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DESARROLLO DE TÉCNICAS COMBINADAS DE SECADO CON AIRE CALIENTE Y MICROONDAS EN LA PRODUCCIÓN DE FIBRA ALIMENTARIA A PARTIR DE SUBPRODUCTOS CÍTRICOS

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D. PEDRO JOSÉ FITO SUÑER, PROFESOR TITULAR DE LA UNIVERSIDAD POLITÉCNICA DE VALENCIA, PERTENECIENTE AL INSTITUTO UNIVERSITARIO DE INGENIERÍA DE ALIMENTOS PARA EL DESARROLLO Y **Dª MARTA CASTRO GIRÁLDEZ** INVESTIGADORA DE LA UNIVERSIDAD POLITÉCNICA DE VALENCIA, PERTENECIENTE AL INSTITUTO UNIVERSITARIO DE INGENIERÍA DE ALIMENTOS PARA EL DESARROLLO

CONSIDERAN: Que la memoria titulada DESARROLLO DE TÉCNICAS COMBINADAS DE SECADO CON AIRE CALIENTE Y MICROONDAS EN LA PRODUCCIÓN DE FIBRA ALIMENTARIA A PARTIR DE SUBPRODUCTOS CÍTRICOS que presenta Dª CLARA TALENS VILA para aspirar al grado de Doctora por la Universidad Politécnica de Valencia, reúne las condiciones adecuadas para constituir su tesis doctoral, por lo que **AUTORIZAN** a la interesada para su presentación.

Valencia, Julio 2015

Fdo: Pedro J. Fito Suñer
Director de tesis

Fdo: Marta Castro Giráldez
Director de tesis

A Carcaixent

A Grècia, a Irlanda, a Bilbao

A València

Als meus amics

A la música

A la platja

Al mar

A les oles

A la terreta

Als tarongers

Al meu company de viatge

Al futur que vindrà

A la familia

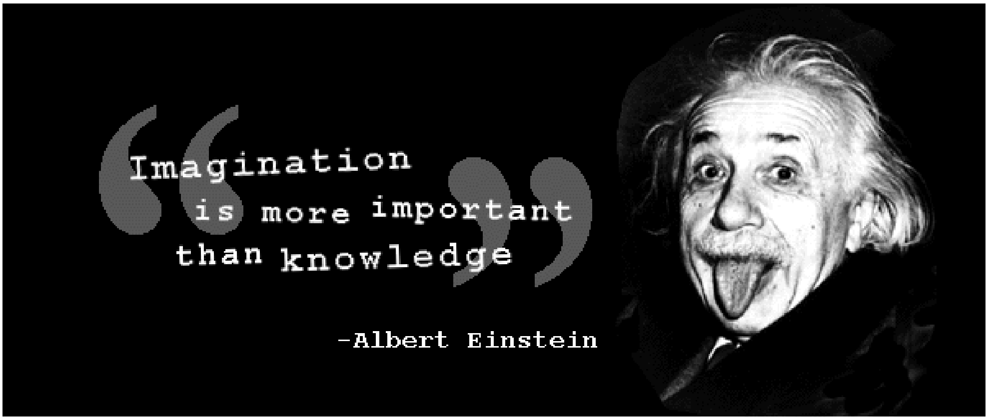
A les meues ***4J****s*

A ***J****uan Carlos*

A María ***J****esús*

A ***J****ordi*

A ***J****uan*


Imagination
is more important
than knowledge
-Albert Einstein

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RESUMEN

La sostenibilidad es una de las apuestas de futuro en cualquier actividad económica. La actual situación de crisis ha tenido un impacto adverso en la mayoría de las industrias, incluyendo las de ámbito agroalimentario. Sin embargo, la industria agroalimentaria ha sido relativamente la menos afectada cuando se compara con otros sectores industriales. Esto se atribuye principalmente al hecho de que los productos alimenticios continúan siendo básicos para los consumidores a pesar de la desaceleración económica. Por lo tanto, esta industria es un pilar fundamental en la economía europea y puede jugar un papel crucial en la consecución de los objetivos marcados en la Estrategia de la UE para 2020: asegurar un marco sostenible de crecimiento de una economía más competitiva. La industria agroalimentaria europea ha apostado por la eficiencia energética y la reducción de emisiones de gases de efecto invernadero, junto con una mejor gestión de sus recursos como vía para la mejora de su competitividad industrial. En este sentido, la búsqueda de soluciones para transformar los subproductos generados en ingredientes de alto valor añadido, es una de las prioridades. En este contexto, la industria productora de zumos, como subsector

fundamental dentro del sector alimentario, y gran generador de residuos, tiene el deber y la oportunidad de transformar sus subproductos en productos útiles y rentables para la sociedad. Esta transformación presenta algunas dificultades que impiden la rentabilidad del proceso. Estas dificultades están asociadas al subproducto, como su variabilidad composicional o su estacionalidad, y a las técnicas actuales de transformación como el elevado coste energético en procesos de deshidratación.

Esta tesis se plantea como una solución innovadora y sostenible para, más allá de superar los inconvenientes asociados a los altos costes de estabilización, transformar este subproducto en un ingrediente de alto valor añadido, tanto nutricional como tecnológico. Para ello se propone desarrollar una técnica de secado combinado por aire caliente y microondas que permita maximizar beneficios mediante la siguiente estrategia: reducir el tiempo y el coste energético de la operación, produciendo un nuevo ingrediente rico en fibra dietética con propiedades tecnológicas de interés para el desarrollo de alimentos más saludables, estudiando el proceso integral propuesto y analizando los nuevos subproductos generados.

El enfoque metodológico de la tesis ha estado dirigido, por una parte, a estudiar los fenómenos que gobiernan el transporte interno de agua y energía a través de la piel de naranja durante su deshidratación, aplicando termodinámica. Por otra parte, el consumo energético del proceso de secado, las propiedades tecnológicas y sensoriales de la fibra obtenida y su potencial uso como ingrediente sustituto de grasa, se han comparado con el método de secado convencional por aire caliente. Finalmente, el proceso integrado, incluyendo tanto el secado combinado como las etapas previas de extracción de color y compuestos amargos, se propone como una nueva ruta de valorización, en la que se analizan posibles subproductos de interés tales como extractos ricos en polifenoles y carotenoides.

En este estudio se ha analizado el proceso combinado de secado con aire caliente y microondas, desarrollando herramientas que permiten dimensionar adecuadamente la operación de secado adaptándola a los estándares óptimos de calidad del producto final. Se ha diseñado un sistema de monitorización que asegure dichos estándares. Se ha mejorado el proceso de obtención de fibra alimentaria respecto a su calidad y a su gasto energético. Se han optimizado las propiedades asociadas a su inclusión en matrices alimentarias. Se ha desarrollado un proceso innovador y sostenible para la estabilización de subproductos vegetales de origen industrial y para su posterior conversión en fibra dietética y otros compuestos bioactivos, aplicando la tecnología de secado por aire caliente y microondas.

RESUM

La sostenibilitat és una de les apostes de futur en qualsevol activitat econòmica. L'actual situació de crisi ha tingut un impacte advers en la majoria de les indústries, incloent les d'àmbit agroalimentari. No obstant això, la indústria agroalimentària ha sigut relativament la menys afectada quan es compara amb altres sectors industrials. Açò s'atribuïx principalment al fet de que els productes alimentaris continuen sent bàsics per als consumidors a pesar de la desacceleració econòmica. Per tant, esta indústria és un pilar fonamental en l'economia europea i pot jugar un paper crucial en la consecució dels objectius marcats en l'Estratègia de la UE per a 2020: assegurar un marc sostenible de creixement d'una economia més competitiva. La indústria agroalimentària europea ha apostat per l'eficiència energètica i la reducció d'emissions de gasos d'efecte hivernacle, junt amb una millor gestió dels seus recursos com a via per a la millora del seu vaig competirtu

En este sentit, la busca de solucions per a transformar els subproductes generats en ingredients d'alt valor afegit, és una de les prioritats. En este context, la indústria productora de sucs, com subsector fonamental dins del sector alimentari, i gran generador de

residus, té el deure i l'oportunitat de transformar els seus subproductes en productes útils i rendibles per a la societat. Esta transformació presenta algunes dificultats que impedixen la rendibilitat del procés. Estes dificultats estan associades al subproducte, com la seua variabilitat composicional o la seua estacionalitat, i a les tècniques actuals de transformació com l'elevat cost energètic en processos de deshidratació.

Esta tesi es planteja com una solució innovadora i sostenible per a, més enllà de superar els inconvenients associats als alts costos d'estabilització, transformar este subproducte en un ingredient d'alt valor afegit, tant nutricional com tecnològic. Per a això es proposa desenvolupar una tècnica de’assecat combinat per aire calent i microones que permeta maximitzar beneficis per mitjà de l'estratègia següent: reduir el temps i el cost energètic de l'operació, produint un nou ingredient ric en fibra dietètica amb propietats tecnològiques d'interés per al desenvolupament d'aliments més saludables, estudiant el procés integral proposat i analitzant els nous subproductes generats.

L'enfocament metodològic de la tesi ha estat dirigit, d'una banda, a estudiar els fenòmens que governen el transport intern d'aigua i energia a través de la pell de taronja durant la seua deshhotidratació, aplicant termodinàmica. D'altra banda, el consum energètic del procés de d'assecat, les propietats tecnològiques i sensorials de la fibra obtinguda i el seu potencial ús com a ingredient substitut de greix, s'han comparat amb el mètode d'assecat convencional per aire calent. Finalment, el procés integrat, incloent tant l'assecat combinat com les etapes prèvies d'extracció de color i compostos amargs, es proposa com una nova ruta de valoració, en la que s'analitzen possibles subproductes d'interés com ara extractes rics en polifenoles i carotenoides.

En este estudi s'ha analitzat el procés combinat d'assecat amb aire calent i microones, desenvolupant ferramentes que permeten dimensionar adequadament l'operació d'assecat adaptant-la als estàndards òptims de qualitat del producte final. S'ha dissenyat un sistema de monitorització que assegure els dits estàndards. S'ha millorat el procés d'obtenció de fibra alimentaria respecte a la seua qualitat i al seu consum energètic. S'han optimitzat les propietats associades a la seua inclusió en matrius alimentàries. S'ha desenvolupat un procés innovador i sostenible per a l'estabilització de subproductes vegetals d'origen industrial i per a la seua posterior conversió en fibra dietètica i altres compostos bioactius, aplicant la tecnologia d'assecat por aire calent i microones.

ABSTRACT

Sustainability is nowadays an investment for the future of any economic activity. The current situation of crisis has had an adverse impact in most industries, including the agri-food sector. However, this industry has been relatively the least affected when compared with other industrial sectors. This is mainly attributed to the fact that food products continue to be basic for consumers despite the economic downturn. Therefore, the agri-food sector is a key element in the European economy and can play a crucial role in the achievement of the objectives set in the EU's strategy for 2020: ensuring a sustainable framework of growth of a more competitive economy. The European agri-food industry has focused on energy efficiency and on reducing greenhouse gases emissions, along with better management of their resources as a way to improve its industrial competitiveness. In this sense, the search for solutions to transform the by-products generated in high value-added ingredients, is a priority. In this context, the juice industry, as fundamental sub-sector within the food sector, and large waste generator, must exploit the opportunity to transform their by-products into useful and profitable products for society. This transformation presents some

difficulties which impede the profitability of the process. These difficulties are associated with the by-product, such as its compositional variability and its seasonality, and current techniques of transformation as the high energy cost in dehydration processes. This thesis represents an innovative and sustainable solution for overcoming the disadvantages associated with the high costs of stabilization, turning this by-products into high value-added ingredients, from both, nutritional and technological, points of view. The aim is to develop a microwave coupled with hot air drying technique allowing maximizing profits by using the following strategy: reducing time and operational costs, producing a new ingredient rich in dietary fiber, with interesting technological properties for the development of healthy foods, studying the proposed comprehensive process and analyzing the new generated by-products.

The methodological approach of the thesis been focused, on the one hand, on studying phenomena that govern the internal transport of water and energy through the orange peel during its dehydration applying thermodynamics. On the other hand, the energy consumption of the drying process, the technological and sensory properties of the fiber obtained and its potential use as a fat substitute have been compared with the conventional hot air drying method. Finally, the integrated process, including both the combined drying technique and the pretreatments needed for colour and bitter compounds extraction, is proposed as a new route of valorization, in which the new by-products obtained, polyphenols and carotenoid rich extracts, are analysed. This study has analyzed the microwave coupled with hot air process, developing tools that allow the adequate upscaling of the drying operation by adapting it to the best standards of quality of the final product. A monitoring system that ensures these standards has been designed. The quality and the energy consumption of the dietary fiber production process has been improved. The properties associated with its inclusion in food matrices have been optimized. An innovative and sustainable process for the stabilization of industrial by-products and for their further conversion into dietary fiber and other bioactive compounds, applying microwave coupled with hot air drying, has been developed.

Tabla de Contenido

I JUSTIFICACION

Ante las evidencias científicas que demuestran el calentamiento global de forma cada vez más contundente, existen diferentes iniciativas mundiales que tratan de frenar este efecto desde distintos enfoques sociales, energéticos y políticos. La reducción en la producción de residuos y la revalorización de los mismos en productos de alto valor añadido puede representar una pieza clave en este esfuerzo mundial.

Los trabajos de investigación para el aprovechamiento de subproductos buscan disminuir el impacto ambiental de los residuos generados a la vez que conseguir un beneficio económico a través de la valorización de algunos de sus componentes por su potencial aplicación en la industria alimentaria, farmacéutica o cosmética (Awarenet, 2004, Fava et al., 2013, Laufenberg et al., 2003, Schieber et al., 2001). Una de las aplicaciones más antiguas de estos subproductos es su transformación en pellets para alimentación animal (Bampidis and Robinson, 2006), sin embargo, no hay duda del potencial de los subproductos de cítricos y de otros vegetales como fuentes de compuestos bioactivos tales como aceites esenciales, carotenoides, flavonoides, pectinas o fibra dietética (Braddock, 1999, Nafisi-Movaghar et al., 2013, Russo et al., 2014).

En concreto, los cítricos presentan una fibra dietética (DF) de gran calidad debido a la presencia de compuestos bioactivos asociados (flavonoides y vitamina C) con propiedades antioxidantes que proporcionan beneficios adicionales para la salud (Figuerola et al., 2005, Lario et al., 2004, Larrauri, 1999, Lundberg, 2005, Lundberg et al., 2014, Marin et al., 2007, Perrigue et al., 2009). Además esta fibra presenta una elevada capacidad de retención de agua, consiguiendo así, por una parte, aumentar rendimientos de producción al evitar pérdidas por sinéresis, y por otra, reducir el contenido calórico de los alimentos a los que se incorpora como sustituto de grasa, al aportar viscosidad a la matriz (de Moraes Crizel et al., 2013, Fernandez-Lopez et al., 2004, Pszczola, 2006, Sendra et al., 2010). Algunos de sus potenciales aplicaciones ya han sido estudiadas en productos de panadería (Kohajdova et al., 2011, O'Shea et al., 2015, Romero-Lopez et al., 2011), productos cárnicos (Fernandez-Lopez et al., 2004, Viuda-Martos et al., 2010), productos lácteos (Comas e Boff et al., 2013, Crizel et al., 2014, Sendra et al., 2010) y salsas (Chatsisvili et al., 2012).

Las propiedades funcionales de la fibra son las responsables de los efectos fisiológicos que desarrolla y están influenciadas, entre otros aspectos, por la estructura de la fibra, el tamaño de partícula, así como por el tipo de proceso llevado a cabo para su obtención. Dicho proceso puede provocar sobre todo cambios microestructurales, que pueden modificar la manera de interaccionar de la fibra con otra moléculas (Heredia Moreno, 2003). Su solubilidad, capacidad para hincharse y para retener agua, así como su composición química, determinará su capacidad para aumentar la viscosidad cuando interaccione con el agua, influenciando así la actividad metabólica de la fibra a través del tracto intestinal.

La mayoría de procesos que se emplean en la actualidad para la obtención de fibra a partir de subproductos cítricos incluyen las siguientes etapas (Braddock, 1999, Nafisi-Movaghar et al., 2013): TRITURADO; ESCALDADO, EXTRACCIÓN, PRENSADO o CENTRIFUGADO; SECADO; MOLIENDA; ENVASADO y ALMACENAMIENTO. La operación de secado supone el coste más elevado en el proceso de valorización de subproductos de alta humedad, representando un factor clave en la viabilidad económica del proceso (Zhang et al., 2006). El secado se realiza en un secador rotatorio horizontal, con quemador de gas. Esta operación debe llevar al subproducto desde humedades del 85% hasta humedad del 10%, muy por debajo de la humedad crítica del producto. Para realizar esta deshidratación sin tener una longitud infinita de secador, el proceso se realiza a con un flujo de aire en paralelo a una elevadísima temperatura (aproximadamente 650ºC y una temperatura húmeda de 75ºC), produciéndose un consumo de gas que puede representar el 75% de los costes de la planta de transformación. Comparado con otros métodos de secado convencionales, como el secado por aire caliente o la liofilización, el secado combinado aire caliente-microondas es un método más rápido y energéticamente más eficiente, lo que supone menores costes operativos, menores pérdidas de energía al ambiente y una calidad de producto más uniforme (Orsat et al., 2005). El uso del microondas en algunos procesos tiene como principal ventaja un tiempo de procesamiento substancialmente reducido que lleva a un aumento en la capacidad de producción, así como a una mejora de la calidad y vida útil de los productos finales (Zhang et al., 2006). Por lo tanto, la utilización combinada de aire caliente-microondas se hace fundamental, a nivel económico y operativo, en procesos de secado que deben de alcanzar humedades por debajo de la humedad crítica.

La tecnología microondas además de secar, puede generar una expansión del tejido debido a su nivel de penetración y a su rápido aporte de energía para evaporar (Contreras et al., 2008, Rakesh and Datta, 2011, Zivanovic et al., 2000). La expansión de materiales fibrosos con el objetivo de aumentar su superficie específica, generando así una mayor capacidad de retención de agua y/o viscosidad aparente, es una de las estrategias más utilizadas para mejorar la funcionalidad de las fibras vegetales (Gu et al., 2001, Lundberg, 2005, Turbak, 1983). Por lo tanto, los cambios macro y microestructurales que ocurren durante el secado pueden modificar las propiedades funcionales de los productos que se obtengan al final del procesado (Bejar et al., 2011, Ghanem et al., 2012, Santana, 2009).

Debido a la alta complejidad de las estructuras alimentarias, los nuevos modelos cinéticos desarrollados para el diseño de productos y procesos alimentarios, deben incorporar suficiente información acerca de todos los aspectos físicos, termodinámicos, estructurales, químicos y bioquímicos de los mecanismos involucrados en sus transformaciones (Castro-Giráldez et al., 2011a, Castro-Giráldez et al., 2010, 2011b). El estudio de dichos fenómenos resulta arduo en el caso del secado combinado dada la complejidad de cuantificar los efectos de ambas fuentes de energía (aire caliente y microondas).

A la frecuencia de microondas el fenómeno predominante de relajación es el que afecta a las moléculas dipolares, siendo el agua la más importante en sistemas alimentarios, especialmente en frutas. Las frutas poseen un alto contenido en agua, lo que hace que estos productos sean muy sensibles a las microondas y absorban rápida y eficientemente su energía (Sosa-Morales et al., 2010). Los cambios físicos y químicos sufridos en el alimento durante el proceso de deshidratación afecta a las propiedades dieléctricas de manera significativa, ya que reducen no solo en contenido de agua sino que además disminuyen la movilidad de la misma. En general, las frutas poseen una fase líquida importante que provoca que la constante dieléctrica adquiera valores altos; por el contrario, en frutas deshidratadas tanto la constante dieléctrica como el factor de pérdidas toman valores menores. Las propiedades dieléctricas en alimentos, cuando se correlacionan con otros parámetros, como contenido en humedad, pueden ser utilizadas para medir eléctricamente dichos parámetros (Castro-Giráldez, 2010). La monitorización durante el procesado es importante a la hora de optimizar los recursos energéticos, mantener un nivel de seguridad durante el tratamiento y evitar la obtención de productos que no cumplan con las especificaciones requeridas de calidad. La espectroscopia dieléctrica ofrece importante y, en algunos casos, información única sobre los procesos y sobre el estado en el que se encuentran los componentes en los alimentos, además puede ser empleada en línea y no es destructiva. Por ello, el estudio del comportamiento de las propiedades dieléctricas cuando existen cambios en la composición del alimento es necesario a la hora de estudiar la viabilidad de estos métodos basados en las microondas y radiofrecuencia de señal para su aplicación como sensores de monitoreo en línea no destructivos.

En resumen, la presente tesis se justifica bajo dos puntos de vista. En primer lugar, el aspecto teórico, ya que se pretende analizar el proceso combinado de secado con aire caliente y microondas, desarrollando herramientas que permitan dimensionar adecuadamente la operación de secado adaptándola a los estándares óptimos de calidad del producto final, así como diseñar un sistema de monitorización que asegure dichos estándares. Además, también se pretende mejorar del proceso de obtención de fibra alimentaria respecto a su calidad y a su gasto energético así como optimizar las propiedades asociadas a su inclusión en matrices alimentarias. En segundo lugar, el aspecto práctico de la tesis se centra en desarrollar un proceso innovador y sostenible para la estabilización de subproductos vegetales de origen industrial para su posterior conversión en fibra dietética, aplicando la tecnología de secado por aire caliente y microondas. De nuevo, no existen métodos publicados para la obtención de fibra dietética a partir de piel de naranja que incorporen el secado combinado por aire caliente y microondas, por lo tanto, es necesario estudiar las propiedades físicas, químicas y tecnológicas de dicha fibra, para determinar si existen ventajas adicionales a la reducción del tiempo de proceso y los costes operativos. Estas ventajas adicionales pueden suponer una mejora de las propiedades tecnológicas de la fibra que aumenten su capacidad de sustituir grasa en determinado tipo de alimentos.

De esta manera, con esta tesis se reportan tanto beneficios a la comunidad científica en forma de nuevos conocimientos sobre ingeniería de procesos, como al medio ambiente en forma de nuevas rutas de valorización de subproductos, así como a la sociedad en forma de ingredientes que permiten desarrollar alimentos más saludables manteniendo su calidad sensorial.

II

INTRODUCCIÓN

INTRODUCCIÓN

2.1 Generación de subproductos en la industria transformadora de cítricos

La industria de alimentos y bebidas representa un sector amplio y económicamente importante en la Unión Europea. El procesado de frutas se ha incrementado considerablemente durante los últimos 25 años, en su mayoría como consecuencia de que los estudios epidemiológicos relacionan el consumo diario de frutas en la dieta con una disminución en la incidencia de cáncer y mortalidad por enfermedades cardiovasculares (Doll, 1990, Rimm et al., 1996).

La transformación de frutas en zumos genera grandes volúmenes de residuos y subproductos (20-60% w/w de la fruta procesada) (Awarenet, 2004) con alta demanda biológica y química de oxígeno y con elevados costes asociados.

Los datos de producción de cítricos a nivel mundial para la campaña 2013/2014 se estiman en 89,3 millones de toneladas (Mt), incluyendo naranjas, mandarinas, tangerinas, pomelos, limones y lima (USDA, 2014). Aproximadamente el 56% de la producción de cítricos son naranjas, siendo Brasil, China, EEUU, Europa y Méjico los principales productores. Aproximadamente el 60% de las naranjas producidas se destinaron al consumo doméstico y el otro 40% fueron procesadas. En Europa la producción se estima en 6,1 Mt.

España figura entre los 10 primeros productores mundiales de cítricos y ocupa la sexta posición como productor mundial de naranjas (2,93 Mt en 2012/2013, (FAOSTAT, 2015)

La industria transformadora de cítricos genera una gran cantidad de subproductos cítricos, teniendo en cuenta que el rendimiento de obtención de zumo a partir de una naranja fresca es del 40-50% de su peso (Braddock, 1999).

En 2012/2013 la producción a nivel mundial de zumo de naranja fue de 1,89 Mt, de las cuales 105.000 t se produjeron en Europa, siendo Alemania y España dos de los principales países productores de zumo de naranja concentrado (Figura 2.1).

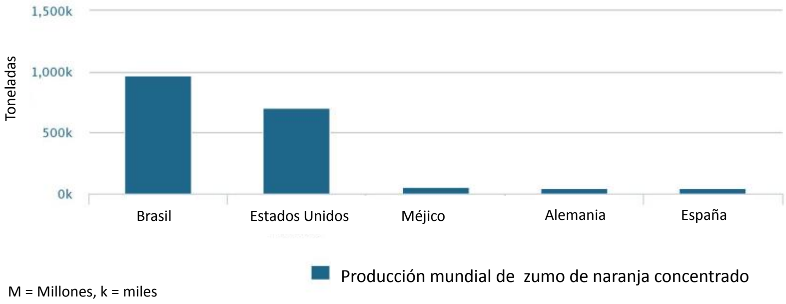

Figura 2.1. Producción de zumo de naranja concentrado de los 5 principales países productores (miles de toneladas) (FAOSTAT, 2015).

Existe escasez de información respecto a la cantidad de subproductos cítricos generados, pero partiendo de datos facilitados por algunos autores, (Fava et al., 2013) aproximadamente el volumen de subproductos cítricos, principalmente naranjas, en la zona europea y mediterránea puede estimarse en 1 Mt por año.

La prevención, minimización y valorización de residuos son las soluciones más ampliamente reconocidas para la gestión de los residuos. La legislación a nivel europeo está promocionando tales enfoques pero aún deben desarrollarse y optimizarse estrategias y tecnologías para garantizar soluciones económicas que den salida al problema de los residuos alimentarios.

Actualmente, los residuos procedentes del procesado de frutas son sólo parcialmente reciclados en función de su valor añadido (alimentación animal, compostaje, producción de metano, obtención de bioalcohol, etc.), sin embargo, existe una fracción importante que va a vertedero con los correspondientes efectos negativos que esto conlleva sobre la sostenibilidad global de la industria agroalimentaria. Estas matrices contienen valiosas sustancias como azúcares, ácidos orgánicos, sustancias colorantes, proteínas, aceites y vitaminas, además de otras macromoléculas (fibra dietética) y compuestos bioactivos, entre otras, que pueden ser de interés en las industrias alimentarias, farmacéuticas, químicas y de cosméticos, fundamentalmente (Castells, 2012).

En efecto, después de tratamientos previos específicos con agentes físicos y biológicos, seguidos por procedimientos de recuperación diseñados para cada caso, estos residuos pueden transformarse en fuente de ingredientes de gran interés para nuevas formulaciones alimentarias (Laufenberg et al., 2003). No obstante, el reto reside en convertir los subproductos generados en materia prima estable que sirva de base para la obtención de nuevos ingredientes y/o alimentos. Poco se conoce sobre la viabilidad técnica y económica de este alcance, en particular para la formulación de nuevos alimentos, pero se considera de enorme relevancia ya que permitiría (i) cerrar el círculo dentro de algunas grandes industrias alimentarias, que podrían utilizar sus residuos como materia prima para la producción de nuevos productos, y (ii) crear sinergias entre las pequeñas y medianas empresas relacionadas con el procesado de frutas, tanto las generadoras de subproductos, como las productoras de nuevos alimentos, que podrían aprovechar los subproductos de las primeras transformándolos en su propia materia prima, y contribuyendo así a la sostenibilidad, competitividad e innovación del sector alimentario.

2.2 Composición y propiedades de los subproductos cítricos

Los cítricos se consumen principalmente como fruta fresca o procesados en forma de zumo, ya sea fresco, refrigerado o concentrado.

El 88,6% de la parte comestible de la naranja es agua, de la restante, la mayoría corresponde a azúcares solubles (aproximadamente un 10%), siendo fundamentalmente sacarosa y azúcares reductores. Un 1% del peso total del fruto corresponde a ácidos orgánicos, que son los responsables del carácter agrio. Las sustancias nitrogenadas representan un 1%. Los lípidos son un componente menor, apenas un 0,2% ó 0,3%. Las cenizas son un componente significativo, entre el 0,48% y 0,50% del peso del fruto (Guardiola Bárcena, 1998).

Los componentes de la naranja se muestran en la Figura 2.2. El subproducto cítrico representa, aproximadamente, la mitad del peso húmedo de la fruta entera (Ensminger et al., 1990, Sinclair, 1984), con la piel representando casi ¼ del total del peso.

Figura 2.2. Componentes de la naranja

Tanto las propiedades intrínsecas de la materia prima de partida (composición química) como el tratamiento mecánico que sufre durante su procesamiento confieren al subproducto cítrico sus características físico-químicas y sensoriales de las que dependerá su posterior aprovechamiento.

Tras la extracción del zumo de la fruta (40-50% w/w) queda un residuo compuesto por piel (flavedo, 8-10% w/w y albedo, 15-20% w/w), pulpa (residuo del zumo) y membranas (25-30% w/w), y semillas (0,5-1,5 w/w %) (Figura 2.3).

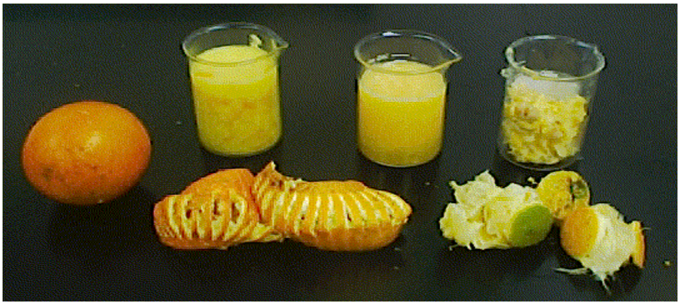

Figura 2.3. Principales subproductos obtenidos en el proceso de extracción de zumo: piel, pulpa (residuo del zumo) y membranas, semillas.

2.3 Transformación y uso actual de los subproductos cítricos

A continuación se describe el proceso general de obtención de zumo a partir de naranjas frescas.

Las etapas básicas del proceso de elaboración de zumo de naranja son:

1.- TRATAMIENTO PREVIO DEL FRUTO. Consiste en la limpieza (eliminación de residuos de pesticidas polvo, etc), selección y clasificación por tamaños para favorecer la extracción. Previamente, las naranjas se descargan de los camiones y se almacenan en silos.

2.- EXTRACCIÓN. Una vez clasificadas las naranjas se les realiza un raspado previo con rodillos de superficie rugosa para separar la capa más superficial del flavedo que es donde se encuentran las glándulas de aceite esencial. Este serrín se prensa en frío obteniéndose el aceite esencial.

Para la extracción del zumo de las naranjas raspadas se utilizan dos sistemas:

a) por EXPRIMIDORES (piñas rotativas). Consiste en cortar el fruto entero transversalmente por la mitad, extrayendo el zumo por presión contra un cono acanalado que gira a gran velocidad. Este sistema, aunque incorpora poco aceite de la corteza, tiene el inconveniente de airear demasiado el zumo y de provocar un excesivo contacto con otros tejidos, que le comunican gusto amargo.

b) Sistema IN-LINE de la Food Marchinery Corporation (F.M.C.). El principio de este sistema se presenta en la Figura 2.4 y se basa en introducir una cánula en la fruta y prensarla entre dos émbolos. Se recogen así separadamente el zumo, que sale por la cánula, el aceite esencial y las cortezas aplastadas; se obtiene de esta forma un zumo que no ha estado en contacto con la parte exterior de la fruta y exento de aceite esencial, que se recupera y constituye un valioso producto utilizado en perfumería.

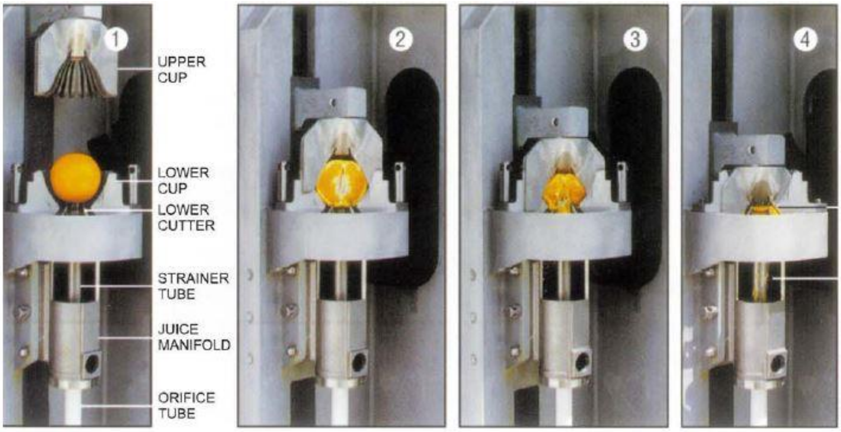

Figura 2.4. Extractor de zumo en línea (cortesía de JBT Foodtech (antes FMC)

La piel de los cítricos tiene numerosas aplicaciones que dependen de las propiedades funcionales de la materia prima así como la aplicación final buscada. Como en la mayoría de las frutas, después de eliminar el agua de la piel, los principales componentes son carbohidratos solubles e insolubles. La fracción soluble en agua contiene glucosa, fructosa, sacarosa y pequeñas cantidades de xilosa; mientras que la parte insoluble está constituida por pectina, hemicelulosa y celulosa (50-70% de la parte insoluble) (Braddock, 1999).

Además, las pieles poseen una gran variedad de compuestos bioactivos que podrían ser considerados como potenciales fuentes de compuestos funcionales (Schieber et al., 2001). A excepción del ácido ascórbico, las pieles contienen más compuestos bioactivos que los zumos: ácidos fenólicos, flavonoides - hesperidina, narirutina, naringina y eriocitrina (Fernandez-Lopez et al., 2004) - limonoides y fibras (Bocco et al., 1998, Gorinstein et al., 2001, Manthey and Grohmann, 2001).

Estos compuestos han atraído una importante atención debido a sus propiedades para la salud humana, que fueron atribuidas a su actividad antioxidante y secuestradora de radicales libres (Bocco et al., 1998, Gorinstein et al., 2001, Imeh and Khokhar, 2002, Manthey and Grohmann, 2001). Poseen además actividad anti-microbiana, antiinflamatoria, y agentes preventivos contra el cáncer (Tripoli et al., 2007).

