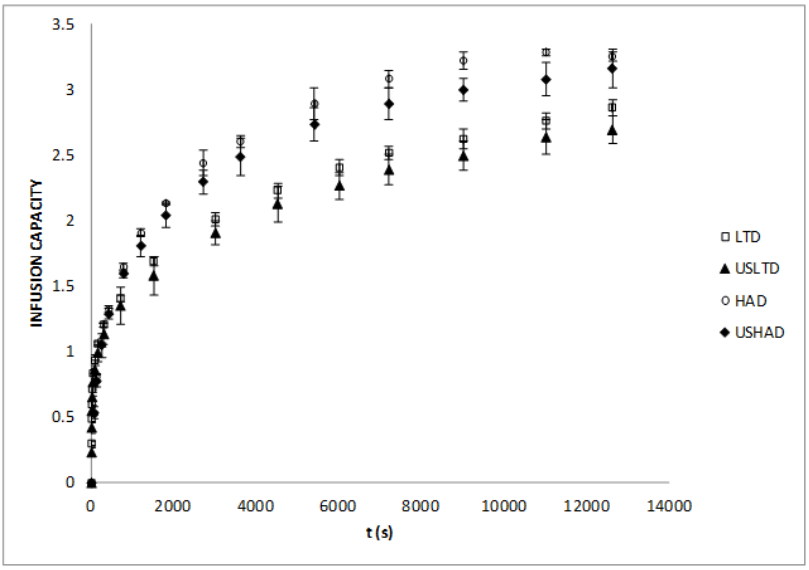

Figure 4. Infusion kinetics of olive leaf extract into LTD, USLTD, HAD and USHAD dried apple cubes (side 10 mm).

3.4. Influence of drying method on antioxidant potential

The apple cubes impregnated with the olive leaf extract were further stabilized by a final drying operation. According to the results reported by Ahmad-Qasem et al. (2015), the influence of which final drying method was used on the apples that had been impregnated with the olive leaf extract was negligible compared to the influence of the method employed to dry the fresh apple. For this reason, the same drying method was used to dry the impregnated samples (hot air dried at 60ºC and 2 m/s). Therefore, in the following sections, it is reported how the drying method used on the fresh apple affects the TPC, AC and the main polyphenols infused into the dried apple.

3.4.1. Total phenolic content (TPC)

The TPC value obtained for fresh apple was 0.40±0.05 mg GAE/g d.m. This value is lower than the reported for Fu et al. (2011) for different apple varieties. After infusion, the lowest value of TPC was obtained in LTD (14.0±355 0.8 mg GAE/g d.m.) samples, while the highest one was found in HAD (30.2±1.6 mg GAE/g d.m.)

(Figure 5). That means that, in all cases, the infusion of olive leaf extracts significantly increased the phenolic content of fresh apple. The difference between LTD and HAD samples could be due to the high temperatures which can induce the formation of some phenolic compounds and inactivate enzymatic reactions of phenolic compounds degradation (Ahmad-Qasem et al., 2013a).