Durante las últimas décadas ha aumentado la industrialización de subproductos de cítricos con los siguientes objetivos (Castells, 2012):

- Aprovechamiento de las cortezas de cítricos como ingredientes de piensos para alimentación animal, melazas y licor de prensado (Tripodo et al., 2004).
- Aprovechamiento de la pulpa para mejorar el aroma y la sensación bucal de zumos reconstituidos (agente de turbidez o cloud).
- Extracción de aceites esenciales empleados como aromatizantes en bebidas y perfumería y otras aplicaciones químicas.
- Extracción de D-limoneno (principal molécula constituyente de los aceites esenciales) con numerosas aplicaciones en la industria química como resinas adhesivas, aromas, disolvente y agentes desengrasantes.
- Obtención de pectinas empleando como materia prima el albedo, ingrediente que se emplea a menudo para aumentar la viscosidad de líquidos o productos semisólidos (Laufenberg et al., 2003).
- Extracción de flavonoides hesperidina y naringina de la corteza de cítricos, empleados en la industria farmacéutica. La naringina se usa como materia prima para la obtención de una sustancia de alto poder edulcorante, que no aporta calorías, llamada dihidrochlaconoa. Además añadida en pequeña cantidad al aceite de palma inhibe su oxidación térmica. También se ha encontrado que

desempeña un papel importante en los tratamientos de resfriados, quemaduras por frío y por irradiación.

- Aprovechamiento de carotenoides como pigmentos naturales para la mejora de la coloración de los jugos simples y concentrados, bebidas refrescantes, jaleas, caramelos duros, helados, yogur, etc.
- Obtención de fibra dietética (DF). Considerando el residuo que queda después de la extracción de pectina, el material seco fibroso resultante se compone de fibra dietética (600g DF/ kg, Aravantinos-Zafiris et al. (1994)), la mitad de la cual es celulosa. La fibra cítrica es de gran interés no solo por sus propiedades nutricionales sino también por sus propiedades funcionales y tecnológicas, por ejemplo como estabilizadores en productos lácteos ácidos o como miméticos de grasa.

2.4 Obtención de fibra dietética a partir de subproductos cítricos

Las constantes recomendaciones de aumentar el consumo de fibra dietética (28-35 g/día), por sus claros beneficios en la salud, han llevado a buscar nuevas fuentes de este componente o a diseñar nuevos alimentos con una mayor aceptación, que contribuyan a aumentar la ingesta diaria recomendada de fibra dietética (Pszczola, 2006). Cuando la importancia nutricional de la DF ganó popularidad, empezó a desarrollarse un interés considerable en obtener fibra a partir de piel de cítricos.

Las fibras cítricas se consideran de mayor calidad que las provenientes de cereales dado su mejor ratio entre fibra dietética soluble e insoluble y, también, debido a su mayor capacidad de retención de agua y aceite (Larrauri, 1999, McCready, 1977). La ventaja adicional de la DF cítrica es su contenido en compuestos bioactivos asociados (flavonoides y vitamina C) con propiedades antioxidantes, que pueden tener un mayor efecto sobre la salud que la fibra misma (Lario et al., 2004).

Para beneficiarse de estas biomoléculas y transformar frutas y subproductos vegetales en valiosos ingredientes, son necesarios procedimientos previos de estabilización. Estos tratamientos previos representan pasos cruciales debido a la necesidad de evitar pérdidas de compuestos bioactivos y de obtener ingredientes microbiológicamente estables que cuenten con una amplia variedad de efectos beneficiosos para la salud (Larrauri, 1999).

Los subproductos de la industria alimentaria son materiales muy susceptibles a la descomposición microbiana, a la fermentación o al deterioro químico debido a una microflora residente y a actividades enzimáticas endógenas. Por lo tanto, todos los procesos de valorización deberán considerar un tratamiento previo o un procedimiento de estabilización que reduzca al máximo el efecto negativo de estos procesos o agentes biológicos y químicos en los compuestos objetivo. Además, comparado con la porción comestible de la fruta, para la mayoría de las aplicaciones destinadas al consumo humano, la piel de los cítricos debe ser procesada para eliminar el amargor, los microbios y otras impurezas.

La mayoría de procesos que se emplean en la actualidad para la obtención de fibra a partir de subproductos cítricos incluyen las siguientes etapas (Braddock, 1999, Nafisi-Movaghar et al., 2013):

- TRITURADO; para conseguir una adecuada reducción del tamaño de partícula y una mayor homogeneización, mejorando la eficiencia de las etapas posteriores.
- ESCALDADO con agua para eliminar las sustancias no deseables y reducir la carga microbiana.
- EXTRACCIÓN con agua (solvente) para reducir los azúcares solubles, el amargor y el sabor.
- PRENSADO o CENTRIFUGADO; para eliminar agua.
- SECADO; con el objetivo de reducir la humedad del producto.

- MOLIENDA; para reducir el tamaño de partícula a polvo; El tamaño final de partícula dependerá del tipo de fibra y de su aplicación. Esta operación debe realizarse cuidadosamente para evitar que se degrade la estructura física de la fibra, disminuyendo su capacidad de retención de agua.
- ENVASADO y ALMACENAMIENTO a condiciones que impidan el desarrollo de malos sabores, mohos o insectos.

2.5 Termodinámica irreversible en sistemas alimentarios

Una vez conocidas las propiedades termodinámicas del aire, se aborda a continuación la teoría sobre las propiedades termodinámicas del alimento que interacciona con el aire, y que determinarán los fenómenos de transferencia, tanto de masa como de calor durante el secado de alimentos. La termodinámica irreversible estudia sistemas alejados del equilibrio, como son aquellos en donde ocurren fenómenos de transferencia y supone una herramienta de gran valor para determinar la evolución de un sistema compartimentado, no equilibrado, con especies químicas en transformación como son los alimentos y su entorno. Las propiedades termodinámicas del alimento y su entorno (i) determinan el punto hasta el cual el alimento debe ser deshidratado para alcanzar la estabilidad deseada (ii) permiten calcular la cantidad teórica de energía requerida para eliminar una cantidad de agua determinada del alimento y (iii) suponen una mejor comprensión de la microestructura asociada con la interfase alimento-agua (Aviara y Ajibola, 2002).

El desarrollo de modelos físicos y matemáticos es importante para simular lo que ocurre durante el proceso y por lo tanto para predecir los valores de las propiedades deseadas. Debido a la alta complejidad de las estructuras alimentarias, los nuevos modelos cinéticos desarrollados en el diseño de productos y procesos alimentarios, deben incorporar suficiente información acerca de todos los aspectos físicos, termodinámicos, estructurales, químicos y bioquímicos de los mecanismos involucrados en sus transformaciones (Castro-Giráldez, 2010, Castro-Giráldez et al., 2011a, Castro-Giráldez et al., 2011b).

Los alimentos son mayoritariamente estructuras coloidales o celulares, con una elevada complejidad, debido a su compartimentación en fases que no se encuentran en equilibrio. Dichas fases se componen a su vez de distintas especies químicas que sufren transformaciones físicas desacopladas entre ellas. La termodinámica irreversible permite acoplar todos los mecanismos involucrados en las transformaciones únicamente en los potenciales termodinámicos. En el caso de los fenómenos de transporte, el potencial termodinámico es el químico. Onsager (1931) propuso que todo flujo (transporte), ya sea de materia o de energía, es una combinación lineal de las fuerzas impulsoras de un sistema, cuyos coeficientes pueden obtenerse en función de variables de estado tales como temperatura, presión, composición, volumen, energía, etc. y son por definición independientes de los flujos y de las fuerzas impulsoras (coeficientes fenomenológicos). Por ejemplo, la relación de Onsager demuestra que la influencia de un gradiente de concentración sobre el flujo de calor es la misma que la influencia de un gradiente de temperatura sobre el flujo de materia (Lévy, 1992).

La primera relación de Onsager describe un flujo de una especie química determinada como la relación entre la fuerza impulsora (potencial químico) y un coeficiente fenomenológico que describe la relación de la especie química en movimiento con el medio a través del cual se transporta. Si la primera relación de Onsager se aplica sobre la termodinámica irreversible se obtiene la siguiente expresión:

$$J_i = L_i \Delta\mu_i \qquad \text{(Ec. 1)}$$

Donde J_i representa el flujo, L_i es el coeficiente fenomenológico y $\Delta\mu_i$ es el potencial químico, el subíndice i hace referencia a la especie química.

Si experimentalmente es posible conocer el flujo de la especie i (mol/$s^{-1}m^{-2}$), entonces se puede, gracias a la relación de Onsager, calcular el coeficiente fenomenológico o el potencial químico del sistema ($\Delta\mu_i$) a partir de la ecuación 1.

Por otra parte, la tendencia de los componentes a dejar una fase se expresa mediante el valor del potencial químico o energía libre de cada componente presente en cada fase. Los alimentos son sistemas compartimentados, separados por interfases, en cuyas fases se definen las variables de estado, por esta razón todas las variables de estado presión (P), temperatura (T), volumen (V), entropía (S) y concentración de las especies químicas (n_i) afectan al valor de la energía libre (G), y por consiguiente a los fenómenos de transporte. En este sentido, la propiedad termodinámica que permite cuantificar los cambios asociados a las propiedades de los alimentos, es la variación en la energía libre (ΔG), esta propiedad mide la capacidad del sistema para transformarse. Las reacciones con un valor ΔG negativo tienen lugar de forma espontánea. Las reacciones en las que ΔG es positivo es necesaria una aportación de energía para que se produzca la transformación. De tal manera que la proximidad al equilibrio y los flujos de especies químicas que se producen al transformar un alimento se determinan en función de la variación de energía libre de Gibbs (G) (Nicolis and Prigogine, 1977).

Para un sistema multicomponente, a presión y temperatura constante, en el que ocurren cambios en la composición, produciéndose un fenómeno de transferencia de especies químicas entre fases, siendo G únicamente función de T, P y n_i, se obtiene la ecuación simplificada de Gibbs-Duhem (Demirel, 2013). La ecuación de Gibbs-Duhem en termodinámica describe la relación entre los cambios en el potencial químico de los componentes de un sistema termodinámico:

$$\Delta G = -S\Delta T + V\Delta P + \sum_i \mu_i \, \Delta n_i \qquad \text{(Ec. 2)}$$

siendo μ_i el potencial químico de la especie i.

En algunos casos, el transporte de materia de i ocurre asociado al acoplamiento de fenómenos mecánicos, térmicos y químicos, asociados a las variables de estado y a otras características del medio. Para cada sistema es necesario definir las principales propiedades físicas que afectan al valor de G, puesto que en la mayoría de los sistemas complejos, las variables de estado no son suficientes para definir la energía libre. La capacidad de hacer un trabajo mecánico (F) y el potencial eléctrico (ψ), necesarios para elongaciones (l) y movimiento de cargas eléctricas (e), respectivamente, son dos potenciales de energía que pueden contribuir a la energía libre. La energía libre podría expresarse de una manera extendida como (Castro-Giráldez, 2010):

$$\Delta G = -S\Delta T + V\Delta P + F\Delta l + + \sigma_w \Delta A + \psi\Delta e + \sum_i \mu_i \, \Delta n_i \qquad \text{(Ec. 3)}$$

A partir de la ecuación de Gibbs-Duhem extendida para cada caso particular, puede calcularse la variación de G (ΔG) en el sistema, asociada a la pérdida (o ganancia) de Δn_i moles de i, como el potencial químico. Para sistemas a presión y temperatura constante, que no presentan interacciones con otras especies químicas se puede expresar como:

$$\mu_i = \left(\frac{G}{n_i}\right)_{T,P,n_{j\neq i}} = RT\ \mathrm{Ln}\ a_i \qquad \text{(Ec. 4)}$$

Siendo R la constante de los gases ideales, T la temperatura expresada en K y a_i la actividad de la especie química estudiada. De la ecuación de Gibbs-Duhem extendida (3) dividida por Δn_i resulta en:

$$\Delta\mu_i = \frac{\Delta G}{\Delta n_i} = -\ \bar{S}_i \Delta T + \bar{V}_i \Delta + F\Delta l + \psi\Delta e + \mu_i|_{T,P,n_{j\neq i}} + \sum \mu_j\Big|_{T,P,n_{i\neq j}} \qquad \text{(Ec. 5)}$$

2.6 Teoría de secado por aire caliente

Se entiende por secado la operación de deshidratación de un producto, poniéndolo en contacto con un fluido que tenga un potencial químico del agua menor. El proceso de extracción de agua se puede producir con o sin cambio de estado. En el caso del secado con aire caliente el principal factor que induce un gradiente de potencial químico de agua es un caudal de aire con baja humedad relativa y un producto con alta actividad del agua. El gradiente del potencial químico de agua en sistemas biológicos, en la interfase fluido/alimento se puede definir como en la ecuación 6 (Castro-Giráldez et al., 2014):

$$\Delta\mu_w = \frac{\Delta G}{\Delta n_w} = \bar{\nu}_w \Delta P - \bar{s}_w \Delta T + \bar{F}\Delta l + \psi\Delta e + \sigma_w \Delta A + RT\Delta \ln a_s \frac{\Delta n_S}{\Delta n_w} + RT\Delta \ln a_w \qquad \text{(Ec. 6)}$$

Donde $\Delta\mu_w$ es el gradiente de potencial químico del agua en la interfase fluido/alimento, G es la energía libre de Gibbs, ν_w es el volumen específico del agua, P la presión absoluta, s_w la entropía parcial molar del agua, T la temperatura, F la fuerza parcial polar del agua, l la variación de elongación del sistema, Ψ el potencial eléctrico, e movimiento de cargas eléctricas, σ_w la tensión superficial del agua, A el área, R es la constante de los gases ideales, a_s la actividad de la especie química del soluto, a_w la actividad del agua, n_s el número de moles de los solutos y n_w el número de moles de agua.

En concreto, en una operación de secado con aire caliente a una temperatura inferior a la de cambio de estado del agua (Traffano-Schiffo et al., 2014):

$$\Delta\mu_w = \frac{\Delta G}{\Delta n_i} = \bar{\nu}_w \Delta P - \bar{s}_w \Delta T + RT\ln\frac{\varphi}{a_w} \qquad \text{(Ec.7)}$$

Donde φ es la humedad relativa del aire caliente expresada en tanto por uno.

Un gradiente de potencial químico del agua induce una inercia termodinámica que impulsa el transporte de agua del alimento (líquido) al aire caliente (gas) lo que exige un cambio de estado de primer orden o lo que es lo mismo, un aporte de energía térmica que induzca este cambio de estado. Esta energía generalmente es obtenida de la energía interna del aire, disminuyéndola, pero si en el entorno donde se produce la inercia termodinámica aparecen fuentes de energía con más disponibilidad, el sistema evoluciona empleando dicha energía para cambiar de estado el agua.

Para que un proceso de secado con aire caliente alcance la máxima velocidad de secado inducida por el potencial químico del agua, el aire debe proporcionarle toda la energía necesaria, para ello, el proceso de secado no debe presentar una barrera externa a la transmisión de calor (Capa límite equivalente). Esto se alcanza al superar una velocidad del aire de 5,13 m/s (Green and Perry, 2007). A partir de esta velocidad se alcanza la velocidad máxima de secado inducido por el gradiente de potencial químico, produciéndose una bajada de la temperatura del aire hasta la temperatura de saturación adiabática. Durante este periodo la entalpia del aire se mantiene constante ya que las pérdidas de energía interna (U) se compensan con el incremento del trabajo de flujo (PV) al pasar a formar parte del aire el vapor de agua generado. A velocidades inferiores, esta máxima velocidad de evaporación no se alcanza, siendo menor la disminución de la energía interna del aire y bajando menos la temperatura del mismo (temperatura húmeda del aire). En el caso de secado a velocidades inferiores del aire, un aporte extra de energía puede permitir al sistema trabajar a la máxima capacidad que le confiere el gradiente del potencial químico del agua en la interfase.

En el proceso de secado con aire caliente a elevadas temperaturas (muy baja humedad relativa o incluso a temperaturas de cambio de estado del agua) o velocidades del aire próximas a 5,13 m/s permite deshidratar cualquier producto alimenticio hasta niveles de humedad final muy baja que confieran al producto final mucha estabilidad, sin embargo, estas cinéticas elevadas de deshidratación asociadas a estas temperaturas elevadas producen en los alimentos transformaciones que pueden alterar su calidad final. Las dos principales transformaciones no deseadas son las compactaciones del tejido o del coloide, denominadas "encostramiento", inducidas por cinéticas elevadas de secado y las reacciones químicas o bioquímicas inducidas por elevadas temperaturas, como las reacciones de Maillard, Streker (aproximadamente 68ºC) o incluso la pirólisis (a partir de 180ºC). Estos procesos no deseados producen alteraciones en la forma y la textura del producto; composición y estructura no uniforme, cambios de sabor y aroma, modificación del color, degradación de componentes nutricionales, mala capacidad de rehidratación, etc. (Arballo et al., 2010).

El proceso de secado envuelve distintos mecanismos acoplados, existiendo distintos puntos críticos que separan las etapas en las que se divide fundamentalmente dicho proceso. Tradicionalmente se ha considerado tres etapas dependiendo de la velocidad de secado. La primera etapa corresponde al período de inducción, donde comienza un transporte de agua promovido por una diferencia de potencial químico del agua entre el aire y el alimento. En este periodo se producen tres fenómenos que inicialmente aparecen de manera independiente y que durante este periodo se acoplan (transporte interno del agua, evaporación superficial y transporte del agua y del calor a través del aire) estos distintos mecanismos conforman simultáneamente el flujo de agua. La segunda etapa representa el período en el cual la velocidad de secado es constante y máxima. En estas etapas, la temperatura de la superficie evoluciona hasta la temperatura húmeda del aire (periodo de inducción) o hasta la de saturación adiabática en función de la velocidad del aire. La superficie del producto permanece a esa temperatura hasta el final del periodo de velocidad de secado constante. Hasta este instante el proceso de secado viene gobernado por la evaporación superficial, siendo el mecanismo más lento. Tradicionalmente, el secado acaba con un periodo de velocidad de secado decreciente que se caracteriza por un lento trasporte de agua por el interior de la muestra, lo que provoca que la superficie se seque incrementando su temperatura hasta la temperatura del aire. Algunos estudios han demostrado que este periodo de velocidad de secado decreciente se compone de distintas etapas ya que los mecanismos de retención y adsorción de agua en el interior del tejido son distintos, así como la procedencia del agua. Al mismo tiempo, a humedades muy bajas, la aparición de una transición vítrea puede inducir una nueva etapa con acumulación de energía mecánica en su interior que cambie sus propiedades físicas frente a la rehidratación (Traffano-Schiffo et al., 2014).

2.6.1 **Fundamentos básicos de la interacción de las microondas con sistemas biológicos.**

Dentro de las cuatro fuerzas universales, la fuerza electromagnética viene transmitida por la partícula fundamental denominada fotón. Es posible utilizar dicha fuerza tanto en procesos de transformación de alimentos como de detección de sus propiedades internas, esto es posible adaptando el comportamiento del fotón a la finalidad del proceso.

INTRODUCCIÓN

Un flujo de fotones genera interacciones eléctricas y magnéticas, el efecto de ambas viene definido por las relaciones de Maxwell. Las partículas elementales expresan su nivel de energía a través de tres movimientos, el rotacional, el vibratorio y el traslacional. El fotón transmite la fuerza electromagnética mediante la vibración transversal (eléctrica) y longitudinal (magnética) de los fotones en movimiento. Por esta razón, en función de la trayectoria del flujo de fotones se maximiza más la fuerza eléctrica o la magnética. Tanto el fotón como el gluon son bosones, partículas transmisoras de fuerza universal, que tienen momento nulo y por tanto no tienen interacción con el campo de Higgs, por esta razón son partículas carentes de masa y se mueven a la máxima velocidad a la que se puede mover una partícula elemental, $3 \cdot 10^8$ $m \cdot s^{-1}$. Por esta razón, la variación de energía en los fotones se muestra exclusivamente en la vibración. Las interacciones eléctricas dependen del nivel de energía del flujo de fotones que generan la fuerza, y se podrán dividir en dos mecanismos de interacción. Un fotón con poca energía tendrá una vibración leve y, por ende, una frecuencia de vibración baja (Hz-GHz). El efecto sobre la materia será leve, y las interacciones estarán asociadas a la resonancia de las ondas producidas por la vibración del fotón; estas interacciones serán de orientación y de inducción molecular. En cambio, los fotones con mucha energía vibrarán intensamente a una elevada frecuencia (THz-ZHz). El efecto sobre la materia será mayor cuanto mayor sea el nivel de energía del flujo de fotones.

En un medio dieléctrico como los sistemas alimentarios, se produce resistencia al flujo de fotones, y esta resistencia produce un desplazamiento en el campo eléctrico y magnético, matemáticamente se expresa como:

$$\overline{D}=\vec{\varepsilon}\cdot\varepsilon_0\cdot E=\left(\varepsilon^{'}\text{-}j\varepsilon^{''}\right)\,\varepsilon_0\cdot E \qquad \text{(Ec. 8)}$$

$$\overline{B}=\vec{\mu}\cdot\mu_0\cdot H=\left(\mu^{'}\text{-}j\mu^{''}\right)\,\mu_0\cdot H \qquad \text{(Ec. 9)}$$

Donde D y B son densidades de flujo, eléctrico y magnético respectivamente, E y H son los campos eléctricos y magnéticos respectivamente, $\vec{\varepsilon}$ es la permitividad compleja y representa la propiedad física que explica la respuesta del medio a un campo eléctrico externo aplicado, y $\vec{\mu}$ es la permeabilidad compleja y representa la propiedad física que explica la respuesta del medio a un campo magnético.

Cuando un flujo de fotones circula a través de un sistema, parte se refleja, parte se transmite y parte se absorbe. La proporción de energía absorbida se define a través de las propiedades eléctricas y magnéticas.

En la descomposición vectorial de la permitividad la ε' es la constante dieléctrica y ε'' el factor de pérdidas.

De tal manera que la constante dieléctrica (ε') representa la proporción de energía eléctrica que es almacenada al orientarse el medio respecto a la dirección del campo, y el factor de pérdidas (ε'') representa el desplazamiento del campo inducido por las transformaciones de energía eléctrica en otras energías. En baja frecuencia genera un aumento en la movilidad molecular, desencadenando entre otros fenómenos colisiones y fricción entre moléculas, disipando la energía eléctrica en forma de energía mecánica y calorífica. Por tanto, los valores de la permitividad son diferentes en cada sistema, debido a los estados de agregación (sólido, líquido y gaseoso) de la materia y fundamentalmente al ordenamiento estructural del mismo.

La interacción de los fotones con los alimentos en el espectro electromagnético se divide, a baja frecuencia, en fenómenos de orientación e inducción y, a alta frecuencia, en fenómenos de partícula. Los fenómenos de orientación se producen a frecuencias características comprendidas entre Hz y GHz, estos fenómenos identifican junto con la conductividad iónica el comportamiento dieléctrico de los sistemas biológicos.

La dispersión alfa (α), también llamada counterion (ion contra ion), viene inducida por la orientación de cargas móviles en el medio dieléctrico. La dispersión beta (β) esta inducida por la orientación de las cargas fijas del medio, pudiéndose deber a las cargas propias de las moléculas o a cargas inducidas por interacciones entre especies químicas, fenómenos de tensión superficial (también denominado Maxwell-Wagner). Por último, el fenómeno que se analiza en esta tesis, la dispersión gamma (γ) se produce por la orientación de dipolos de pequeño tamaño molecular, en sistemas biológicos, principalmente el agua (Markx and Davey, 1999).

La dispersión gamma (γ), fenómeno comprendido entre MHz y GHz, produce la orientación dinámica del spin de rotación de las moléculas dipolares (como por ejemplo, el agua) en la dirección del campo eléctrico, y la inducción o rotación de la molécula a través del spin. Este fenómeno, al igual que las dispersiones α y β, produce una acumulación de energía eléctrica en la reorientación del spin y una transformación de parte de la energía eléctrica en otras energías, mecánicas y/o caloríficas, provocada por las colisiones y fricciones asociadas al incremento en la movilidad molecular. El espectro dieléctrico del agua líquida, presenta una fuerte relajación característica próxima a 18 GHz a 25ºC (Kaatze, 1989), disminuyéndose en presencia de solutos electrolíticos y no electrolíticos (Castro-Giráldez, 2010)

La mayoría de los alimentos presentan una fase acuosa mayoritaria, si se tiene en cuenta que las microondas interaccionan mayoritariamente con la polaridad de esta molécula, es posible usar esta tecnología en procesos de calentamiento (microondas de potencia) o en sistemas de monitorización para describir la estructura del alimento (microondas de señal).

Unido a la dispersión gamma se produce un fenómeno de pérdida de energía eléctrica por repulsión de cargas (iones o macromoléculas con muchas cargas), transformándose en calorífica y mecánica denominado conductividad (σ). Dicho fenómeno se produce en el rango comprendido entre Hz hasta 1 GHz.

$$\sigma=\varepsilon''\varepsilon_0\omega \qquad \text{(Ec.10)}$$

Siendo ω la velocidad angular y ε_0 la permitividad del vacío (ε_0=8.8542 10^{-12} F·m^{-1}).

En la figura 2.5, se muestra un resumen de todos los fenómenos descritos anteriormente.

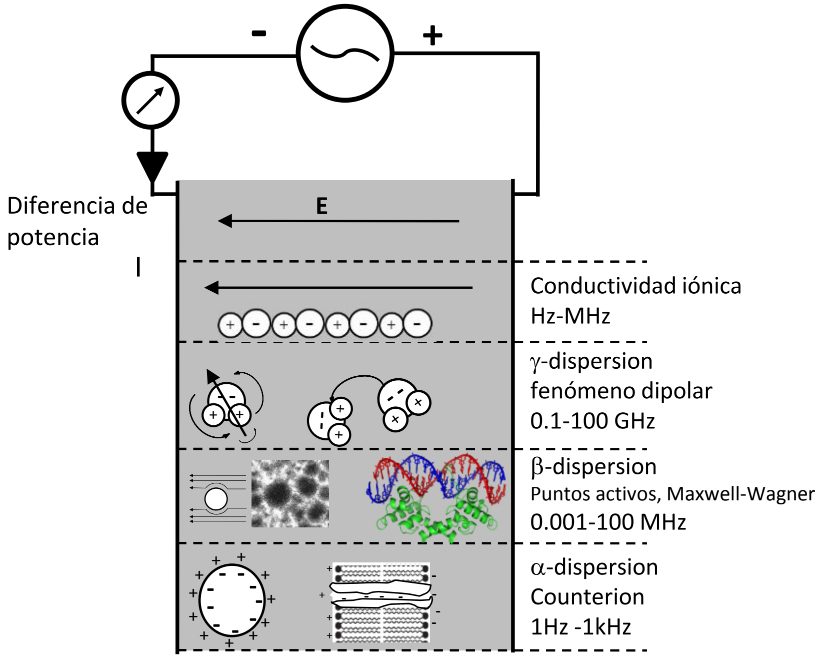

Figura 2.5. Esquema resumen de todos los fenómenos que se producen en el rango de frecuencias entre Hz y GHz.

La penetración del flujo de fotones dentro del alimento dependerá de la constante absorción de energía de los mismos. Esta penetración se puede calcular mediante la siguiente ecuación (Metaxas & Meredith, 1983):

$$Dp = \frac{c}{2\pi f}\frac{\sqrt{\varepsilon'}}{\varepsilon''} \qquad \text{(Ec. 11)}$$

Donde Dp es la profundidad de penetración, c es la velocidad de la luz ($3 \cdot 10^8$ $m \cdot s^{-1}$).

2.6.2 Equipos de microondas de potencia

El calentamiento por microondas se basa en la interacción de los fotones con el agua del alimento y en la elevada penetración de los mismos. La frecuencia de los magnetrones utilizada en Europa es 2450 MHz y en E.E.U.U. es 915 MHz, por esta razón los equipos americanos tienen mayor penetración pero menor calentamiento, mientras que los europeos tienen una penetración menor, próxima a 1 cm dependiendo de la humedad, pero un mayor calentamiento. Las microondas son generadas dentro de una cavidad por intensificación de la corriente alterna desde líneas eléctricas domésticas hasta 2450 MHz. El calentamiento volumétrico acoplado a fenómenos de conductividad térmica acelera la transmisión de calor frente a métodos tradicionales, haciendo de esta tecnología una atractiva fuente de energía térmica.

Los equipos de microondas constan de tres componentes principales (Figura 2.6):

- √ El magnetrón que genera el flujo de fotones a la frecuencia determinada.

- √ Un tubo de aluminio denominado guía, en cuyo interior, el flujo de fotones es conducida hasta la cámara de calentamiento.
- √ Una cámara de calentamiento donde se dispone el alimento para ser calentado y donde existe la posibilidad de agregar una circulación forzada de aire, impulsado por ventiladores y calentado por una resistencia eléctrica.

Figura 2.6: Microondas piloto utilizado para las operaciones de secado.

2.6.3 Equipos de microondas de señal

La espectroscopia dieléctrica en el rango de las microondas proporciona información sobre las interacciones de las moléculas de agua con su entorno. La permitividad en la relajación de la dispersión gamma tiene relación directa con el número de moléculas de agua así como el estado de movilidad de las mismas. De esta manera, también tendrá relación indirecta con todas las propiedades químicas y estructurales que estén relacionadas con el agua. Además, la permitividad en el rango de las microondas resulta muy interesante de medir debido a la comodidad y facilidad de uso. De tal manera que el desarrollo de sensores de control en línea no destructivos resulta de gran interés para la industria, desarrollándose sistemas de control y monitoreo de calidad de productos alimentarios.

La permitividad en el rango de las microondas se puede medir conectando una sonda coaxial conectada a un analizador de redes (Figura 2.7). Mediante esta técnica se obtienen espectros dieléctricos en un amplio rango de frecuencias (0.2-50GHz), y es utilizada principalmente para líquidos y sólidos. Este método es no destructivo y fácil de usar, además no necesita preparación de la muestra. Por otra parte, sus desventajas serían el requerimiento de un determinado espesor de la muestra si esta está muy deshidratada. Este método se utiliza para multitud de alimentos como: margarinas, productos cárnicos, productos de la pesca, etc. (Kent et al., 2002).

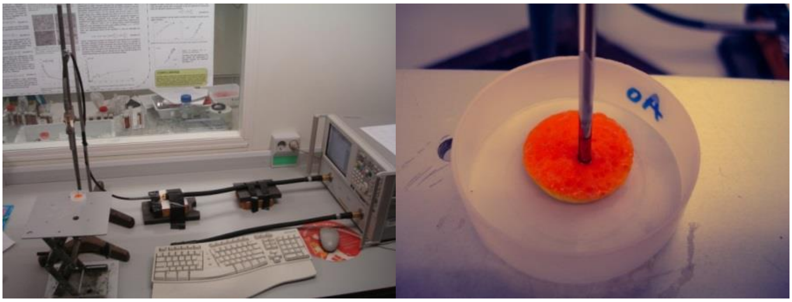

Figura 2.7. Equipo de medida de permitividad del Grupo de Propiedades dieléctricas del IuIAD de la Universidad Politécnica de Valencia.

2.6.4 **Secado combinado microondas-aire caliente.**

Tal y como se ha comentado anteriormente, el gradiente de potencial químico del agua induce una inercia termodinámica que impulsa el transporte de agua del alimento al aire caliente lo que exige un cambio de estado de primer orden o lo que es lo mismo, un aporte de energía térmica que induzca este cambio de estado. Esta energía generalmente es obtenida de la energía interna del aire, disminuyéndola, pero si en el entorno donde se produce la inercia termodinámica aparecen fuentes de energía con más disponibilidad, el sistema evoluciona empleando dicha energía para cambiar de estado el agua. Este es el caso que aparece cuando se combina el secado por aire caliente con microondas de potencia media.

Los fotones en a 2,45 GHz tienen cierta penetración (Ec. 11) en función de la humedad del alimento, por esta razón, el aporte de energía calorífica se produce en un volumen determinado del producto, aportando energía al alimento favoreciendo la transición del agua (de líquido a vapor) inducida por el gradiente de potencial químico del agua. Si esta inercia termodinámica se produce en las vías apoplástica o poros del producto, teniendo en cuenta la penetración del calentamiento por microondas, se producirá vapor en el interior del alimento provocando fenómenos de expansión del tejido.

De esta manera, la tecnología de microondas a potencias medias resulta una atractiva fuente de energía térmica, para mejorar procesos de deshidratación, ya que no solo permite acelerar el proceso de secado abaratando costes sino que además reduce los fenómenos de compactación y encostramiento al expandir el tejido en el interior (Chou and Chua, 2001). Si el calentamiento por microondas se produce a potencia elevada se pueden alcanzar temperaturas de cambio de estado del agua, superiores a 100ºC, generando flujos de vapor independientes del aire. Dichos flujos generan una fuerte expansión del tejido que puede terminar en rotura, además si el alimento es termosensible sufrirá transformaciones químicas o bioquímicas que degradaran en parte las propiedades sensoriales del mismo. En estos casos, la eliminación inmediata del vapor de agua generado es un paso crítico (Bampidis and Robinson, 2006). Procesos de secado con aire caliente combinado con microondas se ha demostrado como una técnica de deshidratación que permite, frente al secado con aire caliente, reducir el tiempo de proceso además de mejorar la calidad del producto y reducir los requerimientos de energía (Erle, 2005, Funebo and Ohlsson, 1998, Okino-Delgado and Fleuri, 2014, Soysal et al., 2006, Tulasidas, 1994, Wu et al., 2004).

2.7 **Propiedades termodinámicas del aire húmedo**

Toda operación de deshidratación requiere de fluido con un potencial químico del agua inferior al del alimento (fluido hipertónico), por esta razón, cuando el fluido empleado es aire, es necesario acondicionarlo para reducir su potencial químico del agua. Los dos mecanismos fundamentales de acondicionamiento del aire pasar por reducir su humedad relativa. El primero es reduciendo la carga neta de agua del aire o deshumidificación y el segundo calentando el aire para que en el proceso de expansión aumente su capacidad de almacenamiento de agua y por ende baje su humedad relativa.

En las operaciones de secado con aire caliente, el proceso de acondicionamiento o calentamiento del aire suele realizarse industrialmente mediante quemadores o mediante resistencias eléctrica, condicionando esta operación la siguiente, el secado. Por esta razón el conocimiento de las propiedades termodinámicas del aire húmedo es crucial para dimensionar correctamente esta operación así como calcular requerimientos energéticos y optimizar la operación de secado.

Las operaciones que usan el aire para deshidratar alimentos constituyen uno de los casos más sencillos de transferencia de materia puesto que sólo hay dos fases: la *fase líquida* constituida por un líquido (agua con diferentes niveles de retención en el tejido y solutos) y la *fase gas* constituida por el aire compuesto por distintos componentes que se mantienen constantes y un único componente capaz de pasar de una fase a otra, ese componente es el agua (Geankoplis, 1993).

La termodinámica es una rama de la física que estudia los efectos de los cambios de la temperatura, presión y volumen de los sistemas físicos a un nivel micro y macroscópico. El término aire húmedo se refiere a una mezcla de nitrógeno, oxigeno, argón, dióxido de carbono y agua, agrupándose en el término aire seco a todos los componentes excepto el agua ya que se trata como si fuera un único componente ya que la relación entre las especies químicas se mantiene casi constante en la atmosfera (Barbosa-Cánovas y Vega-Mercado, 1996).

La Evolución del aire durante su calentamiento y posterior hidratación puede ser calculada utilizando diagramas que agrupan las propiedades termodinámicas del aire que describen la cantidad y estado del agua así como su nivel de energía, estos diagramas se denominan diagramas psicométricos.

Las cuatro propiedades que describen el diagrama psicométrico son las siguientes:

La **humedad absoluta** es la razón másica de agua que tiene el aire y representa el contenido en agua de un volumen de aire expresado en kg agua/kg aire seco. El aire presenta comportamiento ideal en condiciones normales, es por esto que tanto la fracción como la razón molar se pueden explicar, además de molar, de forma volumétrica o barométrica. De acuerdo con esto, la humedad absoluta será la razón molar expresada barométricamente convertida a másica mediante las masas moleculares del agua (18 g/mol) y de la mezcla de gases que se engloba en el aire seco (28,9 g/mol):

$$X = \frac{M_v\, p_v}{M_a p_a} = 0{,}622\ \frac{p_v}{(P\text{-}p_v)} \qquad \text{(Ec. 12)}$$

siendo M la masa molecular (g/mol), P la presión absoluta del aire (mmHg) y p la presión parcial (mmHg) de cada componente del sistema: vapor de agua (v) y el aire seco (a).

En la figura 2.8 se muestran las propiedades físicas necesarias para poder calcular todas las propiedades termodinámicas del aire húmedo.

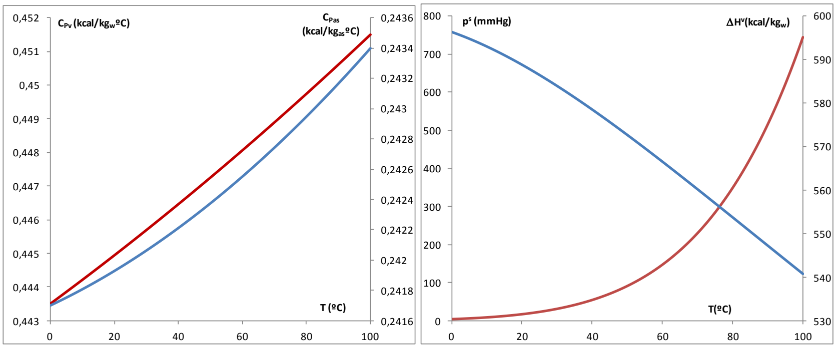

Figura 2.8. A la derecha los calores específicos del vapor (rojo) y del aire seco (azul), y a la izquierda la presión parcial de saturación del agua en el aire (rojo) y el calor latente de vaporización (azul) (Green & Perry, 2007).

Dada una presión absoluta y la temperatura del sistema, habrá un umbral de mezcla máximo de agua con el resto de componentes que forman el aire seco, dicho umbral vendrá definido por la presión de saturación (Figura 2.8.), esta mezcla se volverá totalmente inmiscible a partir de los 335ºC (Treybal, 1980).

Es decir, fijada la presión absoluta, a cada temperatura corresponderá un valor de presión parcial de saturación p_v^s y una **humedad absoluta de saturación** $\mathrm{X_{sat}}$:

$$\mathrm{X_{sat}}=0{,}622\ \frac{\mathrm{p_V^S}}{(\mathrm{P}\text{-}\mathrm{p_V^S})} \tag{13}$$

Este valor es la máxima concentración de agua que puede alcanzar la corriente de aire. Es posible construirse un diagrama psicométrico, en condiciones normales de presión y volumen, en el que se grafique la humedad absoluta en las abscisas frente a la temperatura en las ordenadas. A este tipo de diagramas psicométrico se le denomina diagramas de Mollier (Figura 2.9), donde además se le agregan la humedad relativa y la entalpía.

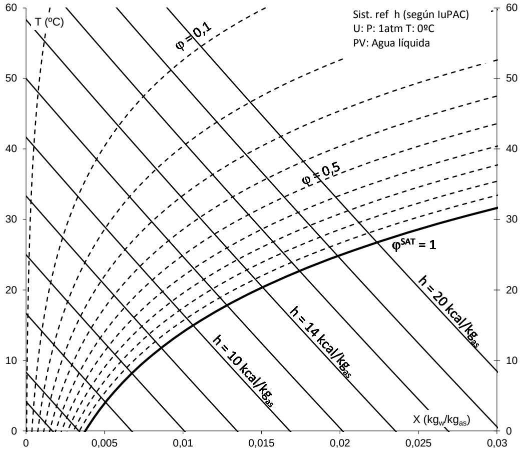

Figura 2.9. Ejemplo de diagrama psicrométrico. Diagrama de Mollier.

La **humedad relativa** es una medida de capacidad y describe la proximidad que tiene un volumen de aire a alcanzar la saturación o máxima concentración de agua. Se define como la relación entre la cantidad de vapor de agua contenida en un determinado volumen de aire y la que tendría si estuviera saturado:

$$\varphi = \frac{\mathrm{p_v}}{\mathrm{p_v^s}} \qquad \text{(Ec. 14)}$$

La humedad relativa es para el aire lo que la actividad de agua para medios líquidos acuosos, expresándose y midiéndose normalmente de la misma manera.

La **entalpía total del aire húmedo** (h) es la magnitud que cuantifica el contenido energético total del aire por unidad de masa, y se descompone en la energía interna (u) y el trabajo de flujo (PV). La entalpía total se calcula sumando la contribución de cada componente de la mezcla:

La entalpia requiere de un sistema de referencia para su cálculo, el más utilizado es el sistema de referencia recomendado por la IuPAC en condiciones normales (P = 1 atm, T = 0ºC y agua en estado líquido), este sistema de referencia marca el umbral de entalpia que se considera cero.

La entalpía del vapor de agua h_v se calcula, teniendo en cuenta que todo el agua está en forma de vapor, quedando la suma de trabajo de flujo más energía interna de la siguiente forma:

$$h_v = \Delta H_v + C_p^v(T\text{-}0) \qquad \text{(Ec. 15)}$$

donde ΔH_v es el calor latente de vaporización del agua (kJ/kg_w); C_p^v es el calor específico (kJ/ kg °C) y T la temperatura a la que se encuentra el aire.

En el cálculo de la entalpia del aire seco habrá que tener en cuenta que no realiza aporte al trabajo de flujo con lo que solo aportara cambios sobre la energía interna, quedando la ecuación como sigue:

$$h_a = C_p^a(T\text{-}0) \qquad \text{(Ec. 16)}$$

Por lo tanto, la variación entalpía del aire respecto al sistema de referencia se puede expresar en base al caudal de aire seco, en pro de facilitar los balances en el diagrama psicométrico con la siguiente expresión:

$$h = u + PV = (C_p^v X + C_p^a)\cdot(T\text{-}0) + X\cdot\Delta H_v \qquad \text{(Ec. 17)}$$

Para el intervalo de temperaturas entre 0 y 100°C en ocasiones se admitirse como valores constantes para los calores específicos: $C_p^a =$ 0,24 kcal/ (kg °C) y C_p^v =0,46 kcal/ (kg °C); y 595 kcal/kg agua para el calor latente de vaporización del agua a 0°C (ver figura 2.8).

Una vez expuestas las herramientas necesarias para calcular los cambios composicionales y energéticos del aire es necesario obtener herramientas que permitan obtener el caudal másico del aire a partir de variables de control manejables en corrientes gaseosas. De esta manera, es posible calcular el caudal volumétrico del aire a partir de la velocidad del aire y sección de las conducciones de circulación, pero la transformación de caudal volumétrico a másico requerirá de las propiedades termodinámicas del aire.

Teniendo en cuenta que se considera al aire húmedo como una mezcla de gases con comportamiento ideal, el **volumen parcial** (m^3/kg_{ah}) será:

$$v_{ah} = \frac{V}{m_a} = \frac{n\,(R\,T/P)}{m_a} = \frac{(n_a+n_v)\,(R\,T/P)}{m_a} = \frac{\frac{m_a}{M_a}+\frac{m_v}{M_v}}{m_a}\,(RT/P) \qquad \text{(Ec. 18)}$$

$$v_{ah} = \left(\frac{1}{M_a} + \frac{X}{M_v}\right)\frac{RT}{P} \qquad \text{(Ec. 19)}$$

La **densidad del aire húmedo** puede calcularse, empleándose la ley de los gases ideales, resumiéndose en la ecuación:

$$\rho_{ah} = \frac{M_a\,P}{RT} - \frac{(M_a\text{-}M_v)\,\varphi \quad p_v^s}{RT} = \frac{28.9\,P}{RT} - \frac{10.9\,\varphi \quad p_v^s}{RT} \qquad \text{(Ec. 20)}$$

De esta forma se obtendrá el caudal másico a partir del volumétrico. Sin embargo, todos los cálculos de humedad en el aire se han expresado en forma de razón másica de agua o humedad absoluta, es decir utilizando como base la masa de aire seco. Por esta razón, para poder realizar balances de materia con corrientes de aire, el caudal de aire también tendrá que transformarse a aire seco (M') mediante la ecuación:

$$M' = \frac{1+X}{m_a} \qquad \text{(Ec. 21)}$$

2.8 **Isotermas de sorción de agua en alimentos**

La actividad de agua (a_w) es un factor único relacionado con la estabilidad de los alimentos que permite controlar su deterioro y predecir su vida útil. Por lo tanto, un gran número de procesos de conservación utilizan la reducción de a_w como estrategia para disminuir el crecimiento microbiano y las reacciones químicas. La a_w, a una temperatura dada, se define como la relación que existe entre la presión de vapor en equilibrio del agua del alimento y la presión de vapor en equilibrio del agua pura a la misma temperatura (Barbosa-Cánovas et al., 2008).

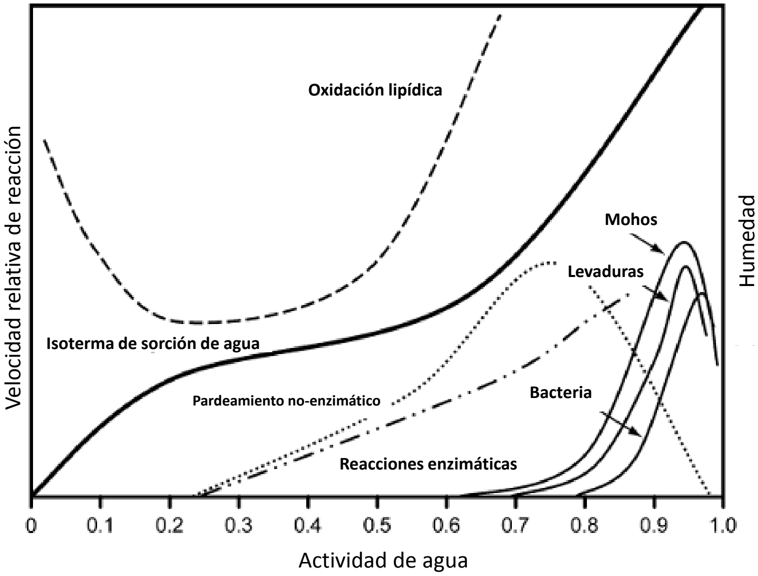

Figura 2.10: Mapa de estabilidad de los alimentos en función de la actividad de agua (adaptado de Labuza y Altunakar, 2007)

La relación entre el contenido en agua de los alimentos y la presión de vapor de la atmósfera en equilibrio con el alimento puede definirse como la humedad relativa en equilibrio ($\varphi_{eq} = p/p_0 = a_w$). A temperatura constante, esta relación de equilibrio se representa en la isoterma de sorción de agua (Figura 2.10).

Las isotermas de sorción de agua representan, de una manera gráfica, la relación entre la a_w de un material y su contenido en agua a una temperatura dada, o dicho de otro modo, relacionan la cantidad de agua presente con la disponibilidad de ésta. Estas isotermas son una de las herramientas más utilizadas en la industria alimentaria debido a que proporciona información muy útil del estado del agua en el alimento, además de poder establecer relaciones entre la humedad de un alimento, otros componentes de éste, o su estructura (porosidad) (Rahman, 2009). Además, permite predecir el comportamiento del producto si se conocen las condiciones a las que va a ser almacenado (Pezzutti and Crapiste, 1997). Por otro lado, las isotermas de sorción de agua pueden ser usadas como herramienta para investigar características estructurales de un alimento, como el área de superficie específica, el volumen de los poros, la distribución y tamaño de estos y la cristalinidad (Ariahu et al., 2006).

La adsorción es un fenómeno superficial que ocurre en la interfase en el cual las moléculas de adsorbato (agua) se fijan sobre la superficie del adsorbente (alimento) en virtud de diversas fuerzas atractivas que entran en juego y se deben, fundamentalmente, a la asimetría de fuerzas que existe en toda interfase. En el fenómeno de adsorción hay dos magnitudes experimentales de interés:

- la cantidad de adsorbato por unidad másica de adsorbente. Depende de la temperatura, de la presión o concentración de adsorbato y de la naturaleza química del sistema. En el caso de isotermas de adsorción de agua se trata de la humedad de equilibrio en base seca.

- calor de sorción, que puede determinarse a partir de la isoterma de sorción, denominándose en este caso calor isostérico de adsorción, y se define como la diferencia de entalpía asociada al proceso de sorción a diferentes humedades.

La medida experimental de estas magnitudes se puede realizar calorimétricamente, no obstante, dado que los calores son muy pequeños (del orden del calor latente de condensación o de evaporación), se necesitan calorímetros muy sensibles. El calor isostérico puede determinarse a partir de las isotermas de sorción pero en muchas ocasiones los parámetros de las isotermas vienen determinados con mucho error y no es posible obtener determinaciones del calor isostérico fiables.

El calor isostérico de sorción puede utilizarse para evaluar los requerimientos energéticos en procesos de deshidratación. El contenido en agua de un alimento en el que el calor isostérico de sorción es cercano a calor latente de vaporización puede dar una idea de la cantidad de agua fuertemente ligada (humedad de la capa monomolecular) (Kiranoudis et al., 1993). A partir de esta a_w, el calor isostérico aumenta cuando el contenido en agua disminuye por debajo de este límite crítico.

El análisis del sistema alimento-vapor de agua se puede realizar cuando los datos de sorción de agua son conocidos a diferentes temperaturas. La ecuación de Clausius-Clapeyron se utilizó originalmente para un equilibrio vapor-líquido (Barbosa-Cánovas et al., 2008). Esta ecuación que aplica los datos sobre temperatura-presión de vapor de un alimento puede utilizarse para evaluar los cambios de entalpía asociados con proceso de sorción a diferentes humedades (calor isostérico de sorción):

$$\ln a_w = - \frac{Qc}{R} \cdot \frac{1}{T} \qquad \text{(Ec. 22)}$$

donde Qc es el calor isostérico de sorción, R es la constante de los gases y T es la temperatura absoluta.

Las isotermas de sorción en alimentos son normalmente no lineares y tienen forma sigmoidal, pero difieren en función de la composición química y el estado físico-químico de los componentes del alimento. Brunauer et al. (1940) clasificó las isotermas de sorción en 5 tipos en función de la teoría de adsorción de gases apolares de van der Waals en diferentes sustratos sólidos no porosos. Sin embargo, cabe destacar que en alimentos, la fase gas es vapor de agua, por lo tanto

es un gas polar, y la mayoría de los adsorbentes polares reaccionan con las proteínas y los carbohidratos. Los tipos I, II y III son los más habituales en alimentos (Figura 2.11).

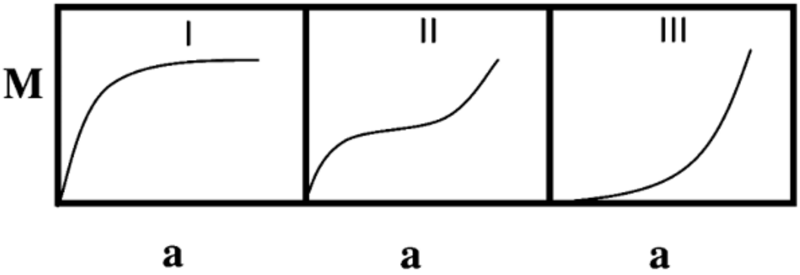

Figura 2.11: Tres tipos de isotermas representando el contenido en adsorbente (M) versus la actividad (a). (adaptado de Brunauer et al, 1940)

El tipo I es típico de los agentes antiaglomerantes ya que pueden contener grandes cantidades de agua a bajas a_w. Este tipo de alimentos adsorbe agua en sitios específicos de manera que el excedente de energía para retener agua (calor isostérico de sorción) es muy elevado. Una vez que todos los sitios de adsorción están ocupados (incluyendo capilares), hay un menor aumento en el contenido de agua al aumentar la humedad ya que los poros están todos completos y no ocurren fenómenos de hinchamiento ni hay solutos que puedan disolverse. El tipo II es la isoterma típica de alimentos procesados donde la $a_w < 0,95$. Se observan dos cambios de pendiente, uno alrededor de a_w de 0,2 – 0,4 y otro a 0,6 – 0,7, debido principalmente a los cambios de magnitud de los efectos físicos y químicos por separado, por ejemplo, la estructuración en multicapas y ocupación de los poros pequeños en la región de a_w baja, seguido por los fenómenos de hinchamiento, la ocupación de poros grandes, y la disolución de solutos en las regiones de a_w alta. Finalmente, los alimentos compuestos principalmente por elementos cristalinos como azúcares y sal, están representados en la isoterma tipo III. El aumento del contenido en agua con la humedad es muy bajo, dado que, a humedades altas los cristales empiezan a disolverse en el agua absorbida sobre la superficie del mismo cristal. Debido a que este fenómeno ocurre en la superficie, el tamaño de partícula del soluto, por ejemplo azúcar, afecta a la cantidad de agua que puede retenerse. A tamaños de partícula menores, la superficie de contacto aumentará y la cantidad de agua retenida a a_w bajas será mayor (Labuza y Altunakar, 2007).

Debido a todo lo comentado anteriormente, resulta importante la posibilidad de modelizar estas isotermas de sorción, de tal manera que permita tanto el estudio de las relaciones agua-sustrato, como la predicción del comportamiento de un determinado alimento en ciertas condiciones de almacenamiento/proceso. En este sentido, la obtención de ecuaciones empíricas o no empíricas que relacionen la actividad de agua con la humedad del producto, puede resultar útil para describir el comportamiento del mismo. Más de 200 ecuaciones de isotermas han sido propuestas para materiales biológicos (Chenoll, 2008), algunas de las cuales permiten predecir parámetros con sentido físico relacionados con las propiedades de adsorción de los alimentos y que ayudan a entender las interacciones agua-producto.

El modelo general de Brunauer-Emmet-Teller (BET) constituye el modelo básico de fisisorción, y junto con el de GAB (Guggenheim-Anderson-de Boer) es uno de los más empleados dentro de la tecnología de alimentos (Labuza y Altunakar, 2007). Del modelo de BET se obtienen dos parámetros: $\mathrm{X_w^0}$ que es la humedad de monocapa para el alimento y C, que es un parámetro relacionado con el calor de sorción. La teoría de BET supone que sobre el complejo de sorción monomolecular (adsorbente), se pueden sorber otras moléculas de gas formando complejos multimoléculas o multicapa (Figura 2.12). Este modelo se considera como el único cuyos parámetros tienen por sí mismos un sentido físico-químico, aunque tiene ciertas limitaciones.

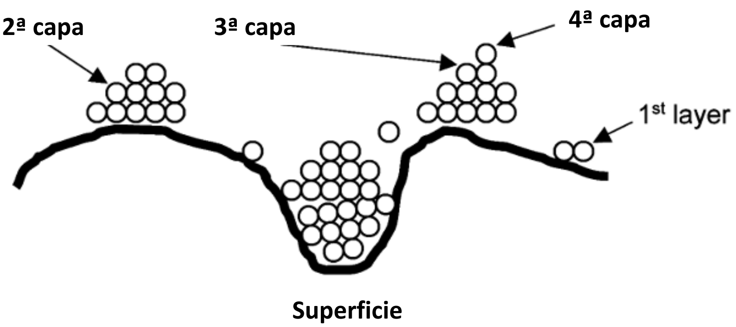

Figura 2.12. Esquema ilustrativo de las capas moleculares de la isoterma de BET (adaptado de Labuza y Altunaker, 2007)

Además del modelo de BET, el otro modelo más frecuentemente usado es el denominado modelo de GAB, que se representa mediante la ecuación:

$$X_w^0 = \frac{X_w^0 \ K \ C \ a_w}{\left[\,1\text{- } Ka_w\right] \left[\,1\text{-}Ka_w + c \ Ka_w\right]} \qquad \text{(Ec. 23)}$$

donde X_w^0 es la humedad de la capa monomolecular en g agua/ g sólidos, el valor de C varía entre 0 y 20, y el valor de la constante K varía de 0,7 a 1. Esta ecuación se puede resolver bien mediante programas informáticos utilizando regresión no lineal en los que al menos se necesitan 5 puntos, o bien, convirtiéndola a un polinomio para aplicar regresión por pasos. La solución de los parámetros de GAB se presenta en las siguientes ecuaciones:

$$K = \frac{\sqrt{\beta^2 - 4\alpha\varepsilon - \beta}}{2\varepsilon} \qquad C = \frac{\beta}{\varepsilon\,K} + 2 \qquad X_w^0 = \frac{1}{\varepsilon\,K\,C} \tag{Ec. 24}$$

$$\alpha = \frac{K}{X_w^0}\left[\frac{1}{C} - 1\right] \qquad \beta = \frac{1}{X_w^0}\left[1 - \frac{2}{C}\right] \qquad \varepsilon = \frac{1}{X_w^0\,K\,C} \tag{Ec. 25}$$

El modelo de GAB es similar al de BET en cuanto a la teoría de adsorción física localizada en multicapas sin interacciones laterales. Sin embargo, la incorporación del parámetro K, asume que las moléculas de la multicapa interaccionan con el adsorbente a unos niveles de energía que varían entre los de las moléculas de la monocapa y el agua líquida. Las ventajas principales del modelo de GAB son: (a) el significado físico de sus parámetros, (b) la descripción del comportamiento de sorción en alimentos abarcando un amplio rango de a_w (de 0 a 0,95), (c) el modelo matemático consta solo de 3 parámetros, y (d) permite describir efectos de la temperatura sobre las isotermas.

Finalmente, el hecho de que ningún modelo de isotermas de sorción se ajuste a todo el rango de a_w no resulta sorprendente debido a que el agua está asociada con la matriz del alimento mediante diferentes mecanismos y en diferentes regiones de a_w. Por ello, resulta conveniente, antes de modelizar una determinada isoterma de sorción de agua en un alimento, conocer las principales características del alimento y del proceso de adsorción/desorción con el objetivo de aplicar los modelos más convenientes en cada situación.

2.9 Histología de la piel de naranja

Puesto que la superficie desempeña también un papel importante en los procesos de sorción es interesante analizar sus características. La superficie externa constituye el límite físico del sólido y nunca es del todo regular a escala molecular. Consta de numerosas rugosidades, prominencias, defectos, etc., que la hacen mayor de lo que podría calcularse macroscópicamente a partir de los datos geométricos. La superficie interna corresponde a los poros que tenga el material. El sistema de poros puede ser muy extenso, llegando a ser en ocasiones de varios órdenes de magnitud superior a la superficie externa. El tamaño de los poros y en particular su diámetro es muy variable. El tamaño de los poros es de considerable importancia, ya que para que su superficie pueda adsorber, es necesario que las moléculas de adsorbato puedan pasar a su través.

La piel de la naranja se compone principalmente de dos partes: albedo y flavedo (Figura 2.13). El flavedo es la parte más externa de la piel, pigmentada debida a la presencia de carotenoides, que restringe el intercambio gaseoso entre el interior y el exterior de la fruta. Las células del flavedo están densamente pobladas, contienen células guarda (estomas) y están además recubiertas con una capa de cera natural llamada cutícula (Ladanyia and Ladaniya, 2010). A lo largo de las células del flavedo se intercalan glándulas de aceite a partir de las cuales se extraen los aceites esenciales, de entre los cuales el más conocido es el limoneno. La parte inferior de las glándulas de aceite se extiende hasta el albedo.

El albedo es la parte interna, esponjosa y blanca de la piel, que se compone principalmente de células parenquimáticas tubulares, de pared celular fina y con grandes vacuolas, presentando rupturas celulares que se producen durante la maduración de la fruta, lo que le confiere una estructura muy porosa (Spiegel-Roy and Goldschmidt, 1996). La fase gas puede moverse a través de esta capa relativamente libre. El albedo es la fuente principal de sustancias pécticas y hemicelulosas (Ting y Rouseff, 1986) y es rica en compuestos fenólicos con importantes propiedades antioxidantes (flavonoides). No obstante, contiene también sustancias amargas como la limonina, por lo que en el proceso de fabricación de zumos se intenta minimizar el contenido de albedo. Finalmente, su peculiar estructura celular le confiere un comportamiento tipo-esponja, con una alta capacidad de impregnación e hinchamiento.

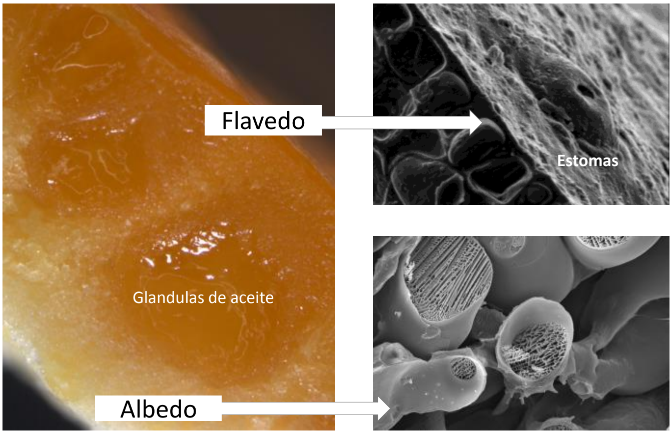

Figura 2.13. Microestructura de la piel de naranja: imagen capturada con estereomicroscopio a 20x aumentos (izquierda) y capturada con Cryo-SEM a 1000x aumentos (derecha). Imagen de estoma adaptado de Fito Suñer, 2002.

2.10 Importancia de los tratamientos previos al secado.

El escaldado es un tratamiento térmico suave que se aplica a los productos vegetales antes de procesarlos con el fin de mejorar su calidad y seguridad. El principal objetivo del escaldado es disminuir la carga microbiana superficial (Jaiswal et al., 2012) pero además supone un tratamiento esencial previo al secado ya que inactiva ciertas enzimas como la lipoxigenasa, polifenololoxidasa, poligalacturonasa y clorofilasa que se asocian con pérdidas de calidad y propiedades nutritivas. El escaldado se realiza principalmente por inmersión en agua caliente o por contacto directo con vapor y se utilizan temperaturas de entre 60 y 100° C, durante períodos de tiempo no superiores a 15 min (Morales-Blancas et al., 2002). El escaldado por inmersión en agua caliente sigue siendo el método industrial más preferido debido a los bajos costos operativos y la uniformidad de tratamiento en todo el producto.

El escaldado de subproductos cítricos es una técnica ampliamente utilizada como tratamiento previo al secado a nivel industrial. Wuttipalakorn et al. (2009) estudiaron los efectos de pretratamientos como escaldado e inmersión en etanol, y de la temperatura de secado (60 – 100 ° C) en las composiciones y la amargura de fibra obtenida a partir de residuos de lima. Estos investigadores demostraron que los pretratamientos y la temperatura de secado reducían significativamente el contenido en limonina, principal responsable de la amargura en subproductos cítricos. La limonina es un triterpeno, responsable también de posibles notas amargas en zumos cítricos. La limonina tiene dos anillos de lactona, designados como anillos de lactona A y D. Maier y Beverly (1968) explicaron el desarrollo del sabor amargo. Según estos autores, la limonina se forma a partir de un precursor no amargo, la monolactona de limonina que se diferencia de la limonina por la ausencia del anillo de lactona D. El precursor de la monolactona, posteriormente reconocido como lactona del Anillo A del ácido limónico, es estable en el tejido intacto de la fruta. Cuando se exprime la fruta y parte del tejido se desintegra como pulpa, tiene lugar una rápida lactonización. Se ha sugerido la existencia de un sistema enzimático que cataliza esta reacción.

Por otro lado, el escaldo y la inmersión en etanol también pueden contribuir a mejorar la capacidad de retención de agua y la capacidad de hinchamiento de la fibra obtenida a partir de subproductos. Peerajit et al. (2012) estudiaron los efectos del escaldado, inmersión en etanol y tamaño de partícula sobre determinadas propiedades funcionales, relacionadas con la salud, de la fibra procedente de residuos de lima. Sus resultados mostraron que las fibras escaldadas y tratadas con etanol presentaron las mejores propiedades nutricionales.

Los subproductos de naranja son además ricos en compuestos bioactivos como polifenoles, con una elevada capacidad antioxidante. Estos compuestos pertenecen al grupo de los flavonoides y son típicos de los cítricos en su forma glicosilada o como rutinósidos (Tripoli et al., 2007). Los flavonoides incluyen a las flavanonas (hesperidina, narirutin, eriocitrin), flavonas y flavonoles. Algunas flavanonas son muy amargas mientras que otras no, según el tipo de azúcar o cadena de glucósido al que están vinculadas. Por ejemplo, los neohesperidósidos son amargos, mientras que los rutinósidos son insípidos. El glicósido de flavanona más común en naranja dulce es la hesperidina (Peterson et al., 2006), que es insípido, mientras que la neohesperidina (neohesperidósido de flavanona) es muy amargo. Además de la hesperidina, las frutas cítricas se caracterizan por la presencia de otras moléculas amargas como la naringina y la neoeriocitrine, ambos neohesperidosides de flavanonas. Los isómeros no amargos correspondientes son narirutina y eriocitrina, respectivamente, que son del rutinósidos de flavanona, también presentes en pieles de cítricos. Por lo tanto, la eliminación de compuestos amargos como la limonina y flavonoides neohesperidósidos de la piel de naranja es crucial para poder transformarlos en ingredientes y productos de valor añadido.

En general los flavonoides presentan efectos beneficiosos sobre la salud humana tales como antiinflamatorios, antimicrobianos, antivirales, antialérgicos, antiulcerosos y efecto hipocolesterolémico (Benavente-Garcia y Castillo, 2008; Bocco et al., 1998; Imeh y Khokhar, 2002; Morand et al., 2011; Rizza et al., 2011). Debido a la importancia de los flavonoides como contribuidores a los efectos beneficiosos sobre la salud, la recuperación e identificación de estos compuestos que se pierden durante procesos industriales tales como el escaldado ha recibido mucha atención en los últimos años. La mayoría de los compuestos polifenólicos presentes en subproductos de naranja son solubles en agua; por lo tanto, una gran parte de ellos serán extraídos durante el escaldado. Algunos autores han demostrado la posibilidad de recuperar los polifenoles del extracto acuoso de procesos de extracción de pectina de orujo de manzana (Schieber et al., 2002) y cáscaras de mango (Berardini et al., 2005) usando resinas adsorbentes. Aunque un alto porcentaje de los compuestos fenólicos pueden degradarse durante el escaldado, su recuperación por adsorción y posterior elución con disolvente parece factible y podría ser una ruta de valorización para aguas residuales de escaldado.

Un control adecuado de la etapa de escaldado previa al secado puede utilizarse como una herramienta para mejorar la extracción de compuestos no deseados de los subproductos cítricos, tales como azúcares reductores y polifenoles amargos, que son al mismo tiempo, compuestos valiosos para su recuperación posterior. Algunos autores han utilizado la espectroscopía dieléctrica para establecer una relación entre las propiedades dieléctricas de un alimento y su contenido en solidos solubles, como técnica para describir y controlar procesos de transferencia de solutos como puede ser el grado de madurez en melones (Nelson et al., 2006) y sandías (Nelson et al., 2007) y manzanas (Castro-Giráldez et al., 2010b), operaciones de salado en productos cárnicos (Castro-Giráldez et al., 2010a). La mayoría de las moléculas de azúcar y los flavonoides son moléculas polares que pueden ser altamente afectadas por frecuencias de microondas. La limonina, es un compuesto de polaridad media y parcialmente soluble en agua que también puede verse afectado. Por lo tanto, la correlación entre las propiedades dieléctricas de un alimento y su contenido en sólidos solubles puede utilizarse como una técnica no destructiva para el control de procesos de extracción tales como el escaldado.

2.11 Definición y composición química de la fibra dietética

La fibra dietética está compuesta por un complejo y heterogéneo grupo de componentes que puede ser definido tanto por sus características fisiológicas como químicas. Los métodos analíticos utilizados para la cuantificación de DF en su totalidad, o por componentes específicos individuales, han sido modificado continuamente (DeVries, 2010, McCleary, 2010). Debido a las avanzadas investigaciones sobre propiedades fisiológicas y nutricionales de los componentes específicos de la DF (fructanos, almidón resistente, polidextrosa y otros), varias agencias y países propusieron definiciones más amplias, correlacionados con los efectos fisiológicos (AACC, 2001, Commision of European Communities, 2008). Con el objetivo de crear un concepto armonizado con el consentimiento de todos los países miembros, el Codex Alimentarius generó una amplia discusión sobre la definición y métodos analíticos de la DF (Codex Alimentarius, 2009, McCleary, 2010, McCleary et al., 2010). En la edición 30 (Codex Alimentarius, 2008) y 31 (Alimentarius, 2009) del Comité del Codex sobre Nutrición y Alimentos para Dietas Especiales – CCNFSDU, acordaron la definición de DF y métodos analíticos para su cuantificación total y la de sus componentes específicos individuales. La Comisión del Codex Alimentarius se conformó con la recomendación de CCNFSDU y adoptó esta definición de DF para el etiquetado sobre propiedades nutritivas. La definición adoptada se presenta a continuación (de Menezes et al., 2013):

Fibra dietética son polímeros[1] de carbohidratos con 10 o más unidades monoméricas[2], que no son hidrolizados por las enzimas endógenas del intestino de los seres humanos pero que pueden ser fermentados por la microflora colónica y/o excretadas parcialmente por las heces; y que pertenecen a las siguientes categorías:

- Polímeros de carbohidratos comestibles que ocurren naturalmente en los alimentos durante su consumo

- Polímeros de carbohidratos que se hayan obtenido a partir de materias primas alimentarias mediante métodos físicos, enzimáticos o químicos y que han demostrado tener un efecto fisiológico beneficioso para la salud mediante evidencias científicas aceptadas por las autoridades competentes
- Polímeros de hidratos de carbono sintéticos que han demostrado tener un efecto fisiológico beneficioso para la salud mediante pruebas científicas aceptadas por las autoridades competentes.