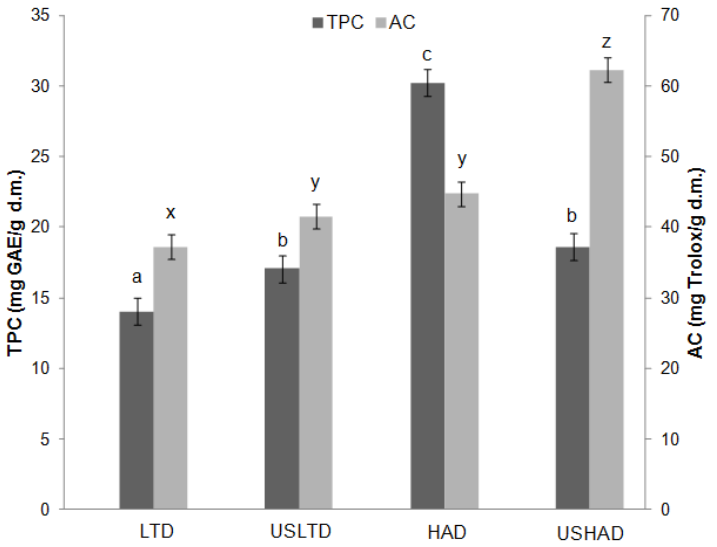

Figure 5. Influence of the drying method used on the fresh apple (LTD, USLTD, HAD and USHAD) on the total phenolic content (TPC) and antioxidant capacity (AC) of samples impregnated with the olive leaf extract. Means±LSD intervals are plotted. Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for TPC and AC, respectively.

The samples dried by means of US application presented intermediate values of TPC, with no significant differences ($p<0.05$) found between samples dried at low (-1ºC; USLTD; 17.1±1.0 mg GAE/g d.m) and high temperatures (60ºC; USHAD; 18.6±0.8 mg GAE/g d.m). Therefore, the application of ultrasound during the drying of fresh apple led to a negligible influence of the drying temperature on the TPC. Thereby, the difference observed between the TPC of HAD and LTD was not found for in the case of USHAD and USLTD. High temperature drying could induce the formation of some phenolic compounds (Ahmad-Qasem et al., 2013c). To a certain extent, this could be different when US is applied due to its widely recognized capacity to form free radicals, which could reduce the amount of available

polyphenols (Paniwnyk et al., 2001). Otherwise, the kinetic intensification caused by US application at low temperatures involved a great shortening (48 hours) of the exposure time to the air flow and so, could reduce the degree of oxidation of the phenolic compounds. In addition to the aforementioned effects, the inactivation of oxidative enzymes by ultrasound waves should also be considered (Islam et al., 2014), something which is almost negligible at high temperatures, but that could be meaningful at low temperature drying where the enzymes are well preserved.

3.4.2. Antioxidant capacity (AC)

The drying method applied to fresh apple also significantly ($p<0.05$) affected the AC (Figure 5), the AC of the samples dried at low temperatures (LTD) being significantly ($p<0.05$) lower than that of HAD ones, which was consistent with the results reported for TPC. As regards the ultrasound application, on the one hand, USLTD showed not only higher TPC, as already reported, but also higher AC than LTD. On the other hand, USHAD also showed a higher AC than HAD and USLTD which, in this case, is not consistent with the behavior found in the TPC. The high figure found for the AC of USHAD samples could be linked to several facts. Firstly, the synergetic effect of the combined high temperature-ultrasound treatment could favor the inactivation of oxidative enzymes, thus preserving the antioxidant capacity of the available polyphenols. Secondly, the new compounds resulting from the binding of the polyphenols with the free radicals promoted by ultrasound could be highly reactive, increasing the antioxidant capacity. Finally, further work focusing on clarifying the biochemical principles should be carried out to elucidate these hypotheses.

3.4.3. Quantification of the main characteristic polyphenols

In order to characterize the infusion process, the main polyphenols of the olive leaf extracts were analyzed in the impregnated apples with the aim of quantifying their retention in the solid matrix after the final drying. The four main polyphenols identified in the olive leaf extract (Table 1) were also found in the impregnated

apple samples (Figures 6 and 7). However, the method employed to dry the fresh apple influenced the content of these compounds.

In the case of oleuropein (Figure 6), no significant ($p<0.05$) differences were found between LTD and HAD samples, showing that the drying temperature did not affect this compound. Ultrasound application greatly increased the oleuropein content, which was especially remarkable at low temperatures (USLTD). As far as we know, this result has not been previously reported. As regards verbascoside (Figure 6), ultrasound application was found to produce the same effect, since it promoted an increase in both LTD and HAD. In this case, it should be emphasized that the verbascoside content of HAD was significantly ($p<0.05$) lower than that of LTD.