[1] Cuando la DF sea de origen vegetal, la definición de DF incluirá fracciones de lignina y/u otros compuestos asociados con los polisacáridos de las células de la pared vegetal. Estos compuestos serán también medidos por determinados métodos analíticos para cuantificar la DF. No obstante, estos compuestos no estarán incluidos en la definición de DF si han sido extraídos y reintroducidos en un alimento.

[2] La decisión de introducir en la definición de DF los carbohidratos compuestos por 3 a 9 unidades monoméricas se dejará en manos de las autoridades nacionales.

Por lo tanto, aunque exista una definición global, actualmente, el concepto de fibra dietética se encuentra todavía en fase de revisión (de Menezes et al., 2013) con el objetivo de llegar a un acuerdo para que su implementación pueda llevarse a cabo en diferentes países. Los dos aspectos principales todavía en debate son (i) la inclusión de polímeros de carbohidratos de entre 3 y 9 grados de polimerización, decisión que se toma individualmente por las autoridades de cada país, y (ii) la necesidad de definir qué efectos fisiológicos de la DF beneficiosos para la salud deben considerar las autoridades nacionales.

Tradicionalmente, la fibra puede clasificarse de acuerdo a su solubilidad en agua en dos tipos:

- fibra insoluble (FI) (celulosa, gran parte de las hemicelulosas y lignina). Las fuentes de fibra insoluble son cereales, granos, legumbres y vegetales.
- soluble (FS) (pectinas, gomas, mucílagos, ciertas hemicelulosas, polisacáridos de algas y celulosa modificada). Las fuentes de fibra soluble son frutas, legumbres y vegetales.

Sin embargo, esta clasificación queda desfasada ya que estudios científicos demuestran que los beneficios de la fibra sobre la salud no están relacionados con la solubilidad de la fibra sino con su viscosidad y fermentabilidad (Institute of Medicine, 2001). Por ejemplo fibras que generan texturas espesas y pegajosas, permanecen más tiempo en el estómago proporcionando una sensación de saciedad.

Aunque la definición de DF se ha debatido durante décadas, los constituyentes que se consideran actualmente parte de la fibra dietética no difieren de los que se consideraban hace décadas. Estos consisten primeramente de polímeros de carbohidratos (no almidonados) que son componentes de la pared celular de las plantas, así como otros polisacáridos procedentes de plantas o algas, como los mucilagos o las gomas, y oligosacáridos como la inulina. Análogos de carbohidratos no digeribles que atraviesan el intestino delgado sin modificaciones pero son fermentados en el intestino grueso también se incluyen, por ejemplo, almidones resistentes, fructoligosacáridos, galactoligosacáridos, celulosas modificadas y polímeros de carbohidratos sintéticos como la polidextrosa. Sustancias asociadas, principalmente lignina, y componentes minoritarios incluyendo ceras, cutina, saponina, polifenoles, fitatos y fitoesteroles también se incluyen ya que se extraen con los polisacáridos y oligosacáridos en diferentes métodos analíticos de fibra dietética. No obstante, estas sustancias asociadas, cuando se aíslan, no pueden describirse como fibra dietética.

A continuación se describen brevemente los principales componentes de las fibras procedentes de frutas:

CELULOSA: La celulosa es un polisacárido lineal y no ramificado que consiste solamente de unidades de glucosa, hasta 10.000 por molécula. Estas moléculas son lineales y se encuentran estrechamente empaquetadas en forma de fibras largas en una estructura que es muy insoluble y resistente a la digestión por enzimas humanas. La celulosa es un componente principal de la pared celular de muchas plantas y está, por lo tanto, muy presente en frutas, vegetales y cereales. Aproximadamente, la celulosa supone 25 % de la fibra dietética en granos y frutas y un 33 % en vegetales y frutos secos.

HEMICELULOSA: Las hemicelulosas son polisacáridos que contienen azúcares diferentes de la glucosa, y que están asociados con la celulosa en la pared celular de las plantas. Incluyen tanto moléculas lineales como ramificadas y es más pequeña que la celulosa, conteniendo entre 50 – 200 unidades de pentosa (xilosa y arabinosa) y de hexosa (glucosa, galactosa, mannosa, rhamnosa, ácido glucurónico y galacturónico). El nombre hemicelulosa describe, por tanto, un grupo heterogéneo de estructuras químicas que están presentes en alimentos de origen vegetal, de forma soluble o insoluble. Aproximadamente, un 33 % de la FD de vegetales, frutas, legumbres y frutos secos está formada por hemicelulosas.

PECTINAS: Las pectinas son polisacáridos solubles en agua caliente que gelifican cuando se enfrían. Se componen principalmente de cadenas de ácido galacturónico intercaladas con unidades de rhamnosa, y están ramificadas con cadenas de pentosa y hexosa. Están presentes en las pared celular y tejidos intracelulares de frutas y vegetales y se utilizan como agentes gelificantes y espesantes en varios aplicaciones alimentarias. Aunque las frutas contienen la mayoría de las pectinas, están también representan por el 15-20 % de la DF en vegetales, legumbres y frutos secos.

OLIGOSACÁRIDOS NO DIGERIBLES: Se incluyen como parte de la FD ya que, debido a su no digestibilidad, exhiben efectos fisiológicos similares a los polisacáridos de mayor tamaño. Su grado de polimerización va de 3 – 10 unidades. Ocurren de manera natural en frutas, vegetales y cereales, pero también pueden sintetizarse química o enzimáticamente a partir de monosacáridos y disacáridos, o mediante hidrólisis enzimática de polisacáridos. Generalmente son altamente fermentables y algunos poseen propiedades prebióticas.

Los más conocidos son los fructanos, que incluyen a los fructoligosacaridos o oligofructosas. Las cebollas, la achicoria y algunas alcachofas son las principales fuentes naturales de inulina y fructoligosacáridos.

COMPUESTOS SINTÉTICOS: Las celulosas modificadas como la metilcelulosa, hidroxipropilcelulosa, carboximetilcelulosa, son gomas semisintéticas porque se sintetizan a partir de un producto natural como lo es la celulosa. A diferencia de la celulosa, estos compuestos son solubles, pero son poco fermentados por la microflora colonica. La polidextrosa y las dextrinas resistentes son algunos ejemplos.

LIGNINA: La lignina no es un polisacárido pero está químicamente unido a la hemicelulosa en la pared celular de las plantas, y por lo tanto, está íntimamente asociada a los polisacáridos presentes. Además, también influye en la fisiología gastronintestinal.

OTROS COMPONENTES MINORITARIOS: Otros compuestos asociados que pueden tener efectos fisiológicos son los polifenoles, las cutinas y los fitoesteroles.

En concreto, la fibra de naranja está formada principalmente por celulosas, hemicelulosa y lingnina, en su fracción insoluble, y por pectinas, en su fracción soluble (Lundberg et al., 2014).

2.12 **Efectos beneficios de la fibra dietética en la salud**

La Agencia Europea de Seguridad Alimentaria (EFSA) considera adecuada una ingesta de 25 gramos de fibra dietética para la función normal del intestino grueso en los adultos (EFSA, 2010). Sin embargo, la ingesta de DF es muy baja, especialmente en las mujeres. Según la Encuesta Nacional de Ingesta Dietética Española (ENIDE, 2011) solo entre el 1,5 y el 7% de la población alcanza los objetivos (EFSA, 2010, SENC, 2001).

Existen multitud de evidencias científicas que demuestran los beneficios para la salud asociados con ingestas de fibra dietética más altas (EFSA, 2010):

- salud gastrointestinal, La presencia de fibra provoca un aumento en el peso de la materia fecal, debido al agua que contiene la fibra y a la fermentación parcial de la fibra, que aumenta la cantidad de bacterias en las heces (Marlett et al., 2002). Una masa más grande y más blanda producida por el consumo de alimentos que contienen fibra hacen que el intestino grueso se contraiga y mueva el contenido hacia la excreción más rápidamente. Esta reducción en el tiempo de tránsito a través del tracto intestinal promueve la regularidad del intestino y tiene una función en la prevención de la constipación y de enfermedades del intestino grueso (Tan and Seow-Choen, 2007).

- cáncer, La relación de la ingesta de fibra con el cáncer de colon es sujeto de investigación permanente. Hay abundante evidencia que respalda la teoría de que la fibra protege al cuerpo contra el cáncer colorrectal (Bingham et al., 2003, Howe et al., 1992). El mecanismo propuesto es que el efecto de la fibra sobre el aumento del volumen y la reducción del tiempo de tránsito ayuda a arrastrar las sustancias que provocan cáncer en el intestino grueso. Sin embargo, hallazgos contradictorios obtenidos a partir de grandes estudios de observación han generado controversia y debate acerca de si la fibra verdaderamente tiene una función en la reducción del riesgo de cáncer colorrectal (Fuchs et al., 1999, Park et al., 2005, Schatzkin et al., 2000). No obstante, los expertos están de acuerdo en que los posibles beneficios de la fibra con relación a la reducción de este tipo de cáncer son motivo suficiente para continuar promoviendo un mayor consumo,

- enfermedad cardíaca, La evidencia de la función de la fibra en la reducción del riesgo de enfermedad cardiaca coronaria (ECC) es lo suficientemente contundente en el sentido de que la ingesta adecuada recomendada de fibra se basa en el nivel de ingesta que, según se ha observado, protege contra la ECC (Pietinen et al., 1996, Rimm et al., 1996, Wolk et al., 1999). Se cree que este beneficio se da principalmente como resultado de los efectos de la fibra sobre la interferencia con el colesterol y la absorción del ácido biliar, reduciendo así los niveles de colesterol total en sangre y de colesterol de lipoproteínas de baja densidad (LDL) en sangre. Otro mecanismo propuesto es la absorción retardada de la grasa y los carbohidratos, lo que provoca mayor sensibilidad a la insulina y menores niveles de triglicéridos en circulación (Trumbo et al., 2002),

- diabetes, De acuerdo con varios estudios de observación, el consumo de alimentos que contienen fibra se ha asociado con un menor riesgo de diabetes tipo 2 (Trumbo et al., 2002). Se cree que la fibra alimentaria tiene una función importante en la reducción del riesgo de diabetes y en el manejo nutricional de la enfermedad porque ayuda a normalizar la reacción a la glucosa y a reducir la concentración y los requerimientos de insulina (Salmeron et al., 1997, Schulze et al., 2004, Weickert et al., 2006)
- mantenimiento del peso corporal, Los alimentos con alto contenido de fibra son procesados más lentamente por el cuerpo, aportan más volumen en comparación con las comidas con menor contenido de fibra y tienden a producir una sensación de saciedad con menos calorías. Además, los alimentos con alto contenido de fibra

requieren más tiempo de masticación y se tarda más en comerlos, lo que limita así posiblemente la ingesta total de energía. Se cree que estas cualidades tienen que ver con el control del equilibrio de energía y el peso del cuerpo (Howarth et al., 2001). Sin embargo, la evidencia más contundente para respaldar la función de la fibra en el manejo del peso corporal proviene de estudios que encuentran una asociación entre una dieta con alto contenido de fibra y un menor índice de masa corporal (IMC) (Trumbo et al., 2002). Si bien la evidencia sugiere que una mayor ingesta de fibra tiene como resultado una mayor saciedad y menos hambre, la pregunta de si estos cambios facilitan una menor ingesta de energía, lo cual lleva a la pérdida de peso, sigue sin responderse. Es necesario realizar nuevos estudios para determinar las cantidades y los tipos de fibra que se requieren para producir los mayores efectos sobre el manejo del peso corporal.

2.13 **Propiedades y aplicaciones alimentarias de la fibra cítrica**

Una mayor comprensión de la función de la fibra en la salud ha traído innovaciones en el desarrollo de alimentos e ingredientes con fibra añadida. Esta tendencia ha llevado al desarrollo y obtención de ingredientes que puedan aumentar el contenido de fibra en diferentes alimentos, algunos de los cuales supuestamente no contienen fibra

(McKee and Latner, 2000). Tradicionalmente el maíz, el trigo y la avena han aportado la fibra para ser usada como ingrediente en otros alimentos. Sin embargo, hay muchas otras fuentes de fibra de frutas, vegetales, legumbres y semillas que también pueden ser extraídas y agregadas a otros alimentos como sustitutos de azúcar

Estas fuentes de fibra concentrada están siendo diseñadas para introducir o aumentar la fibra en varios alimentos, incluidos los productos de grano, los productos horneados, los bocadillos, los cereales, las hamburguesas vegetarianas, los acompañamientos, la pasta y las bebidas.

En el interior del organismo, la fibra actúa como una esponja, reteniendo agua, nutrientes, ácidos biliares y agentes carcinogénicos. Es un hecho comprobado que las distintas fibras tienen efectos diferentes a su paso por el intestino delgado y grueso, dependiendo de sus propiedades físico-químicas y funcionales. Además, debido a la capacidad de retener agua de las fibras cítricas, éstas poseen funcionalidad tecnológica ya que resultan efectivas para mimetizar grasa sin aportar efectos negativos en sabor, color, volumen o textura, como suele ocurrir normalmente en productos a los que se ha reducido el contenido en grasa con otros ingredientes. Cuando las fibras son utilizadas en la elaboración de alimentos, sus propiedades fisicoquímicas influyen también en las características físicas y sensoriales de éstos, especialmente cuando se usan como agentes gelificantes, espesantes y/o estabilizantes. Las propiedades funcionales de las fibras se determinan por lo general in vitro y sirven para dar una idea de su comportamiento in vivo, ya que en este medio están sometidas a un entorno fisiológico muy complejo y a una serie de mecanismos que pueden modificarla (Dervisoglu and Yazici, 2006).

Las propiedades funcionales de la fibra son las responsables de los efectos fisiológicos que desarrolla y están influenciadas por la matriz estructural de la fibra, la relación fibra dietética insoluble/fibra dietética soluble (FDI/FDS), el tamaño de la partícula, la fuente, así como por el tipo de proceso llevado a cabo para su obtención.

La importancia de la fibra alimentaria en la salud humana es por tanto, un hecho incuestionable y el estudio de sus propiedades físico-químicas, que son un factor determinante de sus efectos fisiológicos en el organismo, constituye un reto para la industria alimentaria. El tipo y cantidad de fibra en el alimento inciden en la absorción de nutrientes en el organismo, en el peso de las heces y en otros parámetros relacionados con la digestibilidad de los alimentos. La pared celular, que es la fuente principal de los componentes de fibra alimentaria, presentan propiedades hidrofílicas e hidrofóbicas debido a sus regiones amorgas y cristalinas. También presenta la capacidad de formar soluciones viscosas con el agua, que varían según la concentración, temperatura, pH, tamaño de partícula, etc. Igualmente puede almacenar agua e inmovilizarla dentro de su matriz en cantidades variables, dependiendo del tipo de polisacáridos, influenciando la actividad metabólica del polisacárido a través del tracto intestinal.

En términos genéricos, las principales propiedades físico-químicas de la pared son la hidratación, el intercambio iónico y la adsorción orgánica (Anderson and Eastwood, 1987). Las propiedades físico-químicas que caracterizan a las fibras alimentarias son:

1.-Propiedades de hidratación: solubilidad, capacidad de enlazar agua, capacidad de retener agua, aumento de volumen o capacidad de hinchamiento

2.- Tamaño de partícula, porosidad

3.- Adsorción de moléculas orgánicas

4.- Capacidad de intercambio catiónico

5.- Degradación bacteriana

6.- Otras propiedades: Adsorción de aceite (ORC), capacidad antioxidante, retraso del índice de glucemia.

La propiedades de hidratación y de adsorción, así como el tamaño de partícula y la porosidad son las más susceptibles de verse afectadas durante el procesado, debido a cambios en su microestructura, que pueden modificar la manera de interaccionar con otra moléculas (Heredia Moreno, 2003). Su solubilidad, capacidad para hincharse y para retener agua, así como la composición química de las fibras, determinará su capacidad para aumentar la viscosidad cuando interaccionen con el agua. Tras la solubilización, se produce el hinchamiento debido a que el agua entrante esparce las macromoléculas hasta que estas están completamente expandidas y dispersas. El tamaño y la distribución de los poros, así como la cantidad de agua absorbida y la energía con la que es retenida, determinará la capacidad de retención de agua La estructura química, el peso molecular y la concentración del polímero determinarán la viscosidad de la fibra. Por esta razón, serán las propiedades analizadas en la fibra obtenida en la presente tesis.

III

OBJETIVOS Y PLAN DE TRABAJO

OBJETIVOS Y PLAN DE TRABAJO

III.1 Objetivo general:

El objetivo general de la presente tesis consiste en demostrar la viabilidad de la tecnología de secado combinado por aire caliente y microondas para obtener fibra dietética a partir de subproductos cítricos.

III.2 Objetivo específicos:

Para alcanzar el objetivo mencionado, se plantearon tres objetivos específicos:

1. Analizar el proceso combinado de secado con aire caliente y microondas, desarrollando herramientas que permitan dimensionar adecuadamente la operación de secado adaptándola a los estándares óptimos de calidad del producto final, así como diseñar un sistema de monitorización que asegure dichos estándares. **(Artículos 4.1, 4.2 y 4.3)**
2. Mejora del proceso de obtención de fibra alimentaria respecto a su calidad y a su gasto energético. Optimización de las propiedades asociadas a su inclusión en matrices alimentarias. **(Artículos 4.4 y 4.5)**
3. Desarrollo de un proceso innovador y sostenible para la estabilización de subproductos vegetales de origen industrial

y para su posterior conversión en fibra dietética y otros compuestos bioactivos. Aplicación de la tecnología de secado por aire caliente y microondas.

(Artículos 4.6, 4.7)

Plan de trabajo:

El plan de trabajo de esta tesis se ha llevado a cabo entre dos instituciones: el Instituto de Ingeniería de Alimentos para el Desarrollo (IuIAD) de la Universidad Politécnica de Valencia y el centro tecnológico experto en innovación alimentaria AZTI, perteneciente a la Red Vasca de Ciencia, Tecnología e Innovación (RVCTI), ubicado en Derio (Bizkaia).

Imagen 1: Ubicación de los centros donde se ha llevado a cabo la tesis: AZTI (Derio) y IuIAD (Valencia)

Un total de 3 planes experimentales se llevaron a cabo entre los dos centros de trabajo.

Plan experimental 1:

- Secado de *piel de naranja* por aire caliente y por aire caliente combinado con microondas a tres potencias y a cinco tiempos diferentes, durante 120 min, utilizando el secador a escala laboratorio de la IuIAD. Medida y análisis de energía absorbida, variaciones de masa, volumen, superficie, actividad de agua, humedad, permitividad, microestructura y capacidad de retención de agua.

Imagen 2: Materia prima utilizada para el plan experimetal 1

Plan experimental 2:

- Secado de *subproductos de naranja* por aire caliente y por aire caliente combinado con microondas a una potencia y a diferentes humedades finales, utilizando el equipo de microondas piloto de AZTI. Medida y análisis de las variaciones de masa, consumo de energía, tiempo de proceso. Molienda del producto deshidratado y análisis de la composición físico-química, capacidad antioxidante, color, pH, tamaño de partícula, microestructura, capacidad de rehidratación, propiedades reológicas y funcionalidad tecnológica y nutricional de la fibra obtenida.

Imagen 3: Materia prima utilizada para el plan experimetal 2

Plan experimental 3:

- Definición de las operaciones de picado, escaldado, extracción de color, secado y molido de *subproductos cítricos de origen industrial*. Medida del consumo energético del secado por aire caliente en comparación con el secado por aire caliente combinado con microondas. Análisis del contenido en polifenoles totales, capacidad antioxidante, fenoles individuales, flavonoides, limonina y carotenoides en el producto fresco y en el agua y el etanol resultantes. Análisis de la humedad, el contenido en fibra dietética, el color, la capacidad de retención de agua y aceite y la capacidad de hinchamiento de la fibra obtenida, comparada con un fibra cítrica de alta calidad existente en el mercado.

Imagen 4: Materia prima utilizada para el plan experimental 3

IV

RESULTADOS

Los **RESULTADOS** de la tesis se presentan a continuación, como compendio de artículos enviados, aceptados o publicados en revistas científicas de alto impacto y en revistas técnicas especializadas. Los **MATERIALES Y MÉTODOS** empleados aparecen descritos detalladamente en cada artículo:

1. A thermodynamic model for hot air microwave drying of orange peel
   Journal of Food Engineering, 2015, in press.
2. Effect of microwave power coupled with hot air drying on orange peel
   Journal of Food Engineering, 2015, in press.
3. Study of the effect of microwave power coupled with hot air drying on orange peel by dielectric spectroscopy
   LWT – Food Science and Technology, 2015, in press

4. Effect of microwave power coupled with hot air drying on process efficiency and physico-chemical properties of a new dietary fiber ingredient obtained from orange peel
   Chemical Engineering Journal, submitted (2015)

5. Evaluación de las propiedades tecnológicas y sensoriales de un nuevo ingrediente a base de fibra de naranja como sustituto de grasa en purés de patata.
   Revista Alimentaria 2015, in press

6. A new efficient process for the simultaneous obtention of dietary fiber and bioactive extracts from orange by-products using hot air-microwave drying.
   Journal of Food Science and Technology – Mysore, submitted (2015)

7. New advances in the integrated management of food processing by-products in europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE – EU)
   New Biotechnology . Volume 30, Number 6. September 2013

RESULTADOS: Artículo 4.1

Journal of Food Engineering, 2015, in press

Journal of Food Engineering

A thermodynamic model for hot air microwave drying of orange peel

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ABSTRACT

The citrus juice industry produces a great amount of waste that needs innovation and development to become products. There is a continuous demand to develop innovative approaches for the valorization of citrus by-products by applying environmentally and economically sustainable processes. One of the critical steps for by-products stabilization is the drying operation. The aim of this work was to develop a thermodynamic model for understanding internal heating and water transport mechanisms occurring from the inside to the outside of orange peels during hot air-microwave drying, and to predict the chemical and structural transformations. Different microwave energies (2, 4 and 6 W/g) combined with hot air (HAD) at 55ºC were used for drying citrus peels (5, 15, 40, 60 and 120 min). Mass, volume, surface, water activity, moisture, and permittivity were measured in fresh and dried samples. A thermodynamic model was developed to explain the mechanisms involved in mass and energy transports throughout the combined drying by hot air and microwave. This model allows optimizing the traditional hot air drying, by coupling microwave, of orange peel waste as a novel process for citrus by-products valorization, reducing the process time and therefore process costs.

Keywords: hot air–microwave drying, orange peel, thermodynamics.

NOTATION

a_j	activity of the chemical specie j (-)
R	ideal gases universal constant (J mol^{-1} K^{-1})
q	heat (kJ s^{-1})
T	temperature (K)
s	molar partial entropy (J K^{-1} mol^{-1})
S	entropy (J K^{-1})
P	absolute pressure (Pa)
V	volume (m^3)
l	elongation (m)
L	Phenomenological coefficient (mol^2 J^{-1} s^{-1} m^{-2})
n	number of moles (mol)
M	mass (kg)
Mr	molecular weight (g mol^{-1})
A	surface (m^2)
J	molar flux (mol s^{-1} m^{-2})
t	time (s)
G	free energy (J)
e	charge (C)
E	Energy (W g^{-1})
C_p	Specific heat (W g^{-1} K^{-1})
X	absolute moisture ($kg_w\ kg_{da}^{-1}$)
f	frequency (Hz)
c	light speed (m s^{-1})
H	overall enthalpy (J)
h	partial enthalpy (J kg^{-1})
r, y	distribution ratio
x	mass fraction (kg kg^{-1})

Greek Alphabet

ε	permittivity (-)
ε'	dielectric constant (-)
ε''	loss factor (-)
Ψ	electric potential (J mol^{-1} C^{-1})
μ_j	chemical potential of the specie j (J mol^{-1})
ν_j	molar partial volume of the specie j (L mol^{-1})
ϕ	relative humidity (-)
β	Penetration depth

Subscripts

T	total
air	air
w	water
t	process time
0	initial time
i	any chemical species
HAD	Hot air drying
MW	Microwave power
Abs	Absorbed

Superscripts

n	number of samples
i	interface
v	vapour
HAD	hot air drying
MW	microwave
da	dry air

1. Introduction

Thermodynamics are vital to financially ensure food production due to process variability with time, food heterogeneity, natural variation, complex geometry and temperature dependence of food properties. Drying involves the simultaneous transfer of mass and energy and it is a classical method of food preservation (Orsat et al., 2007), especially for vegetable by-products which are important sources of bioactive compounds such as antioxidants and dietary fiber (Larrauri, 1999).

The second law of thermodynamics involves the reversibility or irreversibility of processes and is very important to follow the changes of enthalpy (total heat) of material as heat is added or removed. In the drying industry, the goal is to use a minimum amount of energy for maximum moisture removal for the desired final conditions of the product. In order to find out the energy interactions and thermodynamic behavior of drying air throughout a drying chamber, heat balances should be performed by applying the first and second law of thermodynamics (Akpinar et al., 2006).

Drying of fruits and vegetables has been traditionally achieved by hot air drying (HAD) (Nijhuis et al., 1998). However, drying may cause irreversible modifications to the cell wall polysaccharides, affecting their original structure and composition, and therefore the final quality of the dried vegetable by-product (Femenia et al., 2003). Energy consumption is another critical issue in the selection of a process and with the increase in fuel prices it becomes an important factor to consider. Applying microwave energy (MW) to a drying process provides an efficient mean of transferring energy for moisture removal (Orsat et al., 2007). Microwave drying uses electromagnetic energy in the frequency range of 300 MHz to 300 GHz, being 2450 MHz the most commonly used frequency in Europe and 915 MHz in USA. Microwaves are generated inside a cavity by stepping up the alternating current from domestic power lines up to 2450 MHz (Orsat et al., 2005).

Tulasidas et al. (1995) demonstrated that the use of microwave energy combined with hot air for drying had relatively low energy consumption, because reduces the drying time in compare with traditional drying. The volumetric heating and reduced processing time make microwaves an attractive source of thermal energy. Since applying only microwaves could be an expensive drying process, it is recommended to combine techniques, such as hot air or vacuum, in order to complete the drying and further improve the process efficiency (Chou and Chua, 2001).

In microwave drying, heat is generated within the product through dipolar molecular induction and orientation caused by the alternating electromagnetic field. The generated water vapor must be coupled to a gradient of water chemical potential, in order to remove it, by using an external air with low relative humidity. Therefore, this process is a combination called 'hot air-microwave drying' (Orsat et al., 2007). A combination of hot-air drying and microwave process has proven to reduce drying time while improving product quality and minimizing energy requirements (Erle, 2005; Funebo and Ohlsson, 1998; Holtz et al., 2010; Igual et al., 2012; Soysal et al., 2006; Tulasidas et al., 1995). The heat flux, induced by the air temperature gradient, is conducted through the product beginning in the surface, nevertheless in case of microwave heating, the energy is absorbed with certain penetration depth.

Castro-Giráldez et al. (2011a,b) suggested considering food as a cellular system, consisting in extracellular space or apoplastic ways, cells with the major quantity of water inside joined with the symplastic ways. Inside the tissue, these authors proposed to share out the liquid water in liquid phase and in the adsorbed water. Therefore, any consideration in mass or energy transport must reflect this point of view and respect the complexity of vegetal tissue.

The mechanisms involved in the microwave-biological systems interaction are dipolar rotation and ionic conductivity. The permittivity of a biological tissue determines how many quantity of electric energy absorbed is distributed in electric energy stored (as a battery) or in mechanical and thermic energy dissipated. Therefore, vectorial permittivity (expressed as complex number, $\varepsilon = \varepsilon' - j\varepsilon''$) is necessary to quantify the overall heating produced when any food product is exposed to microwave radiation. This physical property defines the interaction between the biological systems and the electric field. The real part, ε', is called dielectric constant, and represents the proportion of electric energy absorbed and stored. The imaginary part, the loss factor, ε'', represents the proportion of electric energy absorbed that is dissipated in other energies, such as mechanical or thermal (Traffano-Schiffo et al., 2015).

Physical or mathematical models are important for simulating what happens during the process and therefore to predict the values of the desired properties. The potential use of citrus by-products in different technological applications involves some type of processing, i.e.,dehydration, which can alter their functional properties by affecting its hydration capacity. Garau et al. (2007) concluded that air-drying temperature should be controlled in order to preserve the quality of dietary fiber and antioxidant capacity of orange by-products as they might be degraded or modified either when extended drying periods and/or high drying times are applied.

The aim of this work was to develop a thermodynamic model for understanding internal heating and water transport mechanisms occurring from the inside to the outside of orange peels during hot air-microwave drying, and to predict the chemical and structural transformations.

2. Materials and methods

Oranges (Citrus sinensis (L.) Osbeck var Washington Navel) were bought from a local supermarket in Valencia (Spain). Orange peels were used for the experiments. 60 orange peel cylinders (20 mm diameter and 3 mm thickness) were cut with a core borer. A diagram of the experimental procedure is shown in Figure 1.

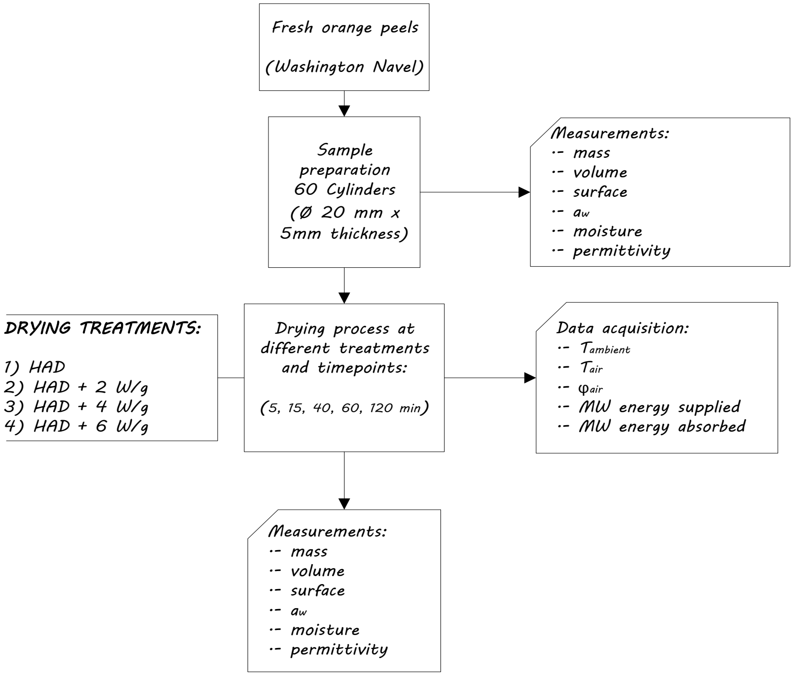

Figure 1. Schematic diagram of the experimental procedure.

Samples were subjected to hot air drying (HAD) and microwave assisted air drying (HAD+MW) (Figure 2), using a specially designed MW-air drying oven (Martín, 2003) with maximum output 2000 W at 2450 MHz, connected to a computer where temperature of ambient air and hot air, relative humidity of ambient air and incident microwave energy could be registered. In order to measure incident and reflected energy a directional coupler with power meter was also connected to the computer. The modified microwave oven presents two parallel connected lines (diameter = 105 mm), one for the application of hot air and another for the generation and application of the microwaves. Drying chamber has a Teflon chamber (edge = 100 mm) and a mode stirrer to ensure a homogeneous microwave distribution. Different variables were measured in drying chamber for process control: air temperature by a Pt100 thermocouple and air velocity by a fan anemometer.

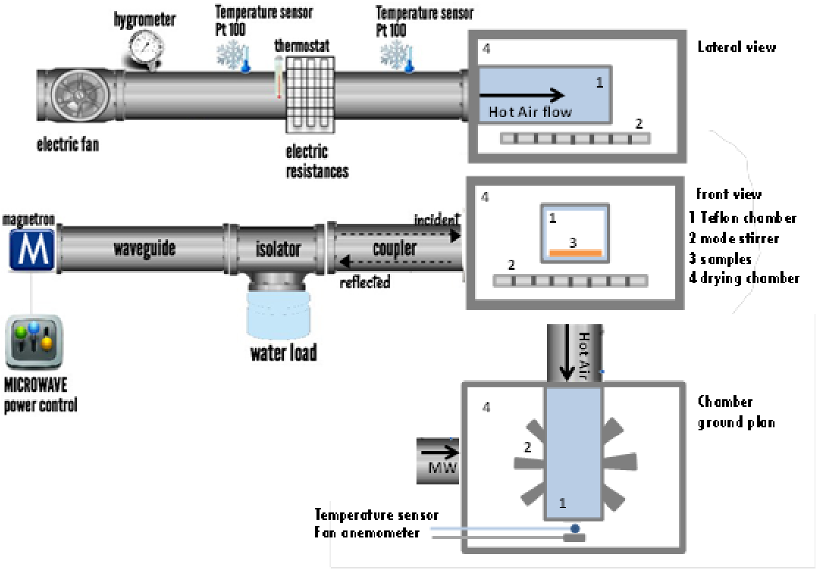

Figure 2. Schematic description of the laboratory equipment used to dry samples.

For the experiments, air velocity was 2.5 m/s, hot air temperature 55 ºC and the MW energy was 0, 2, 4 or 6 W/g. The microwave energy applied (determined by using the IEC-test) was selected such that samples did not burn during drying.

Orange peel samples were placed with flavedo side up on the dryer grid to facilitate mass transfer. Four drying experiments were carried out (HAD, HAD + 2 W/g, HAD + 4 W/g and HAD + 6 W/g). Three orange peels samples were used for each drying time (5, 15, 40, 60 and 120 min). These 3 samples were removed at each time point and were reposed at 25ºC for 1 h on Decagon containers, closed with Parafilm®, in order to eliminate the concentration profiles in samples. The next three samples were then placed in the drier.

Samples weight was determined by a precision balance Mettler Toledo AB304-S (± 0.001g). Surface water activity was determined by a dew point hygrometer Decagon (Aqualab®, series 3 TE), with precision ± 0.003 (Decagon Devices Inc., Washington, USA). Measurements were done in structured samples (not minced), thus a_w obtained was considered surface a_w (Castro-Giráldez et al., 2010). Water content of representative fresh orange peels and 120 min dried samples was determined by drying in a vacuum oven at 60ºC until constant weight was reached (AOAC method 934.06, 2000). The moisture content of the sample at intermediate drying stages was calculated from the weight lost during drying. Volume was determined by Image analysis (Sony T90, Carl Zeiss optics), using Adobe Photoshop© software, obtaining diameter and thickness of the samples by triplicate.

Dielectric properties were measured before and after the drying process for each sample with an Agilent 85070E open-ended coaxial probe connected to an Agilent E8362B Vector Network Analyzer. The system was calibrated by using three different types of loads: air, short-circuit and 25ºC Milli®-Q water. Once the calibration was made, 25ºC Milli®-Q water was measured again to check calibration suitability. The dielectric properties were measured by attaching the probe to the surface of the samples (flavedo). All determinations were made from 500 MHz to 20 GHz (Castro-Giráldez et al., 2011b). The measurements were made in triplicate.

To determine the statistical significance of the results an analysis of variance test (ANOVA) was carried out with confidence levels of 95 % ($p \leq 0.05$) and 99 % ($p \leq 0.01$) using the program Statgraphics Plus 5.1.

Additionally, samples were also investigated by a Leica MZ APO™ stereomicroscope (Leica Microsystems, Wetzlar, Germany) ranging 80 – 200 x magnifications (Castro-Giráldez et al., 2013).

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3. Results and discussion

Hot air–microwave drying involves simultaneous effects of the thermodynamics of hot air in sample surface, and the microwaves effects in depth. The internal effect of microwaves produces mechanical and thermal phenomena, increasing the water mobility, which distinguishes it from other drying methods.

Water mass variation of samples during the drying process can be obtained by the following equation:

$$\Delta M_w = \frac{M^t \cdot x_w^t - M^0 \cdot x_w^0}{M^0} \quad (1)$$

Where M represents the mass of the sample (kg), x_w represents the mass water fraction (kg_w/kg_T) and the superscript t represents the process time, being 0 the initial time. The water mass variation can be observed in Figure 3.

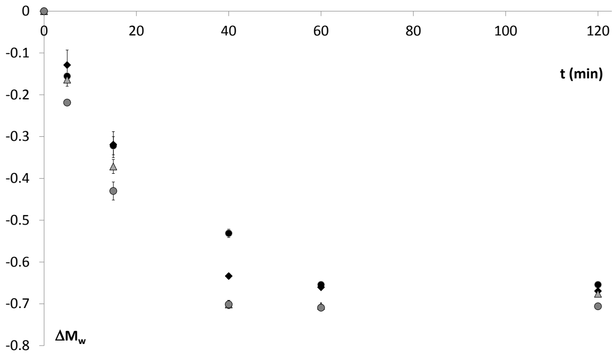

Figure 3. Evolution of water mass variation (ΔMw) in orange peels dried by different treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

A faster water mass reduction can be observed in microwave drying treatments with increasing microwave energy. At 5 and 15 min, very significant differences ($p \leq 0.01$) were found between HAD + 6 W/g and the rest of the treatments. At 40 min, a very significant mass reduction ($p \leq 0.01$) was observed between HAD (-0.53 ± 0.01) and HAD + 2 W/g (-0.63 ± 0.01) and the rest of treatments (HAD + 4 W/g and HAD + 6 W/g, values of 0.70 ± 0.01 for both). No significant difference was found between HAD + 4 W/g and HAD + 6 W/g at this timepoint.

The microwaves absorbed by the samples represent the quantity of electric and calorific energy dissipated throughout the microwaves penetration depth (β). The electric field decreases with β. This calorific energy is absorbed by the water molecules because at 2.45 GHz the relaxations phenomena are caused by the orientation and induction of polar molecules like water (the main dipole molecule in biological tissues). When the characteristic dimension of the sample is higher than the wavelength, β is defined as the distance from the sample surface at which the microwave absorbed energy drops to e^{-1} of its initial value. On the contrary, when the characteristic dimension is lower than the wavelength, heating comes from the inside of the sample. Assuming electromagnetic field as a plane wave that travels along one axis, penetration depth is calculated as it is shown in equation 2 (Meredith, 1998):

$$\beta = \frac{c}{2\pi f}\frac{\sqrt{\varepsilon'}}{\varepsilon''} \tag{2}$$

For all the experiments, β was higher than sample characteristic dimension, therefore heating from the inside was assumed.

Drying rate was also proportional to the intensity of the treatment (Figure 4).

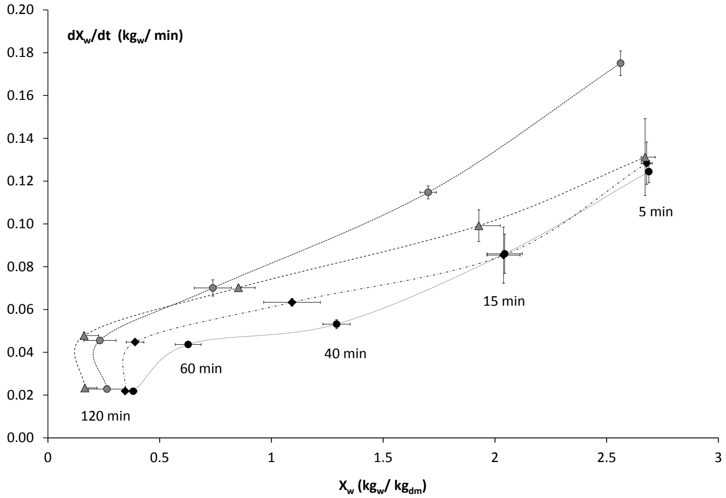

Figure 4. Drying rate of orange peel samples dried by ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

Very significant differences ($p \leq 0.01$) were found between HAD + 6 W/g and the rest of the treatments at 5 and 15 min. At 40 min, no significant differences were found between HAD + 6 W/g and HAD + 4 W/g neither with HAD and HAD + 2 W/g; however the first two were significantly different ($p \leq 0.01$) from the last two.

For instance, at 5 min of HAD, drying rate was 0.12 ± 0.01 kg$_w$/min reaching a moisture in dry basis of 2.69 ± 0.01 kg$_w$/ kg$_{dm}$. However, when using HAD + 6 W/g, at 5 min the drying rate was 0.18 ± 0.01 kg$_w$/min and the moisture in dry basis was 2.56 ± 0.01 kg$_w$/ kg$_{dm}$. No significant differences on drying rate were observed at 120 min, probably due to the low water content remaining in the samples, suggesting that the effect of microwaves on speeding up the drying process could be higher at the initial stages of the drying process.

During microwave convective drying, the energy invested in the drying process (E_T) is that required for evaporating part of the water in the tissue structure. Such evaporation process is induced by the thermodynamic inertia produced at the sample surface (Gibbs free energy gradient - ΔG - occurring at the interface between sample surface and the air in contact with it). This energy can be calculated by the following equation:

$$E_T = \frac{\left(\sum_1^n \Delta M_W\right) \cdot \Delta H^v|_T}{t} \tag{3}$$

being n the number of samples, $\Delta H^v|_T$ (work flow) the heat required for evaporating 1 g of water (data from Green and Perry, 2007) and t time.

E_T comes from two sources: the dissipation of part of the microwave energy absorbed by the water molecules and the energy supplied by the drying air. The proportion of the microwave energy that has been absorbed and transformed into heating energy can be estimated by sample dielectric properties at 2.45 GHz. Heat exchange with air can be determined by the temperature gradient between drying air and sample surface and also by the air thermodynamic inertia for evaporating (ΔG). The total distribution of energy is shown in equation (4):

$$E_T = E_{HAD} + E_{MW} \tag{4}$$

Where E_{HAD} is the energy supplied by the drying air and E_{MW} is the energy supplied by microwaves.

In order to calculate the amount of microwave energy absorbed as heating energy and invested in evaporation, a microwave energy distribution ratio (r_{MW}) has been developed by means of dielectric properties (Equation 5).

$$\mathrm{r_{MW}} = \frac{\varepsilon''}{\varepsilon' + \varepsilon''} \tag{5}$$

Where ε'' is the loss factor at 2.45 GHz and ε' is the dielectric constant at such frequency. Figure 5 shows r_{MW} variation with time for each drying treatment. At 40 min of drying, significant differences appear between 2, 4 and 6 W/g. As shown in Figure 3, the more microwave power applied, the faster the drying. Therefore, at 40 min, the samples treated with 6W/g have less moisture than the rest. On the other hand, the dissipation of microwave energy depends on the amount of water molecules in the samples. Thus, in Figure 5, samples are sorted by treatment, because, actually they are sorted by moisture. As drying process continues, r_{MW} decreases and no significant differences appear after 60 or 120 min. During the first 20 min, where heating is maximum according to Figure 5, β is 1.48 ± 0.015 cm (equation 2), showing a homogeneous heating in whole sample.

Thus the microwave energy absorbed and transformed into heat energy can be calculated as shown in equation 6, where E_{abs} is the overall energy absorbed in W/g:

$$\mathrm{E_{MW}} = \mathrm{E_{abs}} \cdot \mathrm{r_{MW}} \qquad (6)$$

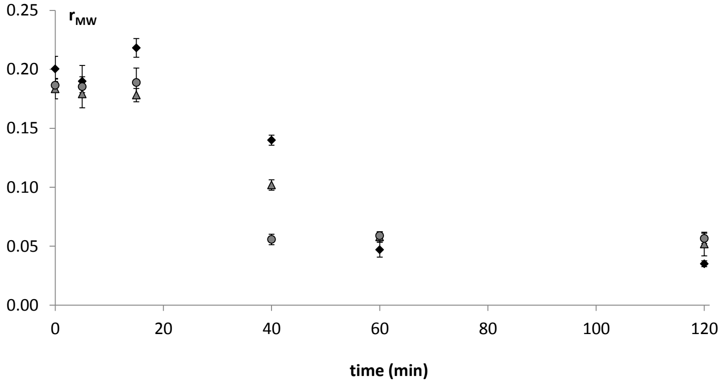

Figure 1. Microwave energy distribution ratio (r_{MW}) at different timepoints during drying at different microwave energies: ◆ HAD + 2 W/g, ▲ HAD + 4 W/g and ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

In order to describe the different behaviors involved during orange peel drying by HAD and MW technology, a thermodynamic approach has been developed. Gibbs free energy variation can be explained by the following equation (Castro-Giráldez et al., 2010):

$$\Delta G = -SdT + VdP + Fdl + \psi de + \sum_i \mu_i \, dn_i \Big|_{T,P,n_j} \tag{7}$$

Where: SdT (entropy and temperature variation) corresponds to the thermal term, VdP and Fdl are the mechanical energies related to the structural changes; where VdP (volume and pressure variation) corresponds to pressure variation and Fdl (force and elongation variation) to the elongation force, finally ψde (electric potential and charge variation) represents the effect of the native electrolytes or external applied electric field, at low frequencies (Hz to kHz), in the sample. The term $\sum_i \mu_i \, dn_i|_{T,P,n_j}$ is the addition of the chemical potentials of all the compounds in the system considering P, T and the molar concentration of the rest of the compounds constant (n_j).

This model fixes an interface between the sample and the air, and determines the free energy variation between them (Figure 6).

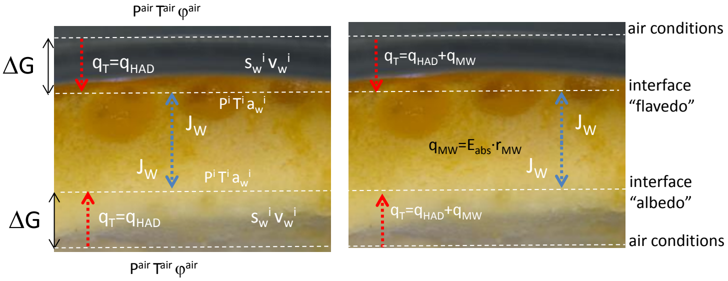

Figure 6. Schematic diagram of heat and water transport during HAD treatments (left) and HAD + MW treatments (right) of orange peel. Images were obtained by a Leica MZ APO™ stereomicroscope (Leica Microsystems, Wetzlar, Germany) at 200x magnification.

Considering the free energy variation per mol of water, it is possible to define the water chemical potential according to the equation 8:

$$\Delta\mu_w = \frac{\Delta G}{\Delta n_w} \tag{8}$$

From equations 7 and 8 it is possible to obtain the equation 9. The terms Fdl and ψde from equation 7 can be neglected because orange peel tissues, flavedo and albedo, are elastic and there is no ions effect since the sample only has the native ions of the peel, respectively. The term of the water chemical potential considering P and T constants and considering no interactions with the rest of the compounds, because only water can evaporate in the interface, is RT ln (φ/a_w), and it is named activity term.

$$\Delta\mu_w = -\, s_w \Delta T + v_w \Delta P + RT \ln \frac{\varphi^i}{a_w^i} \tag{9}$$

In order to calculate the thermal term, $s_w\Delta T$, it is necessary to know the temperature of the interface. For this purpose, the following approach has been developed (see figure 7).

The first consideration of the interface conditions was to consider the molecular water flux crossing the interface sample/air coupled with the internal water flux, explained in figure 6. Therefore the water loss in the samples is equal to the water gained in the air. If it is considered the overall energy invested in process as an energy of evaporation (equation 3), thus, the relation between the microwave energy and the overall energy is approximately equal to the ratio between the increment of the absolute moisture in the air interface produced by microwave and the total increment of absolute moisture (y_{MW}).

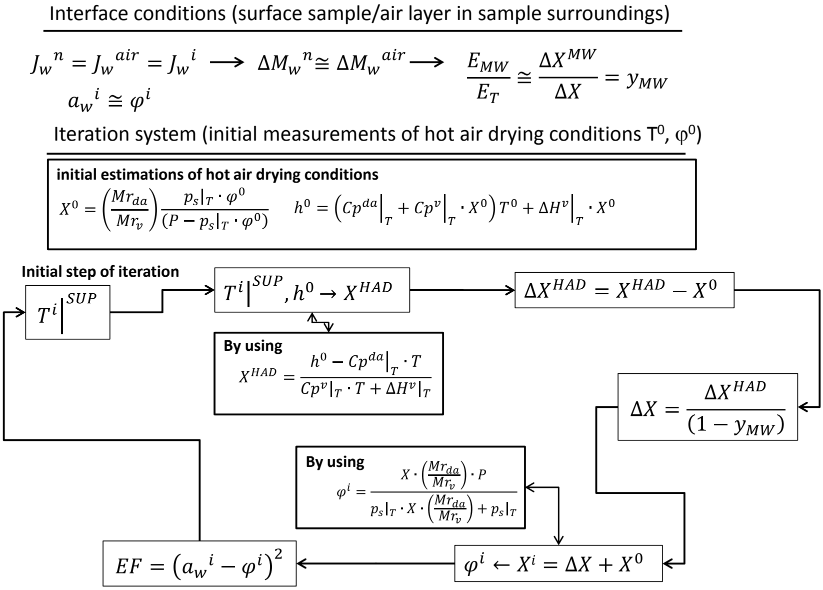

Figure 7. Interface considerations and scheme of iteration.

In order to estimate the surface temperature, an iteration system was developed by using the initial conditions of air drying, temperature and relative humidity, and considering the relative humidity in the interface and the surface water activity in equilibrium, with the same value.

The initial step of iteration is to suppose a surface temperature or temperature in the interface. By using the interface temperature, the absolute moisture of interface air and the increment of absolute moisture induced by hot air drying were estimated. With the y_{MW}, obtained before, it is possible to estimate the overall increment of absolute moisture in the interface, and also the interface relative humidity. The Error Function of the iteration was performed by the subtraction of the squared of the surface water activity and the squared of the interface relative humidity, considering both variables equilibrated in the interface.

Figure 8 shows the evolution of air conditions in the interface, plotted inside a psychometric chart, where it is possible to observe the beginning of drying at the initial value of the water activity ($a_w \approx 0.97$) and finishing at the line of drying conditions. Samples treated by HAD showed an evolution in parallel to the isoenthalpic lines, as a regular hot air drying process, where the energy to evaporate water comes from the internal energy of air, maintaining constant the enthalpy of air (reducing the internal energy and increasing the work flow with the new vapour). Nevertheless, samples treated by HAD and MW showed high levels of enthalpy at the beginning of the treatments, when high water activity produces higher dissipation of microwave energy (as figure 5 shows). This dissipated microwave energy in heat energy, is expended in water evaporation, maintaining, in the air, the level of the internal energy. The increments of enthalpy, shown in figure 8, are sorted with the absorbed microwaves energy, being the maximum value at 6 W/g.

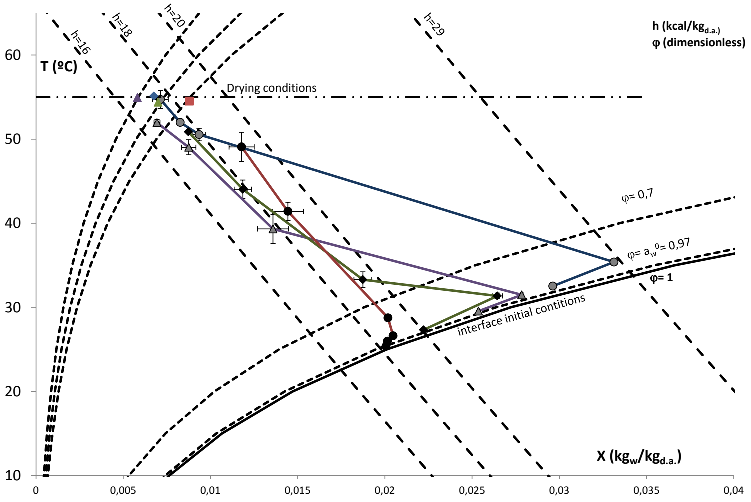

Figure 8. Evolution of interface air conditions throughout the drying process, plotted in a psychometric chart: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g and ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

The interface temperatures were estimated by using the iteration explained in figure 7. In Figure 9 , it is possible to observe how the interface temperature reached the drying temperature as fast as the absorbed microwave energy increased.

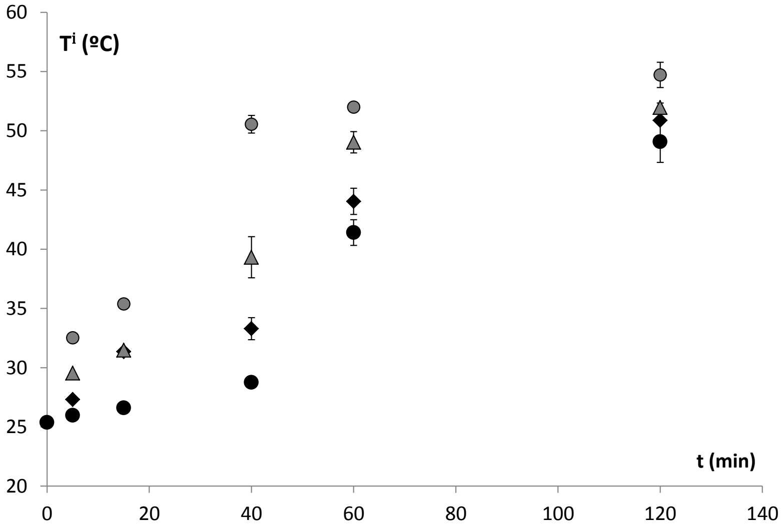

Figure 9. Temperature evolution during the different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

The interface temperature allowed the estimation of the thermal term of the equation 9, by calculating first the water molar entropy in the interface using the next equation:

$$s_w = \frac{Mr_w \cdot \left(C_P^{da} + C_P^{v} \cdot X^i\right) \cdot \left(T^{HAD} - T^i\right)}{T^i \cdot X^i} \tag{10}$$

Where Mr_w is the molecular weight of water (18 g/mol), C_P^{da} is the specific heat of dry air, C_P^v is the specific heat of vapour, X^i is absolute moisture of dry air , T^{HAD} is the temperature of HAD and T^i is the temperature at the interface.

In order to understand how the water transport changes, it is necessary to estimate the water flux with next equation:

$$J_w = \frac{\Delta M_w \cdot M_0}{\Delta t \cdot A \cdot Mr_w} \tag{11}$$

Where J_w is the water flux (mol/s m^2), ΔM_w represents the water mass variation (dimensionless), M_0 is the initial mass of the sample (g), Δt is the process time (s) and A corresponds to the surface area of the sample during the treatment, estimated as an average value between the initial and the final area (m^2).

Figure 10 shows the evolution of the molar water fluxes estimated with equation 11. Statistically significant differences ($p \leq 0.05$) were observed for all treatments at 5 min of drying, increasing water flux with treatment intensity. After 5 min, there are no significant differences among treatments. This also confirms that microwes have a positive effect in accelerating water transport by increasing water flux at the first stages of the drying process.

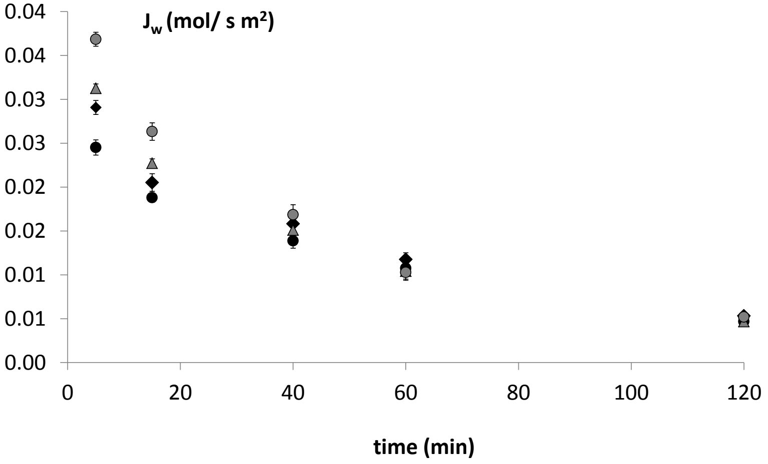

Figure 10. Water fluxes (J_w) of orange peel samples dried by ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

Applying the first relation of Onsager (Castro-Giráldez et al., 2010), the water molar flux is related to the chemical potential, as a driving force for the water transport, by the phenomenological coefficient (equation 12).

$$J_w = L_w \cdot \Delta\mu_w \qquad (12)$$

In order to estimate the mechanical term of the chemical potential (see equation 9), firstly it is necessary to determine the effect of the rest of terms (as equation 13 shows):

$$\Delta\mu_w^* = RT\ln \frac{\varphi^i}{a_w^i} - s_w \Delta T \qquad (13)$$

Where the superscript * represents the water chemical potential without considering the mechanical term.

Applying equations 11 and 13, it is possible to obtain the phenomenological coefficient (equation 14).

$$L_w^* = \frac{J_w}{\Delta\mu_w^*} \qquad (14)$$

Where L_w^* represents the phenomenological coefficient without considering the mechanical terms.

Figure 11 shows the relation between water flux and the phenomenological coefficient without considering the mechanical terms, being linear at the beginning of the dehydration, when the activity and thermal terms are bigger than the rest (amplification on figure 11 shows this range). It can be considered that the relationship between the phenomenological coefficient and water flux is lineal throughout the process. This linear relationship correlates phenomenological coefficient (L_w^*) and molecular water flux (J_w) with high square correlative coefficient for all treatments (table 1).

Table 1. Correlation between phenomenological coefficient (L_w^*) and molecular water flux (J_w) for all treatments.

Treatment	Linear Relationship	R^2
HAD	$L_w^* = 0.168\ J_w$	0.991
HAD + 2 W/g	$L_w^* = 0.166\ J_w$	0.996
HAD + 4 W/g	$L_w^* = 0.131\ J_w$	0.998
HAD + 6 W/g	$L_w^* = 0.139\ J_w$	0.995

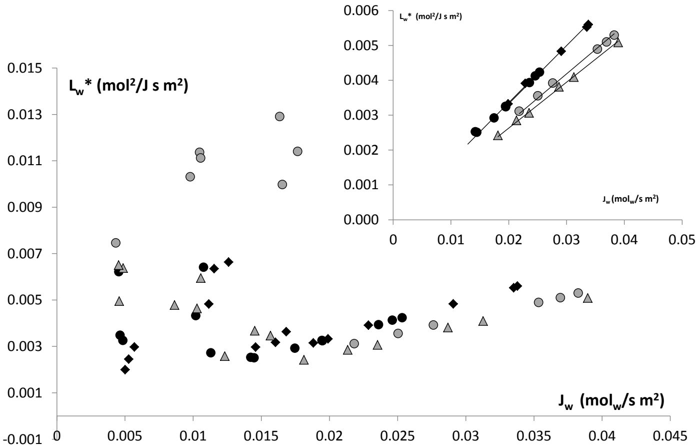

Figure 11. Phenomenological coefficient (L_W) *vs.* water flux (J_W). Amplification shows the linear relationship at the initial stages of the different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g.

Following the linear prediction of phenomenological coefficient with regard to water flux, the real chemical potential could be estimated throughout the drying process. Therefore, the mechanical term can be estimated as follows:

$$v_w \Delta P = \Delta\mu_w - \Delta\mu_w^* \tag{15}$$

The evolution of the mechanical energy, developed in the thermodynamic approach, is plotted in Figure 12.

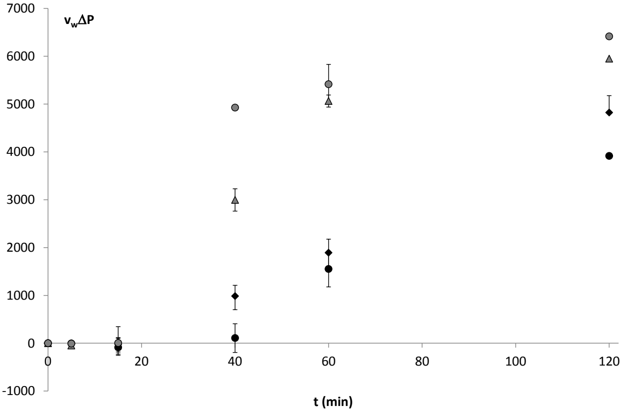

Figure 12. Evolution of the mechanical term (v_w ΔP) in orange peels dried by different treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

The fact that water evaporates at the end of each drying treatment is mainly due to the mechanical term. At the final stages of drying (between

40 and 120 min) the mechanical energy is used for water transport. At 40 min of HAD, the mechanical energy starts to increase at the same time that activity and thermic energies start to decrease at the interface, provoking a govern change in transport phenomena. For all samples dried by HAD + MW, the critical point at which mechanical energies start to increase and activity and thermic start to decrease is at 15 min. Mechanical energies grow faster depending on the microwave energy applied.

Figure 13 showed the volume deformation evolution. It is possible to observe a continuous shrinkage in HAD samples produced by the internal liquid water transport till the interface where it was evaporated. In samples treated by HAD and MW, the mechanisms of surface evaporation and microwave dissipation with penetration are coupled. The result of coupled behaviors produces internal evaporation and therefore induces an internal swelling (volumetric sample expansion). Depending on the predominant mechanisms (HAD shrinkage and MW swelling) samples suffer volumetric expansions or contractions.

For samples dried by HAD + 4 W/g and HAD + 6 W/g, the volume was intensely reduced during the first stages of drying, nevertheless, after 40 min there was an strong expansion of the samples. Samples dried by HAD + 2 W/g showed a volume reduction higher than HAD (non significant) at the beginning of the drying process, but a lower contraction than HAD + 4 W/g and HAD + 6 W/g for the same timepoint. These samples started to expand earlier (15 min) but with lower intensity than higher MW energies.

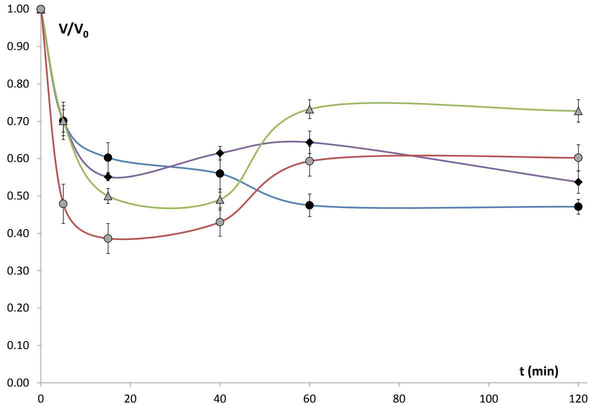

Figure 13. Evolution of the deformation of orange peels (V/V_0) during different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

Figure 14 shows the relation between deformation volume and the mechanical forces applied in water transport (mechanical term of equation 9). This figure shows that at the initial stages of drying (V/V_0 = 1) transport was governed by activity and thermal energies whereas mechanical energy was stored in this period. When mechanical energy starts to be released, small deformations take place, suggesting that water transport at the final stages of the treatment was caused by mechanical energy.

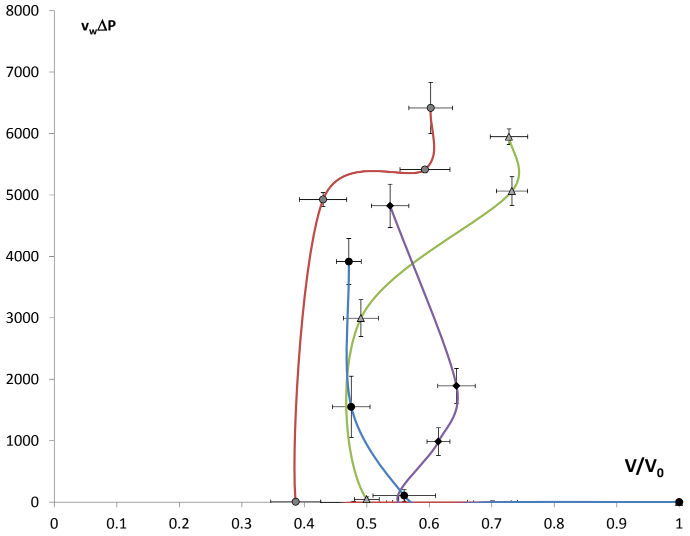

Figure 14. Relationship between mechanical terms (v_w ΔP) and the deformation (V/V_0) of orange peels dried by different treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

4. Conclusions

A thermodynamic model was developed to explain the mechanisms involved in mass and energy transports throughout the combined drying by hot air and microwave. A continuous shrinkage in HAD samples was produced by the internal liquid water losses, and the samples treated by

HAD+MW showed an internal swelling caused by the internal evaporation produced by the microwave energy. Depending on the predominant mechanisms (HAD shrinkage and MW swelling) samples suffer volumetric expansions or contractions.

This model allows optimizing the traditional hot air drying, by coupling microwave, of orange peel waste as a novel process for citrus by-products valorization, reducing the process time and, therefore, process costs.

5. Acknowledgements

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6. References

Akpinar, E.K., Midilli, A., Bicer, Y., (2006). The first and second law analyses of thermodynamic of pumpkin drying process. Journal of Food Engineering 72(4), 320-331.

Castro-Giráldez, M., Fito, P.J., Fito, P., (2010). Application of microwaves dielectric spectroscopy for controlling pork meat (Longissimus dorsi) salting process. Journal of Food Engineering 97(4), 484-490.

Castro-Giráldez, M., Fito, P.J., Fito, P., (2011a). Nonlinear thermodynamic approach to analyze long time osmotic dehydration of àrenchymatic apple tissue. Journal of Food Engineering, 102, 34-42.

Castro-Giráldez, M., Fito, P.J., Dalla Rosa, M., Fito, P. (2011b). Application of microwaves dielectric spectroscopy for controlling osmotic dehydration of kiwifruit (Actinidia deliciosa cv Hayward). Innovative Food Science & Emerging Technologies, 12 (4), 623-627.

Castro-Giráldez, M., Fito, P.J., Ortolá, M.D., Balaguer, N. (2013). Study of pomegranate ripening by dielectric spectroscopy. Postharvest Biology and Technology, 86, 346–353

Chou, S.K., Chua, K.J., (2001). New hybrid drying technologies for heat sensitive foodstuffs. Trends in Food Science & Technology 12(10), 359-369.

Erle, U., (2005). 8 - Drying using microwave processing, in: Schubert, H., Regier, M. (Eds.), The Microwave Processing of Foods. Woodhead Publishing, pp. 142-152.

Femenia, A., García-Pascual, P., Simal, S., Rosselló, C., (2003). Effects of heat treatment and dehydration on bioactive polysaccharide acemannan and cell wall polymers from Aloe barbadensis Miller. Carbohydrate Polymers 51(4), 397-405.

Funebo, T., Ohlsson, T., (1998). Microwave-assisted air dehydration of apple and mushroom. Journal of Food Engineering 38(3), 353-367.

Garau, M.C., Simal, S., Rosselló, C., Femenia, A., (2007). Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. Food Chemistry 104(3), 1014-1024.

Green, D., Perry, R., (2007). Perry's Chemical Engineers' Handbook, Eighth Edition. McGraw-Hill Education.

Holtz, E., Ahrné, L., Rittenauer, M., Rasmuson, A., (2010). Influence of dielectric and sorption properties on drying behaviour and energy efficiency during microwave convective drying of selected food and non-food inorganic materials. Journal of Food Engineering 97(2), 144-153.

Igual, M., García-Martínez, E., Martín-Esparza, M.E., Martínez-Navarrete, N., (2012). Effect of processing on the drying kinetics and functional value of dried apricot. Food Research International 47(2), 284-290.

Larrauri, J.A., (1999). New approaches in the preparation of high dietary fibre powders from fruit by-products. Trends in Food Science & Technology 10(1), 3-8.