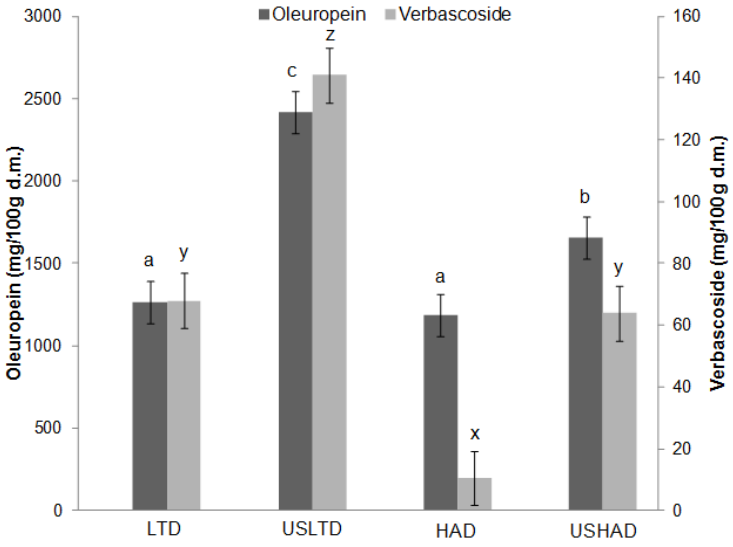

Figure 6. Influence of the drying method used on the fresh apple (LTD, USLTD, HAD and USHAD) on the content of oleuropein and verbascoside of samples impregnated with the olive leaf extract. Means±LSD intervals are plotted. Superscript letters (a, b, c) and (x, y, z) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the content of oleuropein and verbascoside, respectively.

For the minority compounds, luteolin glucoside and apigenin-6,8-glucoside, the influence of the drying method used on the fresh apple was less marked. No significant differences were found in the case of the apigenin-6,8-diglucoside

content (Figure 7), while only the USLTD samples showed a significantly ($p<0.05$) different luteolin-glucoside content.

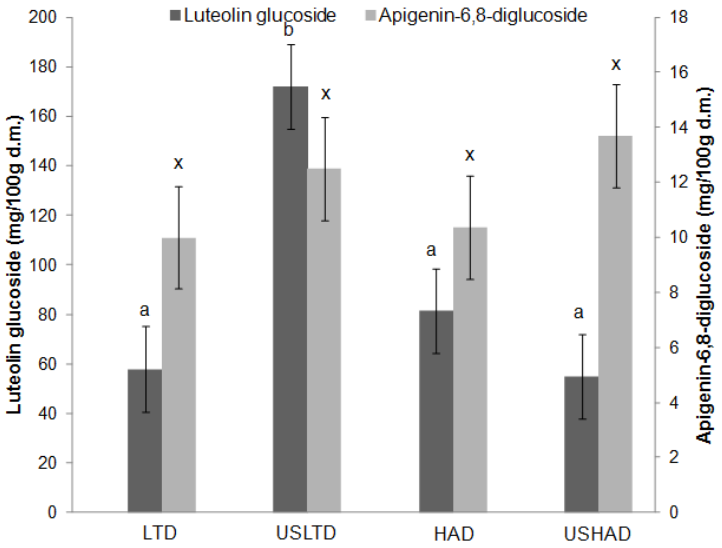

Figure 7. Influence of the drying method used on the fresh apple (LTD, USLTD, HAD and USHAD) on the content of luteolin glucoside and apigenin-6,8-diglucoside of samples impregnated with the olive leaf extract. Means±LSD intervals are plotted. Superscript letters (a, b) and (x) show homogeneous groups established from LSD (Least Significance Difference) intervals ($p<0.05$) for the content of luteolin glucoside and apigenin-6,8-diglucoside, respectively.

Therefore, the drying method applied before infusing the apple with olive leaf extract had a significant influence on the subsequent conservation of the added polyphenols. A probably explanation for this fact is the different sensitivity of the original enzymes of fresh apple to the inactivation caused by the different drying methods applied. Thus, a remarkable influence of the drying method is observed in some infused components, such as oleuropein, but other compounds, like apigenin-6,8-diglucoside, seem to be quite stable. A biochemical study must be carrying out to confirm this fact. The USLTD samples were the ones that showed the highest concentrations of the main compounds: oleuropein (2416±159 mg/100 g d.m.), verbascoside (141±11 mg/100 g d.m.) and luteolin glucoside (172±8 mg/100 g d.m.).

4. Conclusions

The method used to dry fresh apple not only affected the drying kinetic but also the further infusion of olive leaf extract. As regards the drying kinetics, the influence of ultrasound application was more important at the lowest temperature, -1ºC. The application of ultrasound during drying did not significantly ($p<0.05$) affect the infusion capacity of the samples. However, the ultrasonically assisted dried samples showed a greater antioxidant capacity than those conventionally dried at the same temperature. The highest content of polyphenols added with olive leaf extracts (oleuropein and verbascoside) was found in samples that had been submitted to ultrasound assisted low temperature drying. Further research is needed to elucidate the actual mechanisms of influence of the drying method on the polyphenol content.

Acknowledgements

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5. Discusión general

En procesos de secado con aire caliente asistidos por ultrasonidos de potencia, las variables de proceso, tales como la temperatura, la velocidad del aire o la potencia acústica aplicada pueden afectar en gran medida a las cinéticas de secado de los productos agroalimentarios. Además, estas variables presentan una gran influencia en la efectividad de la aplicación de los ultrasonidos, y por tanto, en la magnitud de sus efectos. En la presente tesis doctoral se ha estudiado la influencia que estas variables tienen en procesos de secado a baja temperatura. Así, una de las variables consideradas fue la temperatura y se observó su influencia tanto a valores por encima como por debajo del punto de congelación de tres productos (manzana, berenjena y bacalao). Cuando se utilizaron temperaturas por debajo del punto de congelación de las muestras, se obtuvieron cinéticas de secado mucho más lentas al producirse la salida de agua por sublimación, un proceso bastante más lento que la evaporación que se da a temperaturas superiores al punto de congelación.

La aplicación de ultrasonidos de potencia produjo una reducción del tiempo de secado muy importante en todos los productos estudiados y de mayor magnitud que las que se citan en la bibliografía para procesos de secado con aire caliente (Garcia-Perez et al., 2009; Rodríguez et al., 2014). De hecho, el efecto de la temperatura de secado en la cinética fue menor al aplicar ultrasonidos lo que se atribuyó al aporte adicional de energía mecánica debido a la vibración acústica. En todos los casos, se observó que cuanto menor fue la temperatura, mayor fue la reducción del tiempo de secado producida por los ultrasonidos. Así, en el secado de manzana a 10ºC, al aplicar una potencia ultrasónica de 50 W se redujo el tiempo de secado hasta un 59%, mientras que a -10ºC la reducción alcanzó el 77%. A -10ºC, en berenjena y bacalao se obtuvieron reducciones del tiempo de secado de hasta un 87% y un 60%, respectivamente. Estos resultados muestran la existencia de pequeñas diferencias en la influencia de los ultrasonidos entre los distintos productos estudiados que, en todo caso, fueron mucho menos importantes que las observadas en procesos de secado con aire caliente. Estas diferencias también podrían atribuirse a la distinta estructura de los productos, ya que esta característica está fuertemente relacionada con la efectividad de la aplicación de ultrasonidos (Ozuna et al., 2014b). De hecho, los efectos más intensos de la aplicación de ultrasonidos en la cinética de secado se obtuvieron en

las experiencias realizadas en condiciones de liofilización a presión atmosférica, es decir, utilizando temperaturas por debajo del punto de congelación del alimento. En estas condiciones, la sublimación del agua genera productos con una estructura más porosa a medida que transcurre el secado. Esto facilita la transmisión de los ultrasonidos en la interfase alimento-aire lo que incrementa la cantidad de energía que penetra en el producto y por tanto, la magnitud de los efectos ultrasónicos. Dado que las experiencias de liofilización fueron mucho más lentas que las experiencias de secado por encima del punto de congelación, la reducción de tiempo de secado en términos absolutos que supone la aplicación de ultrasonidos fue mucho mayor, y por lo tanto, resulta muy interesante para aumentar la productividad a nivel industrial.