Martín, M.E., Martínez-Navarrete, N., Chiralt, A., Fito, P., (2003). Diseño y construcción de una instalación experimental para el estudio de la cinética de secado combinado por aire caliente y microondas. Alimentación equipos y tecnología 22(181), 101-107.

Meredith, R.J. (1998). Microwave interaction with dielectric materials. In: Engineers' Handbook of Industrial Microwave Heating. Published by: The Institution of Electrical Engineers, London, UK, pp. 19-50.

Nijhuis, H.H., Torringa, H.M., Muresan, S., Yuksel, D., Leguijt, C., Kloek, W., (1998). Approaches to improving the quality of dried fruit and vegetables. Trends in Food Science & Technology 9(1), 13-20.

Orsat, V., Raghavan, G.S.V., Meda, V., (2005). Microwave technology for food processing: an overview, in: Schubert, H., Regier, M. (Eds.), The Microwave Processing of Foods. Woodhead Publishing, Cambridge, UK, pp. 105-118.

Orsat, V., Yang, W., Changrue, V., Raghavan, G.S.V., (2007). Microwave-Assisted Drying of Biomaterials. Food and Bioproducts Processing 85(3), 255-263.

Soysal, Y., Öztekin, S., Eren, Ö., (2006). Microwave Drying of Parsley: Modelling, Kinetics, and Energy Aspects. Biosystems Engineering 93(4), 403-413.

Traffano-Schiffo, M.V., Castro-Giráldez, M., Colom, R.J., Fito, P.J. (2015). Study of the application of dielectric spectroscopy to predict the water activity of meat during drying process. Journal of Food Engineering, 166, 285–290.

Tulasidas, T.N., Raghavan, G.S.V., Mujumdar, A.S., (1995). Microwave drying of grapes in a single mode cavity at 2450 MHz - I: Drying kinetics. Drying Technology 13(8-9), 1949-1971.

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Effect of microwave power coupled with hot air drying on orange peel

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ABSTRACT

Drying operation is one of the most cost effective processes that make alternative routes for by-products valorisation worthwhile. The two main objectives of this work are to determine the effect of microwave heating coupled to the hot air drying (HAD + MW) on the kinetics of the treatment and on the macro and microstructural properties of the dried product, and to develop engineering tools to predict the dehydration level. Drying by hot air at 55 ºC and by HAD + MW at different power intensities (2 W/g, 4 W/g and 6 W/g) was carried out. At 5, 15, 40, 60 and 120 min mass, surface, volume, water activity and moisture were measured in fresh and dried samples. Sorption isotherms were obtained and fitted by GAB model with high correlation coefficients. Macroscopic and microscopic analyses show that tissue suffers shrinkage/swelling phenomena promoted by MW power. The use of HAD + MW not only resulted in faster moisture reduction of orange peel but also induced microstructural changes that generated higher sorption capacity.

Keywords: hot air–microwave drying, orange peel, isotherm, isosteric heat, microstructure, water retention capacity

1. Introduction

Food industry by-products are materials very susceptible to microbial spoilage, fermentation or chemical deterioration due to a resident microflora and endogenous enzymatic activities. Therefore, every valorization process shall consider a previous pre-treatment or stabilization procedure that minimizes the negative effect of these biological or chemical processes on the quantity and quality of the target compounds. Standard stabilization methods are basically dehydration methods that reduce water activity having a direct effect on the material contaminant microflora (Fava et al., 2013; Fernández-López et al., 2009; Larrauri, 1999; Schieber, Stintzing, & Carle, 2001).

The theoretical basis of drying treatments by hot-air is to produce water fluxes from food sample to the air stream induced by a gradient of water chemical potential (Demirel & Sandler, 2001). The main engine of the water transport is the gradient between a_w and relative humidity (Traffano-Schiffo, Castro-Giráldez, Fito & Balaguer, 2014). In hot air drying, working below 100ºC, the water evaporation is produced in surface. In these cases, it is useful to couple to hot air drying with other techniques in order to increase the process of water removal. A common technique used to be coupled with hot air drying is the MW (Bergese, 2006; Kowalski, Rajewska & Rybicki, 2005).

The magnetron of microwave equipment in Europe works at 2.45 GHz, at this frequency the interaction of the photon flux with biological tissue produces γ-dispersion. This dispersion is due to the dipolar molecules orientation and induction, producing electric storage and dissipation of the electric energy in other energies such as heat. The main dipolar molecule of orange peel tissue is water (Castro-Giráldez, Fito, Chenoll, & Fito, 2010, Castro-Giráldez, Fito, Dalla Rosa & Fito, 2011a, Castro-Giráldez, Fito & Fito, 2011b); therefore, the MW heating is directly related with the quantity and mobility of the water molecules.

The relationship between food moisture and a_w content is described by the moisture sorption isotherm. Moisture sorption isotherms have an important role in shelf-life prediction due to their sensitivity to moisture changes. Aiming to mathematically express the relation between a_w of food and its moisture content diverse models have been developed (Labuza & Altunakar, 2007). The GAB model was developed by Guggenheim Anderson and de Boer as an improved version of the BET model for multilayer adsorption (van den Berg & Bruin, 1981). The GAB equation has been found to effectively represent experimental data in the a_w range of 0 to 0.95 for most foods, and it has been applied in many foods such as corn flour, passion fruit peel, pineapple peel, dried tomato pulp, pear, banana pulp, mango pulp, walnut kernels, etc (Andrade, Lemus, & Pérez, 2011). GAB model uses three constants: the two constants obtained from the BET model that are the monomolecular moisture layer, (X_{w0}), and the energy constant, C, which is related to the isosteric heat of sorption (Q_C). The parameter C represents the strength of binding for water molecules to the primary binding sites on samples surface (monolayer). The larger the value of C, the stronger the bonds between water molecules in the monolayer and the binding sites on the surface of the sorbent. The third constant of the GAB model is K, which is an empirical parameter. The parameter K is a correction factor for multilayer molecules relative to the liquid phase (Quirijns, van Boxtel, van Loon, & van Straten, 2005). This physical meaning, the ability of the GAB equation to predict the moisture sorption isotherms of food products over a wide range ($0.05 < a_w < 0.95$), and the ability to describe some temperature effects on isotherms suggests that the GAB model is the preferred model to fit the moisture sorption behaviour of dried orange products (Edrisi, Sormoli & Langrish, 2015).

Further analysis of sorption isotherm data by application of thermodynamic principles can provide important information regarding the dehydration process energy requirements, food microstructure, physical phenomena on the food surfaces, water properties, and sorption kinetic parameters (Rizvi & Benado, 1984). Within the literature, thermodynamic functions adopted for analysis of sorption phenomena include differential enthalpy and entropy, and integral enthalpy and entropy. The isosteric heat of sorption, or differential enthalpy of sorption, gives a measure of the water–solid binding strength (sorption energy). Knowledge of the isosteric heat is of a great importance when designing equipment for dehydration processes. This is due to the fact that heat of vaporization of adsorbed water may increase to values above the heat of vaporization of pure water as food is dehydrated to low moisture levels. An isosteric heat greater than the heat of vaporization, primarily indicates that the energy of interaction between the water molecules and sorption sites is greater than the energy that holds the water molecules together in the liquid state. Consequently, the level of moisture at which the isosteric heat approaches the heat of vaporization of pure water is often taken as indicative of the amount of bound water existing in the food (Al-Muhtaseb, McMinn, & Magee, 2002).

In previous work carried out by Fava et al. (2013) it was observed that microwave (MW) drying of citrus peels resulted in a stabilized product for further conversion into dietary fiber with optimal microbial, sensory and technological properties such as water retention capacity (WRC). High temperatures or long drying times in hot air drying may cause serious damages to product flavor, color and nutrients, producing shrinkage and decreasing the WRC. MW absorption provokes internal water heating and evaporation, greatly increasing the internal pressure and concentration gradients and thus the effective water diffusion. As a consequence, shorter processing time may be required and higher product quality may be achieved (Igual, Contreras, & Martinez-Navarrete, 2010). It is usual to combine hot air with the MW system when drying with microwave energy. Hot air is, by itself, relatively efficient at removing free water at or near the surface, whereas the unique pumping action of microwaves energy provides an efficient way of removing internal free water (Schiffmann, 2001). Combining properly both unit operations may improve the efficiency and the economics of the drying process. Talens, Castro-Giráldez & Fito (2015) developed a thermodynamic model for hot-air microwave drying of citrus peels that explained the mechanisms involved in mass and energy transports throughout the combined drying by hot air and microwave. These authors showed that depending on the predominant mechanisms (shrinkage during hot-air drying and swelling during microwave) samples suffer volumetric expansions or contractions. Ghanem, Mihoubi, Kechaou, & Mihoubi (2012) studied the MW drying characteristics of *Thompson Navel* oranges at power levels ranging from 5 to 30 W/g and the effect of MW treatment on shrinkage and water retention capacities.

Results showed that drying at low MW power level (5-15 W/g) gave the maximum water retention capacity. Also, Bejar, Kechaou & Mihoubi (2011) showed that when high MW powers were used higher water holding capacities were obtained.

The aim of this work was to determine the sorption isotherms and the isosteric heat of sorption of orange peel treated by hot air-microwave drying and to study its effect on macro and microstructure.

2. Materials and methods

Oranges (*Citrus sinensis* (L.) Osbeck var Washington Navel) were bought from a local supermarket in Valencia (Spain). Orange peels were used for the experiments. 60 orange peel cylinders (20 mm diameter and 3 mm thickness) were cut with a core borer. A diagram of the experimental procedure is shown in Figure 1.

Samples were subjected to hot air drying (HAD) and microwave coupled with hot air drying (HAD+MW), using a specially designed HAD+MW oven with maximum output 2000 W at 2450 MHz, coupled to a balance and connected to a computer where air temperature, air velocity and incident microwave energy could be controlled.

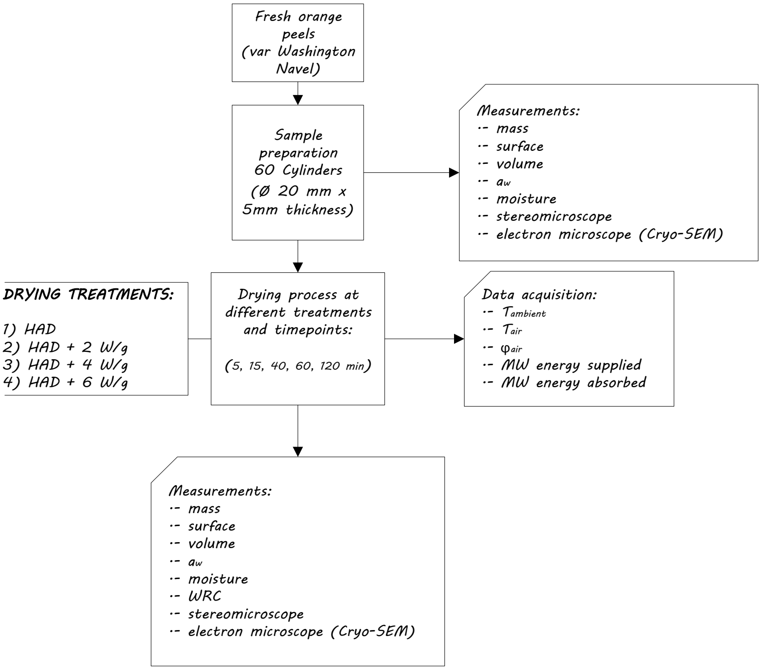

Figure 1. Schematic diagram of the experimental procedure.

In order to measure incident and reflected energy a directional coupler with power meter was also connected to the computer (Figure 2).Different measurement indicators were used for process control (air drying temperature, air velocity, ambient temperature and relative humidity).

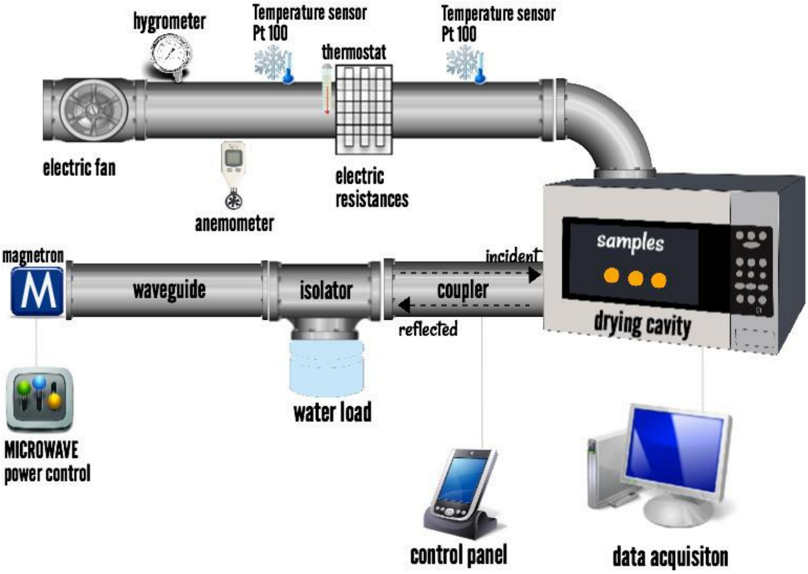

Figure 2. Schematic description of the laboratory equipment used to dry samples.

For the experiments, air velocity was 2.5 m/s, air temperature 55 ºC and the MW energy was 0, 2, 4 or 6 W/g. The microwave energy applied (determined by using the IEC-test) was selected such that samples did not burn during drying.

Orange peel samples were placed with flavedo side up on the dryer grid to facilitate mass transfer. Four drying experiments were carried out (HAD, HAD + 2 W/g, HAD + 4 W/g and HAD + 6 W/g). Three orange peels samples were used for each drying time (5, 15, 40, 60 and 120 min). These 3 samples were removed at each time point and were equilibrated at 25ºC for 5 h in Aqualab® disposable sample cups sealed with parafilm®, in order to eliminate the concentration profiles in samples. The next three samples were then placed in the drier.

Samples weight was determined by a precision balance Mettler Toledo AB304-S (precision ± 0.001 g). Surface water activity was determined by a dew point hygrometer Decagon Aqualab®, series 3 TE (precision ±0.003, dimensionless) (Decagon Devices Inc., Washington, USA). Measurements were done in structured samples (not minced), thus a_w obtained was considered surface a_w. Water content of representative fresh orange peels and 120 min dried samples was determined by drying in a vacuum oven at 60ºC until constant weight was reached (AOAC method 934.06, 2000). The moisture content of the sample at intermediate drying stages was calculated from the weigh lost during drying. Volume was determined by Image analysis (Sony T90, Carl Zeiss optics), using Adobe Photoshop© software, obtaining diameter and thickness of the samples by triplicate.

Microstructure of fresh and frozen samples was analyzed by CryoSEM. A CryoACryostage CT-1500C unit (Oxford Instruments, Witney, UK), coupled to a Jeol JSM-5410 scanning electron microscope (Jeol, Tokyo, Japan), was used. The sample was immersed in slush N_2 (-210ºC) and then quickly transferred to the Cryostage at 1 kPa where sample fracture took place. The sublimation (etching) was carried out at -95 ºC. The final point was determined by direct observation in the microscope, working at 5 kV. Then, once again in the Cryostage unit, the sample was coated with gold in vacuum (0.2 kPa), applied for 3 min, with an ionization current of 2 mA. The observation in the scanning electron microscope was carried out at 15 kV, at a working distance of 15 mm and a temperature ≤ -130 ºC.

Additionally, samples were also investigated by a Leica MZ APO™ stereomicroscope (Leica Microsystems, Wetzlar, Germany) with magnification (8x to 80x) using incident light illumination (light reflected off the surface of the sample). It uses two separate optical paths with two objectives and two eyepieces to provide slightly different viewing angles to the left and right eyes. In this way it allows a three-dimensional visualization of the sample.

The desorption isotherm was fitted following the GAB model using Equation 1 (van den Berg & Bruin, 1981):

$$X_W = \frac{X_{W0}\ C\ a_w}{(1\text{-}K\ a_w)(1+(C\text{-}1)a_w)} \tag{1}$$

Where: X_w corresponds to the orange peel moisture (kg_w/kg_{dm}), X_{W0} is the monomolecular moisture layer (kg_w/kg_{dm}), C is the energy constant and K is an empirical parameter, both dimensionless (Labuza & Altunakar, 2007).

For Water Retention Capacity (WRC) determination, approximately 0.5 g of each sample (precision ± 0.0001 g) was hydrated in 20 mL of distilled water in a 50 mL falcon tube and left overnight to ensure the fiber was fully hydrated. Then the tubes were centrifuged at 1000 × g for 10 min (adapted from Robertson et al., 2000). The supernatant was decanted and the tubes were carefully inverted to drain residual unbound water from the sample. The remaining pellet was dried until constant weight in an oven at 100 ± 5 ºC and weighed to consider possible solid matter losses in the draining step. WRC was calculated as the amount of water retained by the pellet (kg_w/ kg_{dm}).

3. Results and discussion

Figure shows the evolution of the moisture throughout the different drying treatments. A faster moisture reduction was observed in HAD+MW with regards to HAD at the initial stages of the drying. Microwave radiation orientates and induces water molecules, storing electric energy and dissipating part of it as thermal energy. Therefore, the more water molecules in samples, the higher thermal energy is produced by microwave radiation. Thus, the main effect of microwaves in drying process occurs at the beginning, because microwave energy increases the thermal and mechanical energy improving the water motion (increasing the free energy in the media) and increasing the availability of thermal energy for water evaporation, reducing the air internal energy losses. The interaction between water content and microwaves increases with MW power and decreases with water content, this interaction is shown in figure 3, where it is possible to observe how at 5 min, only the maximum MW power, 6 W/g, showed very significant differences ($p \leq 0.01$) with the rest of the treatments. At 15 min very significant differences ($p \leq 0.01$) were appreciated among 4 W/g and 6 W/g microwave powers and the rest of the treatments. At 40 min, very significant differences ($p \leq 0.01$) were appreciated among HAD, 2 W/g and the rest of the treatments, while no differences between them were appreciated mainly because the low level of moisture reduced the effect of the MW energy. After 60 min of drying, treatments converged to the threshold of the thermodynamic properties of dry air ($a_w|^{sample} \approx \varphi|^{air}$).

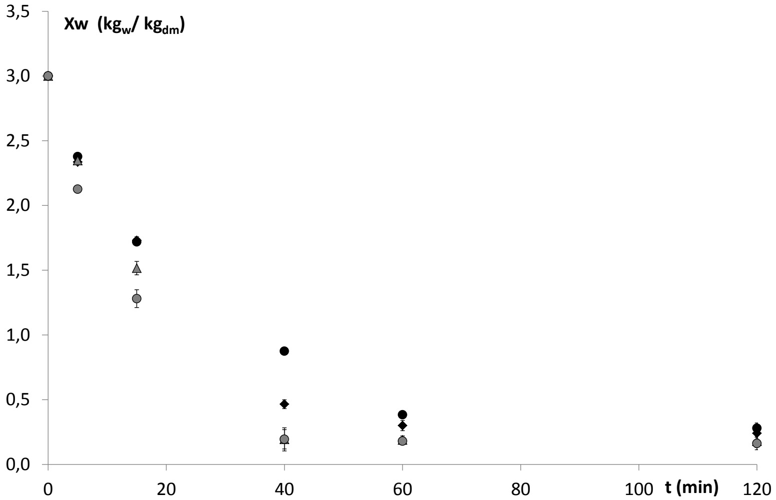

Figure 3. Drying curve of orange peel treated by different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

In order to understand the structural changes produced by the application of MW power throughout the hot air drying, a sorption isotherm for each treatment was obtained (Figure 4). The sorption isotherms were well fitted following the GAB model (Van den Berg and Bruin 1981), with the correlated coefficients of 0.9342, 0.9182, 0.9197, 0.8493 for HAD, HAD + 2 W/g, HAD + 4 W/g, HAD + 6W/g, respectively. Sorption isotherms are sorted by MW power.

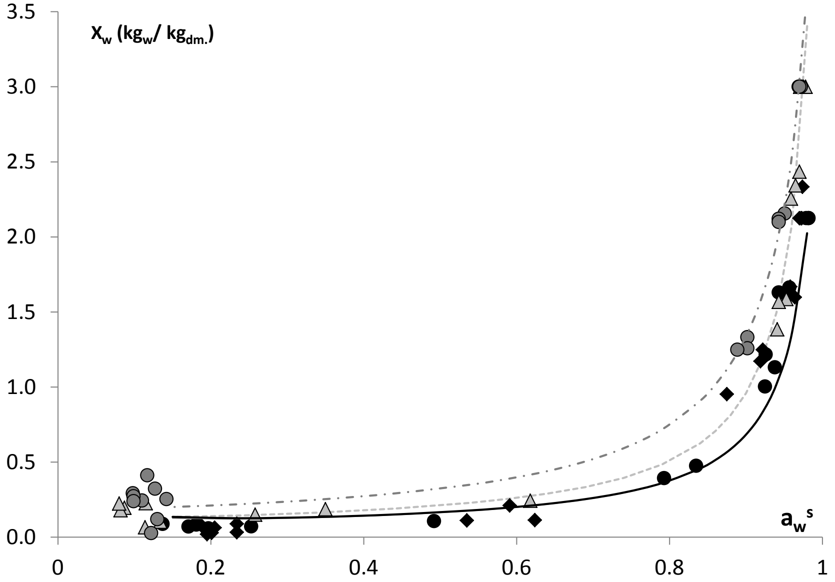

Figure 4. Sorption isotherm of orange peel treated by different drying treatments: experimental points ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g; and GAB model — HAD, — HAD + 2 W/g, - - - HAD + 4 W/g, - · · HAD + 6 W/g.

GAB model uses three constants, being the monomolecular moisture layer (X_{W0}) and the energy constant C (related with the Q_c or isosteric heat of sorption) with physical sense and K parameter an empirical constant. The empirical constant K value was 0.981 ± 0.006 for all drying treatments; this empirical constant produces the exponential shape of the isotherm in order to fit data of samples with liquid phase. This value was the same for all treatments because it depends on the nature of the liquid phase compounds and, for all treatments, the composition of raw material was the same. However the GAB parameters with physic sense are different for each treatment and they could be useful to determine the effect of microwave energy on the final physical properties of dried product (Figure 5). The monomolecular moisture layer increases with the MW power treatment, showing an increase in the adsorption of water in the surface tissue. The energy constant, C, also increases with the MW power treatment, this parameter is related with the isosteric heat of sorption and therefore with the surface tension, improving the capability of the tissue to storage water as a adsorbed water.

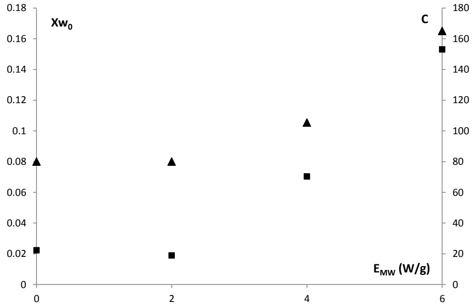

Figure 5. GAB model parameters: monomolecular moisture layer (X_{W0}) (▲) Energy constant (C) (■) for isotherms of orange peels dried by different hot air-microwave treatments.

The isosteric heat can be calculated by using the punctual estimation of the parameter C and the surface temperature of samples obtained from Talens, Castro-Giráldez & Fito (2015), following equation 2 (Labuza & Altunakar, 2007):

$$Q_c = RT \ln C \tag{2}$$

Where Q_c is the isosteric heat of sorption (kJ/mol), R is ideal gas constant (J/mol K) and T is absolute temperature (K).

In figure 6 it is possible to observe the relation between the isosteric heat of sorption and the moisture content of samples. The values obtained (from 1 to 10 kJ/mol) were inside the range reported by other authors: from 0 to 9 kJ/mol for spray dried orange juice using isotherms at 20 - 50 ºC (Edrisi Sormoli & Langrish, 2015), from 1.8 to 8 kJ/mol for orange peel with isotherms at 40 - 60 ºC (Bejar, Mihoubi, & Kechaou, 2012), from 0.8 to 8 kJ/mol for dried banana with isotherms at 10 – 40 ºC (Yan, Sousa-Gallagher, & Oliveira, 2008) and from 5 to 30 kJ/mol for pineapple with isotherms at 20 – 50ºC (Hossain, Bala, Hossain, & Mondol, 2001).

Treatments of higher microwave powers showed a faster reduction of the isosteric heat at the beginning of drying, reaching first a minimum value and then growing faster, reaching the highest values at end of treatment.

This could occur because, at 55ºC of air drying temperature, the evaporation caused by water chemical potential gradients is produced in the surface sample, moving the water in liquid state through the sample; however, the application of MW power produces internal evaporation (caused by the penetration depth of radiation), producing internal vapour fluxes and internal water expansion, thus increasing the internal space in the porous of samples and also the internal surface.

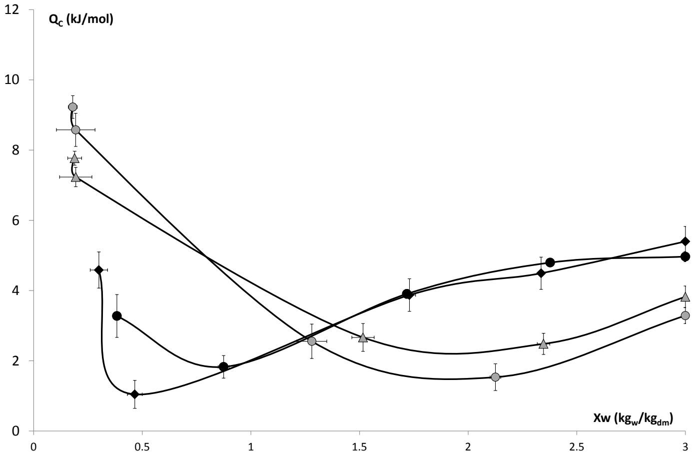

Figure 6. Sorption isosteric heat versus moisture of orange peel samples treated by different MW power: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. The detail of graph shows the Q_c of dried product with regard to the different MW power treatments.

The detail of figure 6 shows that, at the end of drying, isosteric heat increases with MW power, increasing the hygroscopicity of the samples. Surface tension (σ) represents the free energy available to join water molecules to the solid structure represented by the surface area (dG/dA), therefore if the isosteric heat and the internal surface increase with the MW power application, then the surface tension will also increase with the MW power.

Figure 7 shows the volume variation of the samples for the different drying treatments.

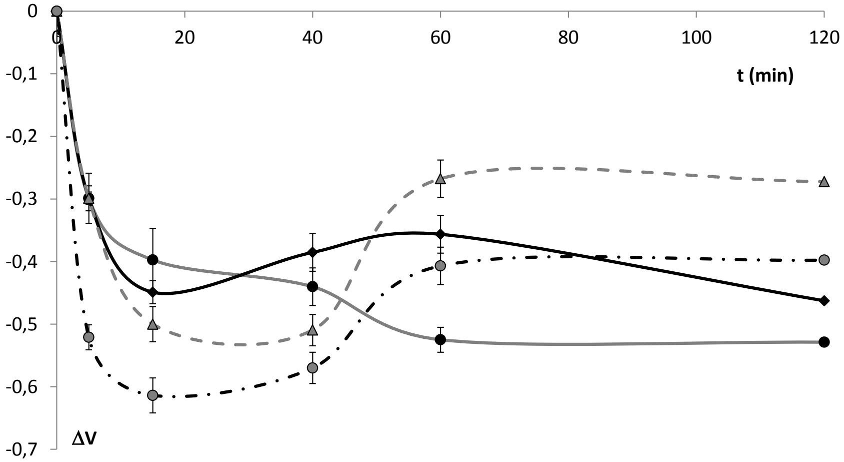

Figure 7. Volume variation of orange peel treated by different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

Samples dried by HAD suffered a continuous shrinkage associated to the water loss. In HAD samples, internal water is transported in liquid state to the surface where it is evaporated, driven by the water chemical potential gradient. These samples reach a volume equilibrium after 60 min of drying associated to the convergence with the thermodynamic properties of dry air ($a_w|^{sample} \approx \varphi|^{air}$). On the contrary, samples dried by HAD+MW showed different stages of volume variation. At the beginning of treatment, samples suffered a drastic reduction of volume associated to the evaporation of water from sample surface. As was explained before, at one time point, microwaves start producing internal evaporation of water coupled to the loss of water surface. This phenomenon of internal vapour fluxes and water expansion caused by MW energy produces the swelling of the samples (Volumetric sample expansion). At the end of the drying treatment (after 60 min), volume equilibrium is reached due to the combined effect of the sample vitreous transition (glass transition moisture was reached) and the low quantity of water molecules present in the samples that can be evaporated (See figure 3).

The WRC is the most common parameter used in the industry to characterize the rehydration capacity of fiber, however this parameter has not a physical sense. This research work tries to develop the engineering tools to produce by-products from citrus juice industry, for this purpose it is necessary to define the physical meaning of this parameter. With this purpose the WRC was measured (Figure 8). In the figure, it is possible to observe that the WRC increases with MW power intensity, being significantly ($p<0.05$) higher at HAD + 4 W/g and HAD + 6 W/g treatments than HAD and HAD + 2 W/g treatments.

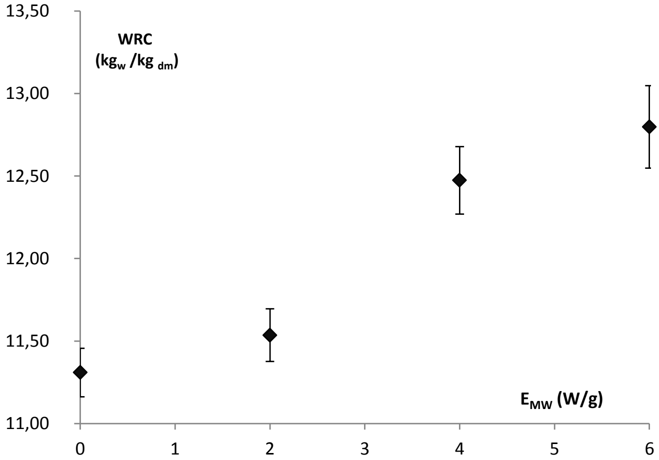

Figure 8. Water retention capacity (kg_w/ kg_{dm}) of orange peel treated by different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

With all the properties explained above, it is possible to describe the rehydration process of samples by giving physical meaning to the WRC, since the hygroscopicity of the sample will depend on the energy to adsorb water molecules and the swelling capacity of the sample when it is in rubbery state. Figure 9 shows the isosteric heat of dried samples with regard to its WRC for each drying treatment studied, in order to understand the physic sense of this parameter. In the figure it is possible to observe that the higher MW power intensity applied the higher isosteric heat and the higher WRC. Isosteric heat is directly related with the WRC, showing that higher energy of adsorption produces higher WRC.

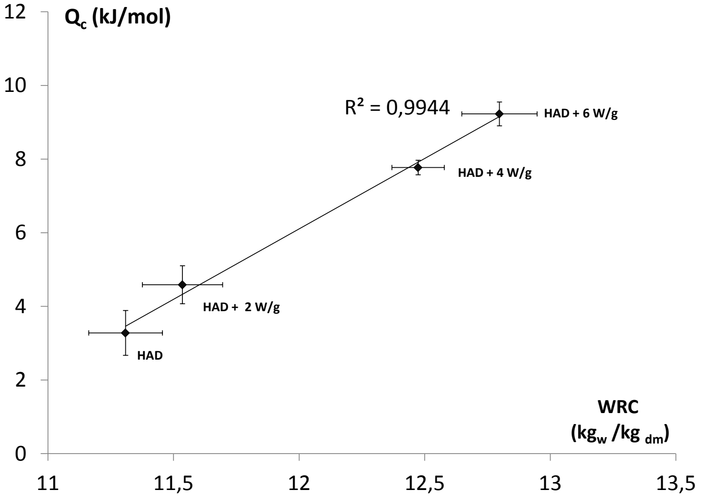

Figure 9. Isosteric heat of dried product with regard to its Water Retention Capacity.

In order to demonstrate and support the theory of shrinkage/swelling explained at macroscopic level in figure 7, it is necessary to analyse the microscopic deformations. In this sense, photographies of fresh and dried samples obtained by stereomicroscope and Cryo-SEM techniques have been analysed (Figure 10). In the figure it is possible to observe fresh samples (Figure 10A) and dehydrated by HAD (Figure 10B) and HAD+MW at three levels of MW energy and after 60 min of drying (2W/g Figure 10C, 4 W/g Figure 10D and 6 W/g Figure 10E). In this figure it is possible to observe the peel tissue or flavedo (F) with the epidermal and hypodermal layers that surround a massive parenchyma or albedo (A) with numerous oil glands cavities or trichomes (T). Micrography of fresh samples shows turgent cells with spherical shape, and the stereography show spherical trichomes (Figure 10A), nevertheless samples treated by HAD showed a general shrinkage of the tissue, being also compacted (low gas phase), and the trichomes are deformed in the sense of the peel contraction induced by the parenchymatic dehydration (Figure 10B). However, these trichomes keep its overall volume because its main content is essential oil (hydrophobic). Micrographies of Figure 10 were taken after 60 min of drying, at this time point the samples treated by HAD + MW showed a macroscopic swelling that was observed in volume variation (Figure 7), this phenomenon is also appreciated in the micrographies which show more gas phase than samples treated by HAD (Figure 10 C, D, E). Moreover, the trichomes were deformed as occurred in samples treated by HAD induced by parenchymatic dehydration. Macroscopic swelling, show in figure 7, and described in figure 10 is not homogeneous, focusing in the parenchymatic tissue (albedo).

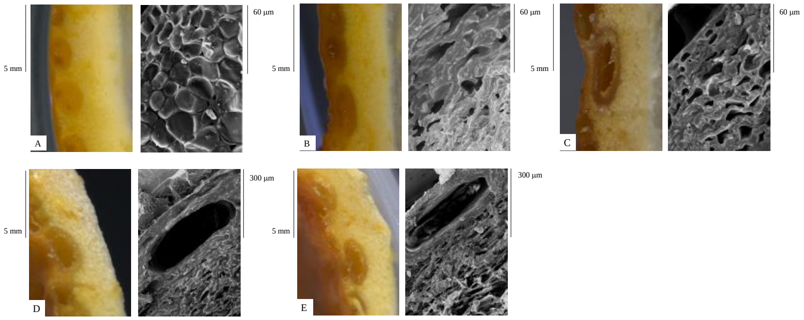

Figure 10. Microstructure analysis of fresh and dried orange peel samples (60 min of drying), where (A) fresh orange peel samples, 1000x; (B) HAD samples, 1000x; (C) HAD + 2 W/g, 1000x; (D) HAD + 4 W/g, 200x; (E) HAD + 6 W/g, 200x. Where: E, Epidermis; IP, Inner parenchyma; GC, Gland cells.

This phenomenon can be better observed in figure 11. As was explained before, at the beginning of drying, samples suffered a drastic reduction of volume associated to the evaporation of water from sample surface, causing the shrinkage of flavedo, producing the crusting effect when the glass transition is reached. The high shrinkage of flavedo and low contraction of the trichomes produces spherical bulges in the surface peel, with the shape of the trichomes (Figure 11C). Nevertheless, the internal evaporation induced by microwaves produces an albedo swelling, causing crispy effect when the glass transition is reached, increasing the available surface to adsorb water and therefore increasing the WRC.

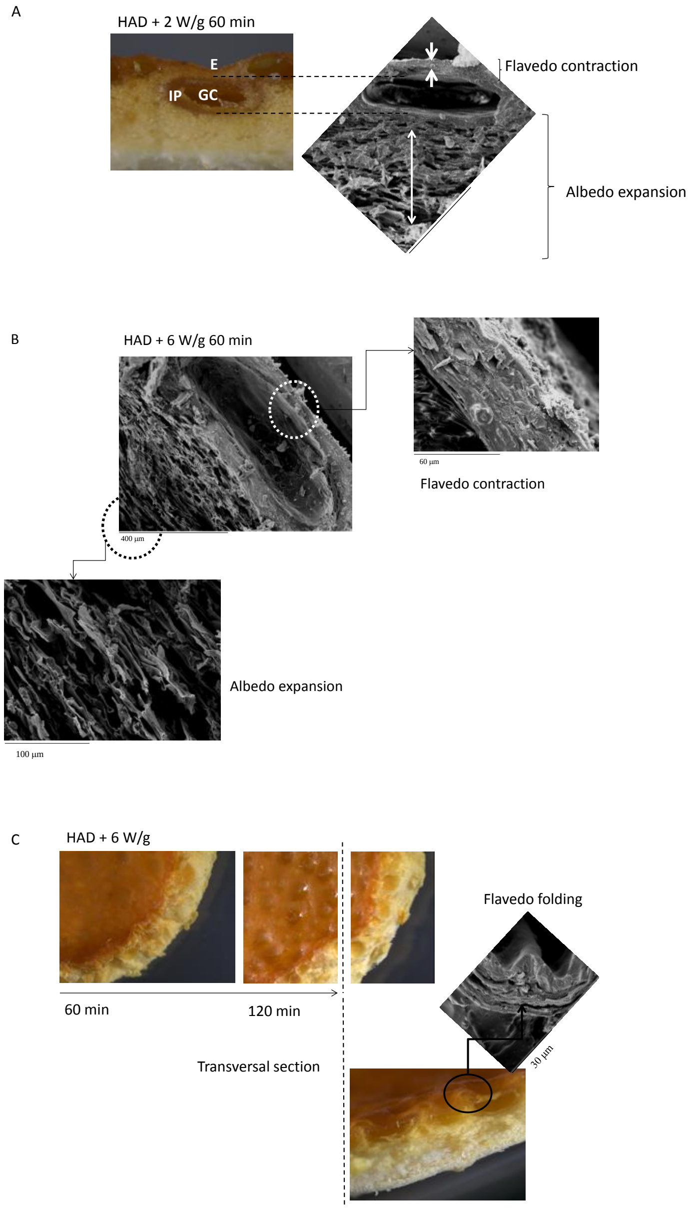

Figure 11. Microstructure analysis of orange peel samples (A) dried by HAD + 2 W/g during 60 min (B) HAD + 6 W/g during 60 min (C) HAD + 6 W/g during 120 min. Where: E, Epidermis; IP, Inner parenchyma; GC, Gland cells.

4. Conclusions

A desorption isotherm of orange peel dried by different treatments (HAD+MW) has been developed and it has been shown that GAB model can be used to predict moisture from a_w measurements. Macro and Microstructural transformations have been described explained by water interactions with tissue. Shrinkage/swelling phenomena have been observed depending on the MW power and on the nature of the tissue.

5. Acknowledgements

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6. References

Al-Muhtaseb, A. H., McMinn, W. A. M., & Magee, T. R. A. (2002). Moisture Sorption Isotherm Characteristics of Food Products: A Review. Food and Bioproducts Processing, 80(2), 118-128.

Andrade, R. D., Lemus, R., & Pérez, C. E. (2011). Models of sorption isotherms for food: uses and limitations. Vitae, 18(3), 325-334.

Bejar, A. K., Kechaou, N., & Mihoubi, N. B. (2011). Effect of Microwave Treatment On Physical and Functional Properties of Orange (Citrus Sinensis) Peel and Leaves. J Food Process Technol, 2(2), 1-7.

Bejar, A. K., Mihoubi, N. B., & Kechaou, N. (2012). Moisture sorption isotherms - Experimental and mathematical investigations of orange (Citrus sinensis) peel and leaves. Food Chemistry, 132(4), 1728-1735.

Bergese, P. (2006). Specific heat, polarization and heat conduction in microwave heating systems: A nonequilibrium thermodynamic point of view. Acta Materialia, 54(7), 1843–1849.

Castro-Giráldez, M., P. J. Fito, C. Chenoll, & P. Fito. (2010). Development of a dielectric spectroscopy technique for the determination of apple (Granny Smith) maturity. Innov. Food Sci. Emerg. Technol. 11(4):749-754.

Castro-Giráldez, M., P. J. Fito, M. Dalla Rosa, & P. Fito. (2011a). Application of microwaves dielectric spectroscopy for controlling osmotic dehydration of kiwifruit (Actinidia deliciosa cv Hayward). Innov. Food Sci. Emerg. Technol. 12(4):623-627.

Castro-Giráldez, M., P. J. Fito, & P. Fito. 2011b. Application of microwaves dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic apple tissue. J. Food Eng. 104(2):227-233.

Demirel Y. & Sandler, S.I. (2001). Linear-nonequilibrium thermodynamics theory for coupled heat and mass transport. International Journal of Heat and Mass Transfer, 44(13), 2439–2451.

Edrisi Sormoli, M., & Langrish, T. A. G. (2015). Moisture sorption isotherms and net isosteric heat of sorption for spray-dried pure orange juice powder. LWT - Food Science and Technology, 62(1, Part 2), 875-882.

Fava, F., Zanaroli, G., Vannini, L., Guerzoni, E., Bordoni, A., Viaggi, D., . . . Brendle, H.-G. (2013). New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). New Biotechnology, 30(6), 647-655.

Fernández-López, J., Sendra-Nadal, E., Navarro, C., Sayas, E., Viuda-Martos, M., & Alvarez, J. A. P. (2009). Storage stability of a high dietary fibre powder from orange by-products. International Journal of Food Science & Technology, 44(4), 748-756.

Ghanem, N., Mihoubi, D., Kechaou, N., & Mihoubi, N. B. (2012). Microwave dehydration of three citrus peel cultivars: Effect on water and oil retention capacities, color, shrinkage and total phenols content. Industrial Crops and Products, 40(0), 167-177.

Hossain, M. D., Bala, B. K., Hossain, M. A., & Mondol, M. R. A. (2001). Sorption isotherms and heat of sorption of pineapple. [Article]. Journal of Food Engineering, 48(2), 103-107.

Igual, M., Contreras, C., & Martinez-Navarrete, N. (2010). Non-conventional techniques to obtain grapefruit jam. Innovative Food Science & Emerging Technologies, 11(2), 335-341.

Kowalski, S.J., Rajewska, K. & Rybicki, A. (2005). Stresses Generated During Convective and Microwave Drying. Drying Technology, 23, 1875–1893.

Labuza, T. P. a. A., B. (2007). Water Activity Prediction and Moisture Sorption Isotherms. In G. V. Barbosa-Cánovas, A. J. Fontana, S. J. Schmidt & T. P. Labuza (Eds.), Water Activity in Foods: Fundamentals and Applications (Vol. 109-154). Iowa, USA: IFT Press and Blackwell Publishing.

Larrauri, J. A. (1999). New approaches in the preparation of high dietary fibre powders from fruit by-products. Trends in Food Science & Technology, 10(1), 3-8.

Quirijns, E. J., van Boxtel, A. J. B., van Loon, W. K. P., & van Straten, G. (2005). Sorption isotherms, GAB parameters and isosteric heat of sorption. Journal of the Science of Food and Agriculture, 85(11), 1805-1814.

Rizvi, S. S. H., & Benado, A. L. (1984). Thermodynamic properties of dehydrated foods. Food Technology, 38(3), 83-92.

Talens, C., Castro-Giráldez, M., Fito, P.J., (2015). A thermodynamic model for hot-air microwave drying of orange peel. Journal of Food Engineering, in press.

Traffano-Schiffo, M.V., Castro-Giráldez, M., Fito, P.J. & Balaguer, N. (2014). Thermodynamic model of meat drying by infrarred thermography. Journal of Food Engineering, 128, 103–110.

RESULTADOS: Artículo 4.3

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Study of the effect of microwave power coupled with hot air drying on orange peel by dielectric spectroscopy

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ABSTRACT

Monitoring moisture t and water activity during drying is crucial for process optimization, avoiding inadequate uses of energy. The main objective of this work was to study the dielectric properties of orange peel during hot air drying at 55 ºC (HAD) and microwave power coupled with hot air drying at different power intensities (2 W/g, 4 W/g and 6 W/g). At 5, 15, 40, 60 and 120 min mass, aw, moisture, and permittivity were measured in fresh and dried samples. Results allowed developing a dielectric isotherm technique by adapting the GAB model to predict aw in dried orange peel by using ' (20 GHz). The physical meaning of the dielectric isotherm parameters (ε_0' and Cd) was studied. The value of ε_0' at 20 GHz (γ-dispersion) represents the induction effect of the minimum quantity of adsorbed water or the monomolecular moisture layer. The parameter Cd is related with isosteric heat, as well as the C parameter of the GAB model. The application of MW power produced an increase of isosteric heat or adsorption energy of the monomolecular layer, improving surface tension of samples and thus the hygroscopicity, explaining the reduction of the ε_0' independently of the quantity of the water molecules adsorbed.

Keywords: permittivity, GAB model, isotherms, orange peel, hot air–microwave drying

1. Introduction

Drying costs are a major issue in most valorization processes, especially when the water content of the material is as high as citrus by-products (85 %), being critical for their economic feasibility. Therefore, moisture monitoring plays a key role in food processing operations such as drying. However, water interaction with air and food depends more on water activity than on moisture, because the reactivity and the mobility of water are directly related with the water activity. The most common and faster tool to obtain the water activity from the moisture is the sorption isotherm. Sorption isotherms relate water activity to water content of a food product at a certain temperature and pressure. The sorption isotherms have an important role in the quantitative approach to the prediction of shelf-life of dried foods, due to their sensitivity to moisture and water activity changes.

On the other hand, the research of electrical properties of food systems has received tremendous attention in the recent years due to the increased development and application in the range of Hz to THz (radiofrequency, microwaves and infrared) for heating, drying or process monitoring in the food industry. The physical properties that define the heating capability of any material are permittivity for the photon electric interactions and permeability for the photon magnetic interactions (Pozar, 2012). They are affected by many different factors, depending on the range of frequency of the photon flux emitted (Castro-Giráldez, Balaguer, Hinarejos, & Fito, 2014), such as amount of water, temperature, structure (i.e. charge conformation of proteins) and chemical composition (i.e. electrolytes), especially on the presence of mobile ions (Castro-Giráldez, 2010). In the case of electric properties, the permittivity must be explained as a vector number, polar or complex. Permittivity explained as a complex number has two parameters, the dielectric constant ε' and the loss factor ε'', being the real and imaginary terms of permittivity (ε), respectively. The dielectric constant is related to the material ability to absorb and store electric energy, and the loss factor is related to the dissipation of the electric energy in other energies such as thermal energy.

In the range of microwaves, the interaction of the photon flux with biological tissue produces two main dispersions, γ-dispersion and ionic conductivity. The γ-dispersion is due to the dipolar molecules orientation and induction, producing electric storage and dissipation of the electric energy in other energies such as mechanical and thermal energies. The main dipolar molecule of plant tissue is water (Castro-Giráldez, Fito, Chenoll, & Fito, 2010, Castro-Giráldez, Fito, Dalla Rosa & Fito, 2011a, Castro-Giráldez, Fito & Fito, 2011b). The other important effect in microwave range is ionic conductivity. It affects only to the loss factor, because it only produces a repulsion of charged molecules, transforming electric energy into others.

Dielectric spectroscopy has been used for many applications as non-destructive technique for monitoring different processes: pork meat salting (Castro-Giráldez, Fito, & Fito, 2010; Kent, Peymann, Gabriel, & Knight, 2002; Lyng, Zhang, & Brunton, 2005), brewing (Velázquez-Varela, Castro-Giráldez, & Fito, 2013), dehydration (Feng, Tang, & Cavalieri, 2002) and osmotic dehydration of apple (Castro-Giráldez, Fito, & Fito, 2011) and kiwi (Castro-Giráldez, Fito, Dalla Rosa, & Fito, 2011) and also for determination of apple maturity (Castro-Giráldez, Fito, Chenoll, & Fito, 2010). Traffano-Schiffo, Castro-Giráldez, and Fito (2015) analyze the viability of monitoring drying meat processes by using dielectric properties measurements at microwaves frequencies. The authors showed that there was a direct relationship between the dielectric loss factor with respect to sample surface and the number of water molecules at 20 GHz, obtaining also the desorption isotherm. This relationship can also be used for determining food product composition by applying dielectric spectroscopy. Iaccheri et al. (2015) studied water features in green and roasted coffee beans by dielectric spectroscopy.

Talens, Castro-Giráldez, and Fito (2015) analyzed the dielectric loss factor at 2.45 GHz (most commonly used MW frequency in Europe) of orange peel dried by hot air-microwave drying in order to quantify the amount of microwave energy that was absorbed and transformed into heating energy. This calorific energy was absorbed by the water molecules because at 2.45 GHz the relaxations phenomena were caused by the induction of polar molecules like water. Fava et al. (2013) also applied microwave drying to citrus by-products in order to dehydrate the final product for further conversion into dietary fiber with optimal microbial, sensory and technological properties.

In microwave assisted drying processes, the knowledge of dielectric properties and parameters that affect their values allows to predict moisture content, water activity and drying kinetics (Barba, 2012). The aim of this work was to develop and to determine dielectric tools to predict the moisture and water activity by using dielectric spectroscopy and sorption isotherms of orange peel dried by microwave power coupled with hot air drying.

2. Materials and Methods

Oranges (*Citrus sinensis* (L.) Osbeck var Washington Navel) were bought from a local supermarket in Valencia (Spain). Orange peels were used for the experiments. 60 orange peel cylinders (20 mm diameter and 3 mm thickness) were cut with a core borer. A diagram of the experimental procedure is shown in Figure 1.

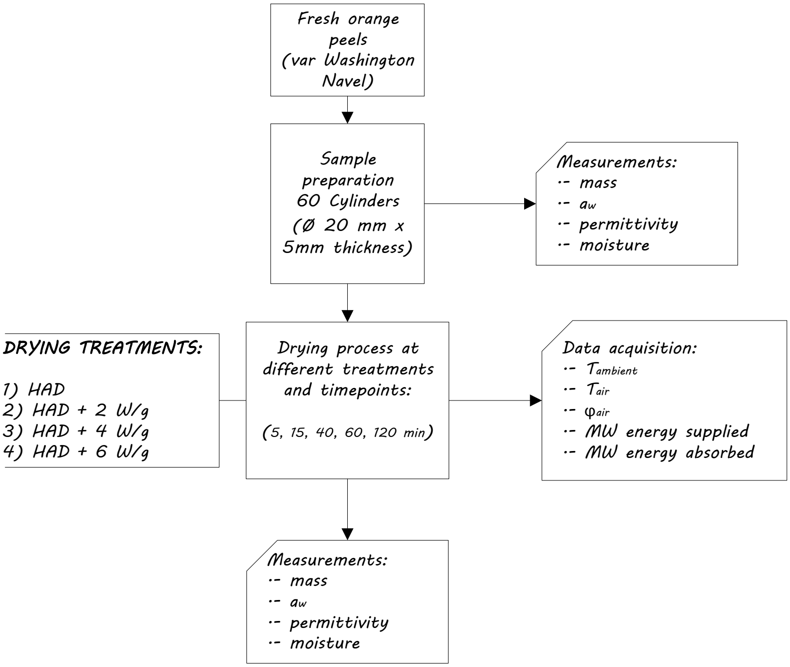


Figure 1. Schematic diagram of the experimental procedure

Samples were subjected to hot air drying (HAD) and microwave coupled with hot air drying (HAD+MW), using a specially designed HAD+MW oven with maximum output 2000 W at 2450 MHz, coupled to a balance and connected to a computer where air temperature, air velocity and incident microwave energy could be controlled. In order to measure incident and reflected energy a directional coupler with power meter was also connected to the computer (Figure 2). Different measurement indicators were used for process control (air drying temperature, air velocity, ambient temperature and relative humidity).

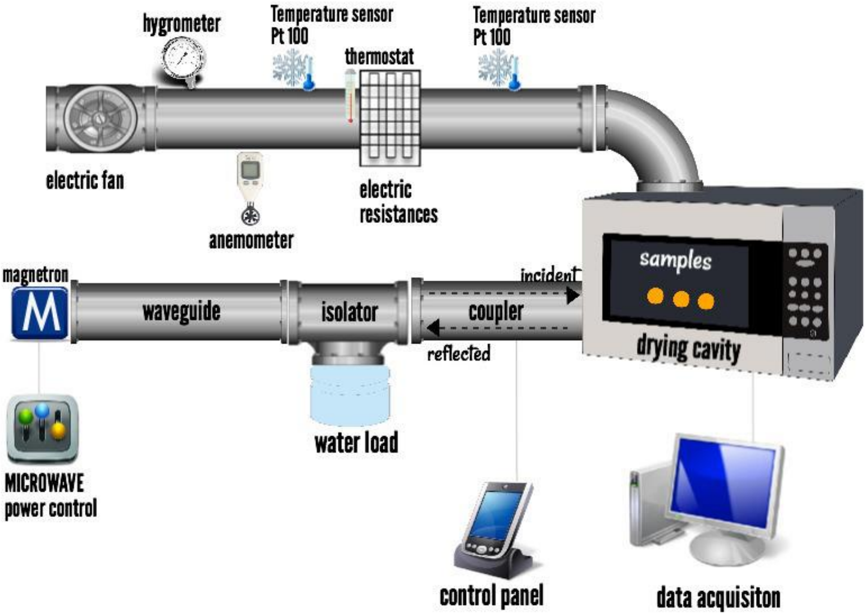


Figure 2. Schematic description of the laboratory equipment used to dry samples.

For the experiments, air velocity was 2.5 m/s, air temperature 55 ºC and the MW energy was 0, 2, 4 or 6 W/g. The microwave energy applied (determined by using the IEC-test) was selected such that samples did not burn during drying.

Orange peel samples were placed with flavedo side up on the dryer grid to facilitate mass transfer. Four drying experiments were carried out (HAD, HAD + 2 W/g, HAD + 4 W/g and HAD + 6 W/g). Three orange peels samples were used for each drying time (5, 15, 40, 60 and 120 min). These 3 samples were removed at each time point and were equilibrated at 25ºC for 5 h in aqualab® disposable sample cups sealed with parafilm®, in order to eliminate the concentration profiles in samples. The next three samples were then placed in the drier.

Samples weight was determined by a precision balance Mettler Toledo AB304-S (precision ± 0.001 g). Surface water activity was determined by a dew point hygrometer Decagon Aqualab®, series 3 TE (precision ±0.003, dimensionless) (Decagon Devices Inc., Washington, USA). Measurements were done in structured samples (not minced), thus a_w obtained was considered surface a_w. Water content of representative fresh orange peels and 120 min dried samples was determined by drying in a vacuum oven at 60ºC until constant weight was reached (AOAC method 934.06, 2000). The moisture content of the sample at intermediate drying stages was calculated from the weigh lost during drying.

The permittivity was measured with an Agilent 85070E open-ended coaxial probe connected to an Agilent E8362B Vector Network Analyser. The system was calibrated by using three different types of loads: air, short-circuit and 25ºC Milli®-Q water. Once the calibration was made, 25ºC Milli®-Q water was measured again to check calibration suitability. Permittivity was measured by placing the probe on the surface of the samples. All determinations were made from 500 MHz to 20 GHz. The measurements were made in triplicate.

The desorption isotherm was fitted following the GAB model using Equation 1 (van den Berg and Bruin, 1981):

$$X_W = \frac{X_{W0}\ C\ a_w}{(1\text{-}K\ a_w)(1+(C\text{-}1)a_w)} \qquad (1)$$

Where: X_w corresponds to the orange peel moisture (kg_w/kg_{dm}), X_{W0} is the monomolecular moisture layer (kg_w/kg_{dm}), C is the energy constant and K is an empirical parameter, both dimensionless (Maroulis, Tsami, Marinos-Kouris, & Saravacos, 1988).

3. Results and discussion

Mass variation of samples during the drying process can be obtained by the following equation:

$$\Delta M = \frac{M^t\text{-}M^0}{M} \qquad (2)$$

Where M represents the mass of the sample (kg), the superscript t represents the process time, being 0 the initial time. The mass variation can be observed in Figure 3.

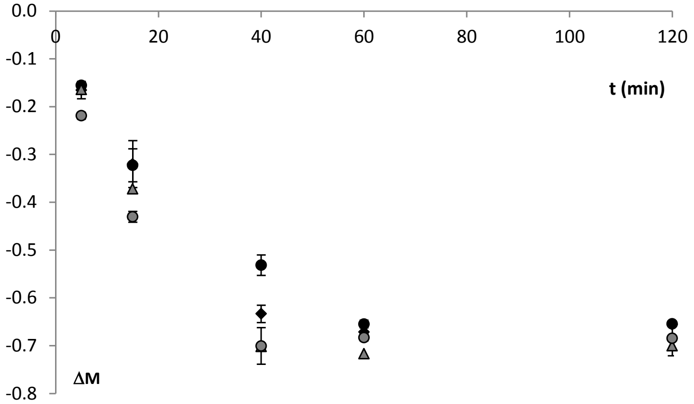


Figure 3. Mass variation of orange peel treated by different drying treatments: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

A faster mass reduction can be observed in microwave drying treatments increasing with microwave energy. At 5 and 15 min, very significant differences ($p \leq 0.01$) were found between HAD + 6 W/g and the rest of the treatments. At 40 min, significant differences ($p \leq 0.05$) were appreciated among HAD and 2 W/g and the rest of the treatments. No differences between 4 and 6 W/g were appreciated mainly because a low level of mass was reached caused by water loss; the low level of moisture reached decreases the effect of MW power. After 60 min of drying, treatments converged to the threshold of the thermodynamic properties of dry air ($\Delta\mu_w|^i = 0$ or $a_w|^{sample} \approx \varphi|^{air}$). Figure 4 shows the sorption isotherms obtained for each drying treatment (experimental points) and the GAB model applied for each treatment. GAB parameters are shown in Table 1.

Table 1: Estimated GAB parameters (X_{W0}, C and K) and correlated coefficient (R^2) of GAB model for desorption isotherms of orange peel dried by hot air (HAD) and hot air coupled with microwaves (HAD + MW).

GAB Parameters				
Drying treatment	X_{W0} (kg_w/kg_{dm})	C	K	R^2
HAD	0.080	22.33	0.98	0.9342
HAD + 2 W/g	0.080	18.90	0.98	0.9182
HAD + 4 W/g	0.105	70.33	0.99	0.9197
HAD + 6 W/g	0.165	153.04	0.97	0.8493

In order to explain the variation of the GAB parameters with physical sense in the different drying treatments, the permittivity in range of the microwaves was analyzed.

Permittivity in microwave range was measured in fresh and treated samples after 5, 15, 40, 60 and 120 min of drying. In Figure 5 it can be observed the dielectric spectra of the fresh and dried orange peels treated at different microwave power energies.

In the range of microwaves, the interaction of the electric field with biological tissue produces two main dispersions, γ-dispersion and ionic conductivity.

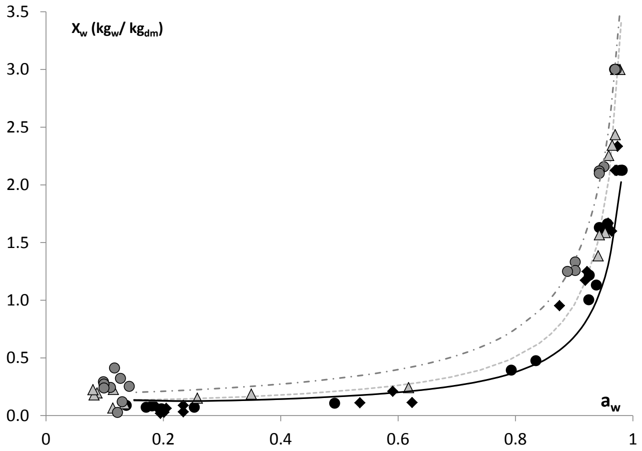
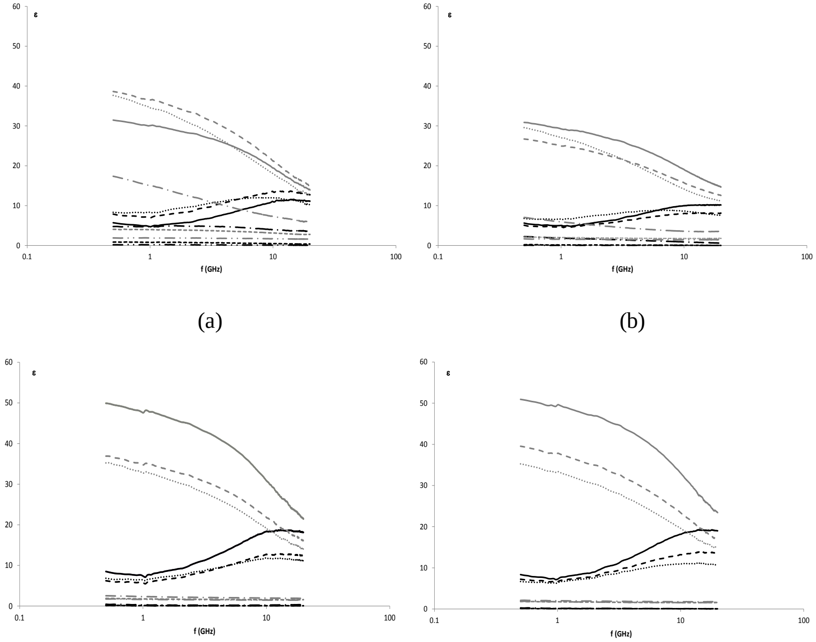


Figure 4. Sorption isotherm of orange peel treated by different drying treatments: experimental points ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g; and GAB model — HAD, — HAD + 2 W/g, - - - HAD + 4 W/g, - • • - HAD + 6 W/g.

The first one mainly represents the induction and orientation phenomena of water, and the second one, represents the conductivity of the electrolytes and weak organic acids. In this figure it is possible to observe at high frequencies (above 1 GHz) the common shape of samples with liquid phase, decreasing the permittivity values with the water losses throughout the treatment. Below 1GHz, in fresh samples, a negative slope of loss factor shows the low ionic strength of the weak organic acids. Ionic conductivity decreases with the drying treatment caused by the limitation of the movement of weak organic acids due to the loss of liquid phase.



(a)

(b)

(c)

(d)

Figure 5. Permittivity (⍰) spectra of orange peels after 0 min (—), 5 min (— — —), 15 min (···), 40 min (-·-), 60 min (−−−) and 120 min (-··-) of drying by different treatments (a) HAD, (b) HAD + 2 W/g, (c) HAD + 4 W/g, (d) HAD + 6 W/g. Grey lines represent the dielectric constant (ε') and black lines represent the loss factor (ε'').

Since there is a progressive loss of liquid phase during the drying process, the dielectric loss factor decreases with time. Therefore it is possible to relate the permittivity at high frequency (dipolar effect) with the quantity of water molecules in equilibrated samples (Traffano-Schiffo et al., 2015). The water molecules can be calculated with the following equation (Eq. 3).

$$N_w = \frac{X_w\ N_A}{Mr_w} \qquad (3)$$

Where N_w represents the water molecules (number of water molecules in dry basis), X_w is the moisture in dry basis (kg_w/kg_{dm}), N_A the Avogadro constant ($6.022 \cdot 10^{23}$ mol^{-1}) and Mr_W the molar mass of water (18 kg_w /$kmol_w$).

Figure 6 shows the linear relation between number of water molecules related with the dry matter (water molecules/kg_{dm}) and the dielectric constant at 20 GHz, frequency close to the dipolar relaxation effect.

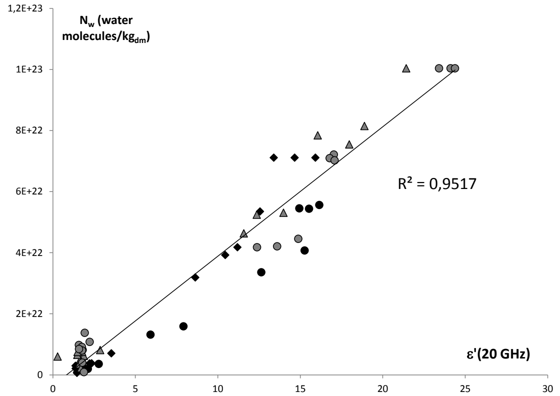


Figure 6. Relation between number of water molecules (N_w) and the dielectric constant at 20 GHz of orange peels dried by different hot air-microwave treatments. Where: ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g.

If the moisture in dry basis explains the dielectric constant, it is possible to develop a dielectric isotherm to predict the water activity in dried samples using equation 4 adapted from GAB model, where ε' (20 GHz) represents the dielectric constant at 20 GHz, close to the water relaxation frequency, ε'_0 is the minimum value of the dielectric constant and C_d and K_d are empirical constants (dimensionless).

$$\varepsilon'(20GHz)=\frac{\varepsilon'_0\, C_d\, a_w}{(1-K_d\, a_w)(1+(C_d-1)a_w)} \qquad (4)$$

Figure 7 shows the dielectric isotherms obtained by adapting the GAB model to dielectric approach previously explained. This figure shows that the dielectric isotherm of HAD treatment is above the rest of treatments. The dielectric isotherm equation (equation 4) applied to the different treatments obtained well fittings (for HAD a R^2 0.8960 for HAD + 2 W/g a R^2 0.9494, for HAD + 4 W/g a R^2 0.8833 and for HAD + 6 W/g a R^2 0.9988).

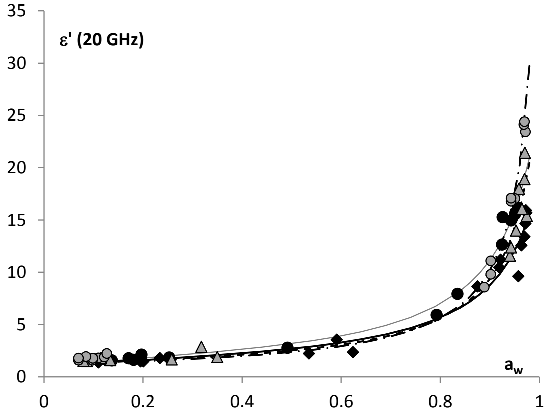


Figure 7. Dielectric isotherm at 20 GHz of orange peel treated by different drying treatments: experimental timepoints ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g and calculated model — HAD, — HAD + 2 W/g, - - - HAD + 4 W/g, - · - HAD + 6 W/g.

The K_d parameters were similar in all treatments and the average value was 0.95 ± 0.02. In order to compare the dielectric isotherms, the parameters of equation 4 have been compared in figure 8. Figure 8 relates in primary axis the minimum dielectric constant with the treatments, where it is possible to observe a linear relation with the MW power showing a negative slope. Minimum value of dielectric constant at 20 GHz (γ-dispersion) represents the induction effect of the minimum quantity of adsorbed water or the monomolecular moisture layer. Therefore, the application of MW power in the dehydration process produces a decrease in the induction of the adsorbed water molecules (ε_0'). This decrease could be caused by the diminution of the X_{w0} (reduction of molecules adsorbed) or the increase of the isosteric heat (increase in the adsorption energy). Figure 8 shows, in secondary axis, the parameter C_d with the treatments. The parameter C_d is a modification of the C parameter of the GAB model, this parameter explains the isosteric heat or the adsorption energy of the monomolecular moisture layer. In this figure, parameter C_d increases with MW power.

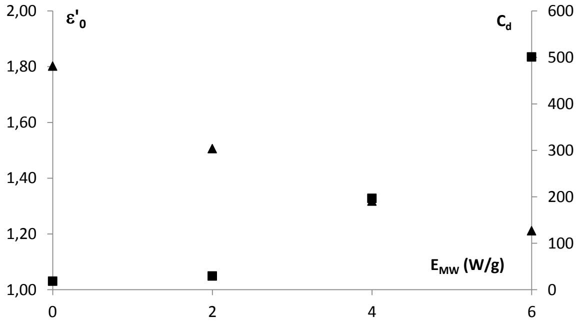


Figure 8. Dielectric isotherm parameters (adapted to GAB model) of orange peels dried by different hot air-microwave treatments: ε'0 (▲) and Cd (■)

Figures 9a and b relate the GAB parameters with the dielectric isotherm parameters. Figure 9a shows the relation between the X_{w0} and the ε'_0, where it is possible to observe that the minimum value of X_{w0} corresponds with the maximum value of ε'_0, in opposite sense the figure 9b shows the linear relation between C and C_d, increasing together with the MW power. Therefore, during a drying process, the application of MW power produces an increase of the isosteric heat or adsorption energy of the monomolecular layer, improving the surface tension of samples and thus the hygroscopicity, explaining the reduction of the ε'_0 independently of the quantity of the water molecules adsorbed.