Respecto a la velocidad del aire, cabe destacar que tuvo muy poca influencia en las cinéticas de secado a baja temperatura. Esto es debido a que la velocidad de aire afecta principalmente a la resistencia externa a la transferencia de materia y, en estas condiciones de temperatura, el factor limitante para la transferencia de agua es la resistencia interna. Así, se observó que, tanto en el secado a baja temperatura de manzana como de berenjena, el incremento de la velocidad de aire no tuvo un efecto significativo ($p<0.05$) sobre la cinética de secado. En cambio, en las experiencias de secado asistidas con ultrasonidos de potencia el uso de altas velocidades de aire produjo una ralentización de la cinética. Este hecho probablemente sea debido a que el aumento del flujo puede crear turbulencias que distorsionan el campo acústico disminuyendo su intensidad (Garcia-Perez et al., 2006b) y, por lo tanto, reduciendo el efecto del mismo.

Como ya se ha comentado anteriormente, la aplicación de ultrasonidos permitió reducir significativamente ($p<0.05$) el tiempo de secado en todas las condiciones experimentales y productos analizados. Pero además, esta reducción dependió de la potencia acústica aplicada. Así, en el secado de manzana a -10 y 10ºC se observó que cuanto mayor fue la potencia acústica aplicada, mayor fue la reducción del tiempo de secado obtenida. Este resultado es lógico ya que a mayor potencia acústica aplicada, mayor es la intensidad de sus efectos, especialmente aquellos que implican una reducción de la resistencia interna. En este sentido, cabe destacar que en las experiencias de liofilización a presión atmosférica, la aplicación de ultrasonidos, incluso a la potencia más baja de las ensayadas,

provocó una reducción muy importante del tiempo de secado. La aplicación de potencias superiores redujo todavía más el tiempo de proceso, aunque en menor medida. Por ejemplo, en el caso de manzana liofilizada a -10ºC, la aplicación de la potencia ultrasónica más baja de las ensayadas (25 W) ya supuso una reducción de tiempo de hasta el 71%. Sin embargo, al aumentar la potencia a 75 W, la reducción del tiempo de secado sólo se incrementó hasta el 80%.

Uno de los apartados importantes de esta tesis fue la modelización matemática de las cinéticas de secado a baja temperatura de manzana, berenjena y bacalao, obtenidas bajo distintas condiciones experimentales (temperatura, velocidad de aire y aplicación de ultrasonidos) con el objetivo de cuantificar la influencia de las variables de secado en la velocidad del proceso. Para ello, se utilizaron modelos difusivos con diferente grado de complejidad. En general, el modelo difusivo sin considerar la resistencia externa a la transferencia de agua resultó adecuado para describir las experiencias sin aplicación de ultrasonidos de los tres productos estudiados, obteniendo porcentajes de varianza explicada superiores al 98%. En el caso de las experiencias asistidas con ultrasonidos, el ajuste a los datos experimentales no fue satisfactorio considerando un modelo difusivo estricto, llegando a porcentajes de varianza del 93%. En este último caso, el porcentaje de varianza explicada mejoró notablemente al incluir la resistencia externa en el modelo alcanzando valores superiores al 99% en todas las condiciones experimentales ensayadas. Esto indicaría que en el caso del secado con aplicación de ultrasonidos, además de los mecanismos de transporte difusivo, cobran importancia los mecanismos convectivos. En todas las experiencias, se observó que la aplicación de ultrasonidos produjo un incremento mayor de la difusividad efectiva que del coeficiente de transferencia de materia. Esta mayor influencia en la difusividad indicaría que la aplicación de ultrasonidos tiene mayor efecto sobre el transporte interno de agua que sobre el externo, lo que resulta especialmente adecuado para estas condiciones de temperatura en las que el factor limitante para el transporte de agua es la resistencia interna.

En el caso de las experiencias realizadas a temperaturas por debajo del punto de congelación, el modelo difusivo estricto pasa de ser un modelo teórico a un modelo empírico ya que no se cumple una de sus principales suposiciones, la homogeneidad e isotropía del material. En este caso, se pierde la homogeneidad

de las muestras ya que durante el secado presentan dos partes bien diferenciadas, una zona interna congelada y una capa externa porosa ya deshidratada. Durante el proceso, el frente de sublimación avanza desde la superficie hacia el centro de la muestra y el vapor de agua difunde hacia la superficie a través de la capa deshidratada. Por este motivo, para las experiencias de liofilización a presión atmosférica se utilizó un modelo de tipo URIF (Uniformly Retreating Ice Front) que considera el avance del frente de sublimación. El modelo se ajustó satisfactoriamente a los datos experimentales proporcionando valores de difusividad efectiva en el orden de magnitud de los del vapor de agua. Los resultados de la modelización se validaron realizando experiencias con muestras de diferente tamaño y geometría. Además, se validaron los perfiles de humedad que proporciona el modelo URIF con experiencias donde se forzó que el transporte de agua fuera unidireccional. Todos estos resultados demuestran que el modelo URIF resulta adecuado para describir el proceso de liofilización a presión atmosférica, con o sin la aplicación de ultrasonidos. A partir de los valores de difusividad obtenidos se identificó que la potencia acústica aplicada fue la variable de proceso que más influencia presentó en la velocidad de secado. La temperatura de secado, aunque menos, también afectó significativamente ($p<0.05$) a dicha velocidad de secado. Por el contrario, la velocidad de aire no presentó una influencia significativa ($p<0.05$) en la difusividad.

Además del efecto de las variables del proceso en la cinética de secado, también se analizó su influencia en diferentes parámetros de calidad del producto obtenido. A continuación se comentan los principales resultados obtenidos en cada uno de los parámetros estudiados.

Una de las características importantes que marcan la calidad de los productos deshidratados es su capacidad de rehidratación. En este sentido, la aplicación de ultrasonidos no afectó a dicha capacidad en ninguno de los tres productos estudiados, manzana, berenjena o bacalao. Del mismo modo, se demostró la nula influencia de la velocidad del aire en el secado de berenjena a baja temperatura en su capacidad de rehidratación. Sin embargo, la temperatura de secado sí que influyó significativamente ($p<0.05$) en dicho parámetro. Así, las muestras deshidratadas a -10ºC presentaron una mayor capacidad de rehidratación que las deshidratadas a temperaturas por encima del punto de congelación. Este hecho

puede estar relacionado con la mayor porosidad que se desarrolla en las muestras deshidratadas en condiciones de liofilización a presión atmosférica, lo que facilita la entrada de agua en la muestra.

Otro parámetro importante de calidad es la dureza del producto secado y posteriormente rehidratado. En este sentido, se observó que, en general, el secado y la posterior rehidratación tienen como consecuencia que el producto obtenido sea más blando que la muestra fresca, lo que se puede atribuir a la degradación de la estructura causada por ambos procesos. En cuanto a la influencia de las variables utilizadas en el proceso de secado, está no resultó muy evidente en el caso de la dureza. Así, en el análisis de la textura de berenjena rehidratada, se concluyó que la temperatura, la velocidad del aire y la aplicación de ultrasonidos no tuvieron un efecto significativo ($p<0.05$) en la dureza de la muestra. En el caso de la manzana, sólo se observaron valores de dureza significativamente ($p<0.05$) inferiores en las muestras deshidratadas a -10ºC, probablemente como consecuencia del daño producido por los cristales de hielo durante la congelación.

En las muestras de manzana deshidratada, se evaluó el impacto del proceso de secado en el potencial antioxidante. Para ello, se evaluó el contenido fenólico y la capacidad antioxidante en muestras secadas a diferentes temperaturas y con aplicación de distintas potencias acústicas. Los resultados mostraron que, en general, el secado produjo una reducción de ambos parámetros. Esta degradación fue generalmente mayor en las experiencias de secado asistido con ultrasonidos. Sin embargo, la diferencia respecto a las experiencias sin aplicación de ultrasonidos sólo resultó significativa ($p<0.05$) en algunos casos y dependió del solvente utilizado para la extracción y/o del método de determinación de la capacidad antioxidante. Por otra parte, las muestras deshidratadas a temperaturas por debajo del punto de congelación mostraron una mayor reducción del contenido fenólico y de la capacidad antioxidante debido al secado.

Otro de los parámetros importantes de los productos deshidratados es el color. En este caso, se estudió la influencia del secado en el color de bacalao, tanto deshidratado como posteriormente rehidratado, debido a la importancia de este parámetro en la aceptación final de este producto por parte del consumidor. Así,

se observó que las muestras deshidratadas a -10ºC fueron más blancas y luminosas, mientras que a 0 y 10ºC resultaron más amarillas y oscuras. La aplicación de ultrasonidos solo tuvo influencia en el color de las muestras deshidratadas a -10ºC, reduciendo ligeramente su luminosidad. Sin embargo, después de la rehidratación, las muestras no presentaron ninguna diferencia ocasionada por las diferentes temperaturas de secado ni por la aplicación de ultrasonidos de potencia.

Se realizaron ensayos de microestructura de manzana deshidratada a diferentes temperaturas, con y sin aplicación de ultrasonidos. Las imágenes de Cryo-SEM obtenidas mostraron que las muestras deshidratadas en condiciones de liofilización a presión atmosférica presentaron una mayor porosidad que las obtenidas mediante secado convectivo a baja temperatura. Esto se debe tanto a la formación como al crecimiento de los cristales de hielo en el interior de la muestra durante su congelación. En las muestras secadas con aplicación ultrasonidos se apreció una porosidad aún mayor. Este hecho puede estar fuertemente relacionado con la aparición de grietas y microcanales en la muestra por el efecto de los ultrasonidos y que contribuyen a la intensificación del proceso de secado.

En todo caso, y como un resultado general, se puede establecer que la aplicación de ultrasonidos de potencia durante el secado a baja temperatura no tuvo una influencia importante en los parámetros de calidad de los productos deshidratados.

Por último, se estudió una posible aplicación del secado a baja temperatura asistido con ultrasonidos: el desarrollo de matrices alimentarias porosas en las que posteriormente se incorporen extractos con actividad antioxidante. Concretamente, se estudió la influencia del secado a baja temperatura asistido con ultrasonidos de manzana en su posterior impregnación con extracto de hoja de olivo. Los resultados obtenidos mostraron que las muestras de manzana deshidratadas a baja temperatura presentaron una menor capacidad de impregnación que las deshidratadas con aire caliente. La aplicación de ultrasonidos durante el secado no tuvo influencia significativa ($p<0.05$) en la capacidad de impregnación. Como se esperaba, la impregnación aumentó significativamente ($p<0.05$) el contenido fenólico y la capacidad antioxidante del producto obtenido respecto al producto fresco. En este sentido, la aplicación de ultrasonidos durante el secado incrementó

la capacidad antioxidante del producto final. Así, las muestras deshidratadas a baja temperatura con aplicación de ultrasonidos fueron las que mostraron un mayor contenido de los principales polifenoles incorporados con el extracto de hoja de olivo.

6. Conclusiones

The main conclusions that can be drawn from the results obtained in this study have been grouped into four sections according to the main topics addressed in the present thesis and are listed as follows:

6.1. Influence of process variables on drying kinetics

- Ultrasound application significantly ($p<0.05$) shortened the drying time under every drying condition and with each product tested. Moreover, the greater the ultrasonic power applied, the shorter the drying time.
- Low drying air velocities and temperatures positively affected the ultrasonic performance in low temperature drying.

6.2. Drying modeling

- A simple diffusion model considering the external resistance to water transfer as negligible accurately fitted the low temperature drying kinetics. In the case of ultrasonically assisted drying, it was necessary to include the external resistance in the model to achieve an acceptable fit.
- Ultrasound application led to a greater increase in the effective moisture diffusivity than in the mass transfer coefficient, which suggests that the impact of ultrasound was greater in the internal transport than in the external.
- The proposed model considering the URIF (Uniformly Retreating Ice Front) theory successfully fitted the atmospheric freeze drying kinetics. This model was validated under different conditions (different size and geometry of the sample) and showed the retreat of the ice front during drying.

6.3. Influence of process variables on product quality

- Ultrasound application and air velocity did not significantly ($p<0.05$) affect the rehydration capacity of the samples dried at low temperatures. As regards the drying temperature, samples dried at temperatures lower than the freezing point showed a significantly ($p<0.05$) greater rehydration capacity.

- The rehydrated products were significantly ($p<0.05$) softer than the fresh ones. The drying process variables (temperature, air velocity and ultrasonic power) did not significantly ($p<0.05$) influence the sample's hardness.
- The drying process reduced both the phenolic content and the antioxidant capacity. In general terms, this reduction was greater both at temperatures below the freezing point and also when ultrasound was applied.
- Ultrasound application only caused a significantly ($p<0.05$) different overall color when desalted cod was dried at -10ºC.
- The Cryo-SEM images of dried apple showed that the atmospheric freeze dried samples were more porous that those dried at temperatures above the freezing point. Moreover, ultrasound application brought about an additional increase in the porosity.

6.4. Prospective application: obtaining new solid matrices to develop functional foods

- Low temperature drying allows highly porous solid matrices to be obtained, which can be used to develop functional foods. In this sense, apple samples dried under different conditions were impregnated with olive leaf extract.
- Ultrasound application during drying did not significantly ($p<0.05$) influence the infusion capacity but did increase the antioxidant capacity of the obtained product. Thus, the samples dried at low temperatures with ultrasound application had the highest content of infused polyphenols.

GENERAL CONCLUSION

In overall terms, power ultrasound could be considered an interesting technology with which to speed-up the low temperature drying processes, making them more affordable and less time-consuming for all kinds of industries without greatly affecting the quality of the obtained product.

7. Recomendaciones

Teniendo en cuenta los resultados obtenidos en la presente tesis doctoral, la investigación sobre la aplicación de ultrasonidos en procesos de secado a baja temperatura debería continuar profundizando en aspectos como los siguientes:

- Sería conveniente realizar un análisis energético del proceso de secado a baja temperatura asistido con ultrasonidos de potencia (US) para determinar si el ahorro del tiempo del proceso se ve acompañado de un ahorro efectivo en el consumo energético. Además, se podría comparar dicho consumo con el de otras técnicas que actualmente se utilizan en la industria agroalimentaria.
- Habría que profundizar en el estudio de escalado de la tecnología con el objetivo de evaluar su viabilidad para tratar mayores volúmenes de producto.
- Convendría determinar de manera precisa el aumento de temperatura ocasionado por los US en el producto a secar con el objetivo de cuantificar el posible efecto térmico de los US y separarlo del mecánico.
- Se deberían de llevar a cabo experiencias de secado con muestras de diferente tamaño y geometría, así como con distintas densidades de carga con el fin de determinar su impacto en la efectividad de la aplicación de US.
- También se debería estudiar la posibilidad de utilizar otro tipo de transductores (placa escalonada) en el secado a baja temperatura y comparar la efectividad de los mismos con el transductor utilizado en este trabajo.
- Sería necesario realizar un análisis sensorial de los productos obtenidos con el secado a baja temperatura asistido con US con el fin de determinar su viabilidad comercial y comparar su calidad con la de otros productos deshidratados que se pueden encontrar en el mercado.
- Evaluar el potencial del secado a baja temperatura asistido con US en productos líquidos, salsas, cremas, etc.

8. Contribución científica

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