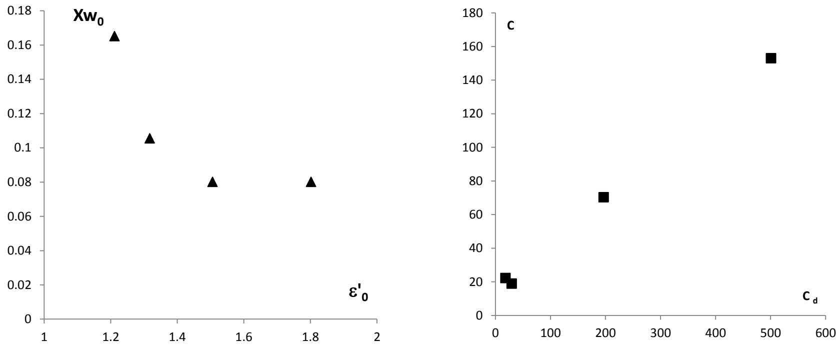


Figure 9. Comparation of the GAB parameters and dielectric isotherm parameters. (a) Relation between X_{W0} and ε'_0 and (b) Relation between C and C_d parameters.

4. CONCLUSIONS

It was possible to develop a dielectric isotherm technique by adapting the GAB model to predict the water activity in dried orange peel by using ε' (20 GHz). The physical meaning of the dielectric isotherm parameters (ε'_0 and C_d) was studied. The value of ε'_0 at 20 GHz (γ-dispersion) represents the induction effect of the minimum quantity of adsorbed water or the monomolecular moisture layer. The parameter C_d is related with isosteric heat or the adsorption energy of the monomolecular moisture layer, as well as the C parameter of the GAB model. The application of MW power produced an increase of the isosteric heat or adsorption energy of the monomolecular layer, improving the surface tension of samples and thus the hygroscopicity, explaining the reduction of the ε_0' independently of the quantity of the water molecules adsorbed.

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6. REFERENCES

Barba, A. A., d'Amore, M. (2012). Relevance of Dielectric Properties in Microwave Assisted Processes, Microwave Materials Characterization

In I. Prof. Sandra Costanzo (Ed.).

Castro-Giráldez, M. (2010). *Estudio de los espectros dieléctricos para el control de calidad de alimentos.* Thesis, Universidad Politécnica de Valencia. (UPV3351)

Castro-Giráldez, M., Balaguer, N., Hinarejos, E., & Fito, P. J. (2014). Thermodynamic approach of meat freezing process. *Innovative Food Science & Emerging Technologies, 23*(0), 138-145. doi: http://dx.doi.org/10.1016/j.ifset.2014.03.007

Castro-Giráldez, M., Fito, P. J., Chenoll, C., & Fito, P. (2010). Development of a dielectric spectroscopy technique for the determination of apple (Granny Smith) maturity. *Innovative Food Science & Emerging Technologies, 11*(4), 749-754. doi: http://dx.doi.org/10.1016/j.ifset.2010.08.002

Castro-Giráldez, M., Fito, P. J., Dalla Rosa, M., & Fito, P. (2011). Application of microwaves dielectric spectroscopy for controlling osmotic dehydration of kiwifruit (Actinidia deliciosa cv Hayward). *Innovative*

Food Science & Emerging Technologies, 12(4), 623-627. doi: http://dx.doi.org/10.1016/j.ifset.2011.06.013

Castro-Giráldez, M., Fito, P. J., & Fito, P. (2010). Application of microwaves dielectric spectroscopy for controlling pork meat (Longissimus dorsi) salting process. *Journal of Food Engineering, 97*(4), 484-490. doi: 10.1016/j.jfoodeng.2009.11.005

Castro-Giráldez, M., Fito, P. J., & Fito, P. (2011). Application of microwaves dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic apple tissue. *Journal of Food Engineering, 104*(2), 227-233. doi: http://dx.doi.org/10.1016/j.jfoodeng.2010.10.034

Fava, F., Zanaroli, G., Vannini, L., Guerzoni, E., Bordoni, A., Viaggi, D., . . . Brendle, H.-G. (2013). New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). *New Biotechnology, 30*(6), 647-655. doi: http://dx.doi.org/10.1016/j.nbt.2013.05.001

Feng, H., Tang, J., & Cavalieri, R. P. (2002). Dielectric properties of dehydrated apples as affected by moisture and temperature. *Transactions of the Asae, 45*(1), 129-135.

Iaccheri, E., Laghi, L., Cevoli, C., Berardinelli, A., Ragni, L., Romani, S., & Rocculi, P. (2015). Different analytical approaches for the study of water features in green and roasted coffee beans. *Journal of Food Engineering, 146*(0), 28-35. doi: http://dx.doi.org/10.1016/j.jfoodeng.2014.08.016

Kent, M., Peymann, A., Gabriel, C., & Knight, A. (2002). Determination of added water in pork products using microwave dielectric spectroscopy. *Food Control, 13*(3), 143-149. doi: http://dx.doi.org/10.1016/S0956-7135(01)00066-4

Lyng, J. G., Zhang, L., & Brunton, N. P. (2005). A survey of the dielectric properties of meats and ingredients used in meat product manufacture. *Meat Science, 69*(4), 589-602. doi: http://dx.doi.org/10.1016/j.meatsci.2004.09.011

Maroulis, Z. B., Tsami, E., Marinos-Kouris, D., & Saravacos, G. D. (1988). Application of the GAB model to the moisture sorption isotherms for dried fruits. *Journal of Food Engineering, 7*(1), 63-78. doi: http://dx.doi.org/10.1016/0260-8774(88)90069-6

Metaxas, A. C., & Meredith, R. J. (1983). *Industrial Microwave Heating*: P. Peregrinus.

Pozar, D. M. (2012). Microwave Engineering: Wiley India.

Talens, C., Castro-Giráldez, M., & Fito, P. J. (2015). A thermodynamic model for hot-air microwave drying of orange peel. *Journal of Food Engineering, in press.*

Traffano-Schiffo, M. V., Castro-Giráldez, M., & Fito, P. J. (2015). Development of a new tool to predict the water activity of meat during drying process by dielectric properties in the microwave range. *Innovative Food Science and Emerging Technologies, in press*.

van den Berg, C., & Bruin, S. (1981). Water activity and its estimation in food systems: theoretical aspects. In L. B. R. F. Stewart (Ed.), *Water Activity: Influences on Food Quality* (pp. 1-61): Academic Press.

Velázquez-Varela, J., Castro-Giráldez, M., & Fito, P. J. (2013). Control of the brewing process by using microwaves dielectric spectroscopy. *Journal of Food Engineering, 119*(3), 633-639. doi: http://dx.doi.org/10.1016/j.jfoodeng.2013.06.03

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Effect of microwave power coupled with hot air drying on process efficiency and physico-chemical properties of a new dietary fiber ingredient obtained from orange peel

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ABSTRACT

Orange by-products are an excellent source of dietary fiber. Hot-air coupled with microwave drying (HAD + MW) can reduce drying time resulting in a more efficient drying process, and can provoke changes in fiber microstructure that modify its technological properties. The main objective of this work was to obtain a fiber ingredient from orange by-products by applying HAD + MW and to compare the efficiency of the process and the physico-chemical properties of the fiber, with conventional hot air drying (HAD). An important reduction in processing time (92 %) and energy consumption (77 %) was achieved, compared to conventional hot-air drying. An increase in particle size due to an increase in porosity during drying improved fiber swelling capacity. Although viscosity of both treatments showed similar values, the higher swelling capacity of HAD + MW-treated fiber provoked a significant decrease in the viscoelasticity of the samples. The drying treatment did not affect chemical composition, water and oil retention capacities, pH or antioxidant capacity of orange fibers. Total dietary fiber content was about 60 % with a ratio of soluble to insoluble fiber of 1:1. Colour was not affected by HAD + MW. The shrinkage-swelling phenomena occurred during drying affected the gradient of the water chemical potential. HAD mainly affects the mechanical term due to the fact that higher mechanical energy is stored during drying and, therefore, more energy could be released during the rehydration. HAD + MW mainly affects surface tension term as it is possible to observe in values of isosteric heat. Therefore, the potential use of HAD + MW as an efficient process for valorisation of citrus by-products into value-added ingredients, with optimum nutritional and technological properties has been shown.

Keywords: hot air–microwave drying, orange peel, energy consumption, dietary fiber particle size, functional properties

NOTATION

MW	microwave drying
HAD	hot air drying
AOC	antioxidant capacity
WRC	water retention capacity
DF	dietary fiber
TDF	total dietary fiber
IDF	insoluble dietary fiber
SDF	soluble dietary fiber
dm	dry matter
j	relative humidity (-)
M	mass per time in wet basis (kg s^{-1})
M'	mass per time in dry basis (kg s^{-1})
x	mass fraction (kg kg^{-1})
X	absolute moisture (kg water kg dry air $^{-1}$)
t	time (s)
h	specific enthalpy (J kg^{-1})
p_s	water saturation pressure (kPa)
C_p	heat capacity at constant pressure (W g^{-1} K^{-1})
ΔH	molar enthalpy (J mol^{-1})
ρ	density (kg m^{-3})
v	velocity (m s^{-1})
S	section (m^2)
E	energy (kW or kWh)
W	microwave energy (W g^{-1})
P	absolute pressure (Pa)
T	temperature (K)
R	ideal gases universal constant (J mol^{-1} K^{-1})
Qc	isosteric heat
Subscripts and superscripts:	
amb	ambient conditions
da	dry air
D	drying conditions
0	initial time
v	vapour
w	water

Introduction

One important source of citrus dietary fiber is the residue from the orange juice industry (Fava et al., 2013). Fiber from citrus can be obtained from edible parts (Lundberg et al., 2014, Pszczola, 2006) and attracts, binds, and manages high levels of water (up to 12 times its weight) in baked goods, meat and poultry products, and sauces. Additionally, citrus peel is a rich source of fiber and antioxidant, but the high levels of astringent compounds make it unsuitable for human consumption (Baker, 1994). Regular consumption of dietary fiber (DF) has been one of the most consistent recommendations of nutritionists and official agencies for the prevention of gastrointestinal and cardiovascular diseases, and also for the prevention and/or treatment of diabetes, hypercholesterolemia and obesity (Howarth et al., 2001, Marlett et al., 2002, Park et al., 2005, Rimm et al., 1996).

The physiological functions of the DF are often attributed to their physico-chemical properties, water holding capacity, swelling, rheological and fat binding properties and susceptibility to bacterial degradation or fermentation (Dikeman Fahey, 2006). By an *in vitro* determination of the hydration or physicochemical properties of dietary fibre *the in vivo* physiological effects of dietary fibre can be predicted (Dreher, 1987; Robertson et al., 2000). In fact, the beneficial healthy effect exerted by soluble fiber, lowering cholesterol and the rate of glucose absorption and post-prandial plasma glucose concentrations, has been associated to their viscosity (Dikeman Fahey, 2006). Insoluble fiber (fiber as part of a plant cell wall) through its increased water holding capacity, promotes laxation by increasing stool mass and softness (McCleary and Prosky, 2008). The principal physiological effect of fiber is its ability to swell after water absorption, which occurs due to three mechanisms: carbohydrates with free polar groups (pectin), interaction with hydrophilic bonds or retention within the matrix (Lopez et al., 1997).

Most fractions of DF are the major constituents of plant cell walls (cellulose, lignin, hemicellulose, pectins, gums and mucilages) (Selvendran, 1984), therefore, functional properties are also related to the chemical structure of the plant polysaccharides, The physico-chemical properties of the original products may be altered during processing operations such as drying, modifying consequently the functional properties of the ingredient (DF) obtained (Bocco et al., 1998).

A main disadvantage of conventional hot-air drying (HAD) is that it takes a long time, even at high temperature, which in turn may cause serious damage to the product's quality attributes, such as flavour, colour, texture, nutrient status and beneficial substances to health (Nijhuis et al., 1998, Tsami et al., 1998). The application of coupled drying technologies such as hot-air microwave drying (HAD + MW) could reduce the drying time and preserve the quality of orange by-products (Fava et al, 2013, Talens et al, 2015). Microwave drying have achieved considerable attention in the recent past, gaining popularity because of its advantages over conventional heating such as reducing the drying time of biological material with small quality loss (Arslan and Ozcan, 2010). The theoretical basis of drying treatments by hot air is to produce water fluxes from food sample to the air stream induced by a gradient of water chemical potential (Demirel and Sandler, 2001). The main engine of the water transport is the gradient between a_w and relative humidity (Traffano-Schiffo et al., 2014). In hot air drying, working below 100ºC, the water evaporation is produced in the surface of the food product. In these cases, it is useful to couple hot air drying with other techniques in order to increase the process of water removal. A common technique used to be coupled with hot air drying is MW (Bergese, 2006, Kowalski et al., 2005). Talens et al. (2015) reported higher expansion phenomena in orange peel at 14 % moisture after HAD+MW drying at 6 W/g. The expansion of fibrous materials with the aim of increasing its specific surface area, thus generating a greater retention of water and/or apparent viscosity, is one of the strategies used to improve the functionality of vegetable fibers (Gu et al., 2001, Lundberg, 2005, Turbak, 1983). At the same time, the microstructural changes that occur during drying allow to explain the functional properties of the products obtained at the end of the processing (Bejar et al., 2011, Ghanem et al., 2012, Santana, 2009).

Therefore, the aims of this work were to compare the energy consumption of two drying methods (hot air and hot air-microwave drying) and the physico-chemical and technological properties of the orange fiber obtained from citrus by-products.

Materials and methods

Fiber obtention process

Orange peels (*Citrus sinensis* (L.) Osbeck var Lane Late) were obtained after juice extraction by using a rotary press machine (Zumex, Valencia, Spain). Orange by-products were minced to 0.5 - 1 cm particle size using a cutter (Stephan UMC-5, Stephan, Germany) and blanched in water (vol 1:4) at 65 ºC for 5 min. Afterwards, samples were centrifuged at 1000 g for 5 min using a high performance centrifugal machinery (Comteifa, Barcelona, Spain).

Blanched samples were treated in batches of 500 g by two different drying methods in order to compare process efficiency and the physico-chemical and rheological characteristics of the fiber ingredient obtained. A pilot scale 2450 MHz electromagnetic microwave equipment (MMP20T, Sairem S.A., Miribel, France) was used. Drier dimensions were 0.66 m x 0.66 m x 0.83 m, air velocity was 7 m/s, ambient temperature was 15 ºC and relative humidity was 60 %. For the energy consumption calculations, HAD, HAD + 2 W/g, HAD + 4 W/g and HAD + 6 W/g were studied. For physico-chemical analysis, samples treated by HAD and HAD + 6 W/g were compared. Ambient temperature was 15 ºC, relative humidity was 60 %, hot air temperature was 55 ºC and air velocity was 7 m/s. Drier dimensions were 0.66 m x 0.66 m x 0.83 m. For HAD experiments, blanched samples were dried at 55 ºC in the same equipment as described above without applying microwaves. Samples weight at different times (5, 15, 40, 60 and 120 min) was measured by a precision balance Mettler Toledo AB304-S (± 0.001g).

After drying, samples were milled using an ultracentrifuge mill (ZM 100, Retsch, Germany) with a sieve of 500 µm. At this stage, powder samples were sealed in plastic bags for further characterization.

Compositional analysis

Samples were analyzed according to the ISO recommended standards: Moisture by 1442:1997, (ISO, 1997), ash by ISO 936:1998 (ISO, 1998), protein content by ISO 937:1978 (ISO, 1978) and fat content by ISO 1443:1973 (ISO, 1973). Total sugars were analyzed by Luff–Schoorl method for reducing sugars (Lees, 1968)

The total protein content was determined by the Kjeldahl method using the Digestion Unit K-435 and a distillation unit B-324 (Buchi Labortechnik AG, Switzerland). A correction factor of 6.25 was used. Crude fat was extracted with petroleum ether using a Soxtec HT 1043 extraction unit (Foss Tecator, Denmark). The ash content was performed in a muffle furnace (Carbolite CWF 1100, Carbolite, UK) set to 550 ºC. The moisture content was determined at 105 ºC (Memmert, Germany), for approximately 18 h until constant weight. The carbohydrate content was determined by the difference. Total, soluble, and insoluble dietary fiber was determined by the AOAC enzymatic-gravimetric method, 991.43. Neutral detergent fiber and acid detergent fiber was analyzed by the gravimetric method AOAC 973.18. Cellulose content was calculated as the difference between acid detergent fiber and acid detergent lignin. Finally, hemicellulose content was determined according to NF V 18-122 (AFNOR, 1997) .

The total caloric value was calculated by adding up the calories provided by the energy-containing nutrients and considering 4 kcal/g for protein, 9 kcal/g for fat, 4 kcal/g for carbohydrate and 2 Kcal/g for dietar fiber (Regulation EU No 1169/2011, 2011)

Antioxidant capacity

The antioxidant capacity (AOC) was measured by DPPH method using Trolox as standard (0-225 mg/L) adapted from Brand-Williams et al. (1995) to a plate reader spectrophotometer (Varioskan, Thermo Scientific, USA). Briefly, 20µl of citrus extract (without dilution) or Trolox standards were added to 280 µl of 25 mg/l DPPH solution (dissolved in methanol). The absorbance of the remaining DPPH was measured after 30 min at 515 nm. The final results were expressed as mg of Trolox equivalents (TE) per kg of citrus dry matter (mg TE/kg dm)

Colour

Colour was measured following CIELab scale. L*, a* and b* parameters were measured using a Minolta CM 3500d colorimeter (Osaka, Japan), where L* is the parameter that measures lightness, a* the tendency towards red and b* the tendency towards yellow.

Measurement of pH

The pH was determined using a pH-meter (GLP 21, Crison Instruments,Spain) ccording to Andrade et al. (2014) with minor modifications. The instrument was calibrated with standard pH values of 4.0 and 7.0. Concentrations of 2% sample in distilled water (w/v) were prepared in triplicate and placed in a magnetic stirrer for 30 minutes and pH was measured.

Particle size distribution

Analysis of the particle size distribution was carried out using a laser diffractometer Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK) which has a particle size distribution range of 0.02 – 2000µm. The Mie theory was applied by considering a refractive index of 1.5 and absorption of 0.01. The samples were analyzed on laser diffraction with wet analysis using the Hydro S dispersion unit. Dry analysis was also performed using the Scirroco dry dispersion unit. Samples were diluted in de-ionised water at 2,000 rpm during 10 min. An obscuration rate of 15 % was obtained at each measurement. $D_{3,2}$ (surface weighted mean diameter) and $D_{4,3}$ (volume weighted mean diameter) were obtained. The volume-weighted average diameter is sensitive to the presence of large particles, whereas the surface-weighted average diameter is more sensitive to the presence of small particles.

Water and oil retention capacity

For water retention capacity (WRC) samples (0.5 g ± 0.0001 g) were hydrated in 20 mL of distilled water in a 50 mL falcon tube and left overnight to ensure the fiber was fully hydrated. Then, the tubes were centrifuged at 1000 × *g* for 10 min (adapted from Robertson et al., 2000). The supernatant was decanted and the tubes were carefully inverted to drain residual unbound water from the sample. The remaining pellet was dried overnight in an oven at 105 ºC and weighed to consider possible solid matter losses in the draining step. For oil retention capacity (ORC), 20 mL of sunflower oil was added to 0.5 g of sample in a 50 mL falcon tube and left overnight. The tubes were then centrifuged at 1000 × *g* for 10 min. The supernatant was decanted and the tubes were carefully inverted to drain residual oil from the sample. WRC and ORC were calculated as the amount of water or oil retained by the pellet (g/g_{dm}).

Swelling capacity

Swelling capacity, defined as the ratio of the volume occupied when the sample is immersed in excess of water after equilibration to the sample weight, was measured by the method of Raghavendra et al. (2004). To 0.2 g of dry sample placed in a graduated test tube; around 10 mL of water was added to hydrate the sample for 18 h; then the final volume attained by fiber was measured and expressed as volume/g of original sample (dry weight).

Rheology

The rheological characterization of the samples was carried out using a controlled-stress AR 2000 rheometer (TA Instruments, Leatherhead, United Kingdom). Stainless steel parallel plate geometry of 40 mm diameter was used with a gap of 2 mm. A Peltier plate was used to equilibrate and maintain the samples temperature at 20°C during the measurements. A spoon was used to carefully load the sample on the bottom plate, trying to minimize the structure breakdown. Samples rested for 2 minutes before any determination was carried out to allow the stress induced during loading to relax.

Large and small deformation analyses were used for samples characterization. A flow curve (large deformation) analysis was performed at increasing logarithmic shear rates, from 0.001 to 100 s^{-1} to determine the samples viscosity. Casson model was applied to calculate the yield stress and the apparent viscosity of each sample (Lundberg et al., 2014). Dynamic oscillatory stress sweeps (small deformation) were applied to investigate the viscoelastic behavior of the samples with a range of stress values from 0.1 to 2000 Pa at a constant frequency of 1 Hz. All the measurements were carried out at least by triplicate.

Microscopy

Dehydrated particles were examined under a light microscope (DMLM Leica Microsystems) with a CCD camera incorporated which allowed acquiring images for further analysis. Description of dehydrated samples was based on examining sample surface variation each second over 40 s from dry until fully hydrated. Subsequent treatment and measurement of the images was carried out by using Adobe Photoshop v 7.0; Image J, 1.36 b free version. Measurements consisted of obtaining the surface area of each sample. The response of particles to rehydration was assessed by examining 5-10 particles per treatment.

Statistical analysis

To determine statistical differences among samples, the non-parametric Wilcoxon signed rank test was used with confidence levels of 95 % ($p \leq 0.05$) using the program Statgraphics Centurion XVI 16.1.

Results and discussion

The basic composition of the citrus fibers obtained in this study is shown in Table 1. There were no significant differences ($p \leq 0.05$) on moisture, protein, fat, ash, sugar or carbohydrates among the fibers obtained by HAD or by HAD + MW. Considering the variability due to seasonality, cultivar, production process and region these values can be considered consistent with those reported by Lundberg et al. (2014) for moisture (7.42 ± 0.73), protein (8.15 ± 0.45 %), fat (1.05 ± 0.12 %), ash (2.65 ± 0.26 %), carbohydrates (80.73 ± 0.92 %) and sugar (7.36 ± 2.68 %) of commercial citrus fiber obtained from by-products of orange juice production. Total dietary fiber content was not significantly different among samples. The value obtained (60.85 ± 5.25 for HAD and 59.10 ± 1.75 for HAD + MW) was lower than that reported by Lundberg et al. (2014) which was approximately 73 %, this might be due to differences among cultivars as reported by Grigelmo-Miguel and Martín-Belloso (1998).

Soluble and insoluble dietary fibers contents represented respectively approximately 50 % of total dietary fiber, with a slightly higher value for insoluble dietary fiber. This ratio represents an equilibrated balance for a fiber ingredient as insoluble DF is important to intestinal regulation, whereas the soluble fraction is involved in reduction of both blood cholesterol and intestinal glucose absorption (Fabek et al., 2014). Furthermore, The main advantage of DF from orange peel, compared with other alternative sources, such as cereals, was its higher proportion of soluble dietary fiber (Wang et al., 2015). It is known that generally, the most suitable SDF:IDF ratio for food ingredients is close to 1:2 (Andrade et al., 2014, Primo-Yúfera and Carrasco-Dorrien, 1987), hence this ingredient is optimum for human consumption from the digestibility point of view. In addition, the percentage of soluble fiber was higher than other reported by other authors who also obtained dietary fiber from orange peel. Andrade et al. (2014) reported a ratio SDF:IDF ranging from 1:1.2 to 1:1.4; and Grigelmo-Miguel and Martín-Belloso (1998) obtained a ratio ranging from 1:1.7 to 1:2.2.

The structural makeup (i.e. the polymeric backbone and side chain units of fibers varies with the source, strongly influencing the properties of high-fiber ingredients (Nelson, 2001). Its structural make up determines fiber two dimensional structure which influences its three-dimensional structure (i.e. how the polymer interact with itself and other polymers). The soluble fraction of orange fiber is mainly composed by carbohydrates such pectins that dissolves in water to form a viscous, or gel-like, substance.

The insoluble fraction of orange fiber is mainly composed of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose contents were lower than those reported by Lundberg et al., 2014, 15.95 ± 0.02 % and 10.06 ± 0.15 %, respectively. However, lignin content was higher than that estimated in another study carried out by Grigelmo-Miguel and Martín-Belloso (1998) where lignin content ranged from 2.2 – 3 %. These differences in fiber composition might be due to another important factor which is the ripening of the plant cell, associated with a gradual shift in fiber composition toward increasing proportions of cellulose and lignin (McPherson, 1982).

The caloric content of this ingredient was estimated as 2.40 Kcal/ g, which is in accordance with the Regulation EU No 1169/2011 2011) that accounts for 2 Kcal/g of dietary fiber. Therefore, its use as ingredient for fat replacement in food is viable as it accounts for less calories than fat and it mimics fat thick and viscous texture.

Another beneficial aspect of citrus-derived fibers is their antioxidant capacity (AOC) due to the presence of bioactive compounds such as polyphenols. The AOC found in the orange fibers obtained in this study was 997.19 ± 70.70 and 925.56 ± 68.91 mg TROLOX/ g fiber. There were no significant differences among treatments, which means that HAD + MW drying did not reach temperatures higher than HAD that could inactivate antioxidant capacity.

Table 1: Chemical composition (g/ 100 g) of the fiber obtained by hot air drying (HAD) and hot air + MW drying (HAD + MW) of orange peel.

g/ 100 g fiber	Orange fiber	
	HAD	HAD + MW
Moisture	9.38 ± 0.16	9.77 ± 0.08
Protein	6.81 ± 0.46	6.75 ± 0.33
Fat	2.66 ± 0.26	2.12 ± 0.31
Ash	3.26 ± 0.12	3.42 ± 0.41
Carbohydrates	78.74	77.94
Sugar	10.16 ± 1.0	13.42 ± 3.19
TDF	60.85 ± 5.25	*59.1 ± 1.75*
SDF	*29.6 ± 3.7*	*28.3 ± 1.32*
IDF	*31.25 ± 1.56*	*30.8 ± 1.6*
SDF:IDF	*1:1*	*1:1*
cellulose	*9.23 ±1.2*	*11.19 ± 1.15*
hemicellulose	*7.22 ± 2.91*	*5.85 ± 1.2*
*lignin**	*12.51 ± 1.93*	*10.98 ± 1.21*

TDF (Total dietary fiber); IDF (Insoluble dietary fiber); SDF (Soluble Dietary Fiber); AOC (Antioxidant Capacity). *Lignin is not a carbohydrate but it accounts for the insoluble part of dietary fibers. Data represent mean and standard deviation.

Colour is another attribute that could be affected by temperatures reached during drying. No significant differences were find on lightness (L*) nor hue on a green (-) to red (+) axis (a*) or either on b*, blue (-) to yellow (+) axis showing that HAD + MW did not negatively affect the molecules responsible for colour in orange peel, such as β-carotene (Hecker, 2014) (Table 2).

Table 2: Colour parameters (CIELab) of orange fibers obtained by different drying methods: hot air drying (HAD) and hot air coupled with microwave drying (HAD + MW).

	HAD	HAD + MW
L	77.5 ± 0.8	76.9 ± 1.0
a	3.4 ± 1.3	3.0 ± 1.5
b	66.1 ± 2.4^{a}	60.7 ± 3.6^{b}

Data represent mean and standard deviation. ^{a,b}Values with different superscript are significantly different

Hydration properties are also related to pH due to the presence of charged groups such as carboxyl in pectin. Samples pH was not affected by the drying treatment (5.06 for HAD and 5.08 for HAD + MW). These results are in accordance with Andrade et al. (2014) as this authors did not found significant differences on pH of orange by-products after drying by different treatments.

Energy consumption was estimated as explained in Figure 1. The total energy required for the hot air-microwave drying process described in this work was estimated as the sum of the energy required by hot air (E_{HAD}) and the energy required by microwaves (E_{MW}) per time.

E_{HAD} was calculated applying thermodynamics of humid air as explained in Green and Perry (2007). Considering the specific enthalpy (h) as the amount of heat (KJ/Kg) used or released in a system at constant pressure, E_{HAD} was calculated as the difference between the enthalpy of hot air at 55ºC ($h_{D\ air}$) and the enthalpy of ambient air at 15ºC (h_{amb}) per kg of dry air (M'). The total energy consumption of microwaves was calculated as the total microwave power applied (W) per kg of wet product (M_0).

As air is a homogeneous mixture of dry air and water vapour, the enthalpy of hot air is found taking the sum of the enthalpy of dry air and enthalpy of water vapour in the moist air. The specific enthalpy of dry air is a product of the specific heat of dry air (Cp_{da}) and the temperature of drying (T_D). The enthalpy of water vapour depends on the specific heat of water vapour at that temperature (Cp_v), the absolute moisture (X) and the latent heat of vaporization (ΔH^v). The absolute moisture (kg_w/kg_{da}) is related to the partial pressure of water vapour, which at the same time is a product of relative humidity (φ) and the vapour pressure of saturated air at that temperature (ps), the latter being dependent only on temperature. Thus, at T_{amb} and T_D it is possible to obtain the vapour pressure of saturated air at those temperatures ($ps^{amb}$and p_s^D).Assuming that the absolute moisture of ambient air (X_{amb}) is equal to the absolute moisture of drying air at the beginning of the drying process (X_D^0), it was possible to calculate the specific enthalpy of ambient air and drying air (h_{amb} and h_D, respectively). Finally, the mass of dry air (M') was calculated from the mass of moist air (M_D) and its absolute humidity (X_D^0). Also, M_D is a product of air density (ρ_D), air velocity (v_{air}) and the drier section (S_{Drier}). For air density estimation, at 1 atm it was possible to apply the perfect gases law, therefore, ρ_D was calculated from φ_D and p_s^D.

The relative humidity of drying air (φ_D) is defined as the relationship between partial pressure of water vapour and the vapor pressure of saturated air at T_D so it was possible to calculate it as previously explained.

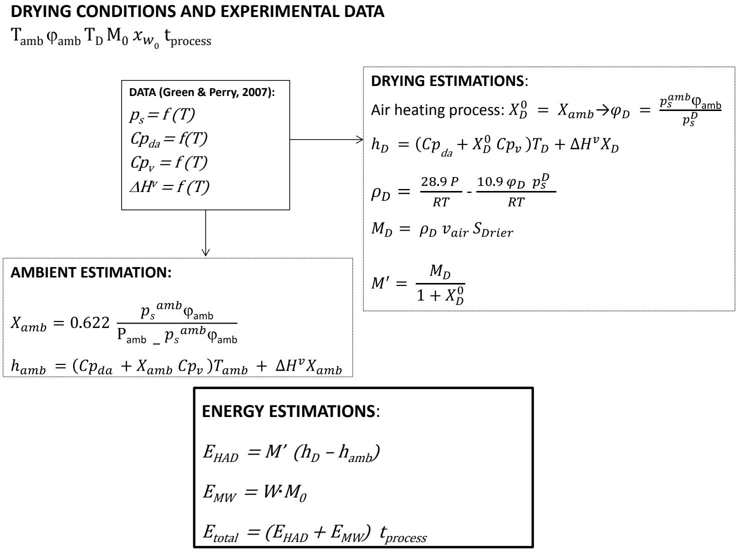


Figure 1. Drying conditions and experimental data for calculating energy consumption of two different drying processes applied to orange by-products: hot air drying (55 ºC) and hot air combined with microwave drying at different power intensities (2, 4 and 6 W/g).

Table 3 showed that at higher microwave levels, the time needed to reach different moisture levels was highly reduced. A strong time reduction was observed in all treatments by HAD+MW with regards to HAD at the initial stages of the drying (x_w = 50%). Microwave radiation orientates and induces water molecules, storing electric energy and dissipating part of it as thermal energy. Therefore, the more water molecules in samples, the higher thermal energy is produced by microwave radiation. Thus, the main effect of microwaves in drying process occurs at the beginning, because microwave energy increases the thermal and mechanical energy improving the water motion (increasing the free energy in the media) and increasing the availability of thermal energy for water evaporation, reducing the air internal energy losses (Talens et al., 2015b). It is possible to observe how for reaching a moisture content of 50 %, 122.5 min were needed when drying by HAD, whereas only 9.6 min were needed if drying at HAD + 6 W/g, which represents a 92.1 % time reduction.

Table 3: Drying time needed for reaching 10 %, 20 %, 30 %, 40 % and 50 % water content of orange by-products dried by hot air drying (HAD) and hot air drying coupled with microwaves (HAD + MW) at different powers (2, 4 and 6 W/g).

x_w (kg_w/kg_T)	time (min)			
	HAD	HAD + 2 W/g	HAD + 4 W/g	HAD + 6 W/g
0.5	122.5	27.0	15.2	9.6
0.4	144.0	31.0	17.3	10.8
0.3	159.5	35.0	19.2	12.1
0.2	174.5	40.0	21.2	13.3
0.1	191.5	44.0	23.0	14.6

Process yield was 125 g fiber/ kg fresh by-product. Figure 2 shows the energy required to achieve different reductions of moisture content by using HAD (0 W/g) or HAD + MW at different powers (2, 4 and 6 W/g). It is possible to observe how MW drying reduced energy consumption by up to

77.5 % For instance, 608.9 kWh were estimated for reducing samples moisture content from 85 % to10 % when applying HAD, whereas only 47.2 kWh where needed when using HAD + 6 W/g.

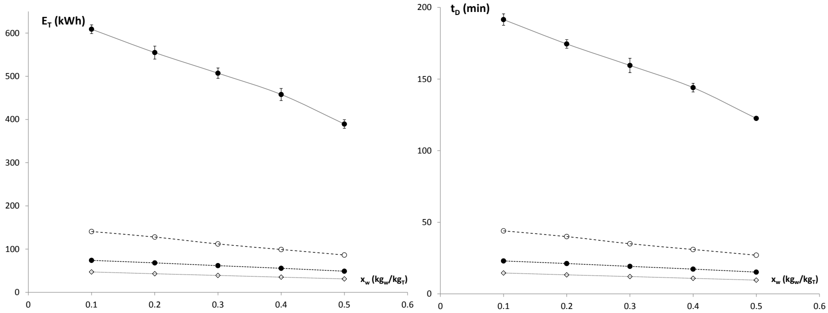


Figure 2. Energy consumption (kWh) for drying orange by-products at different moisture contents: 10 % (——), 20 % (······), 30 % (------), 40 % (- - - -), 50 %,(—) applying ● HAD, ◆ HAD + 2 W/g, ▲ HAD + 4 W/g, ● HAD + 6 W/g. Data represent means and standard deviation of experiments performed in triplicate.

Hot air–microwave drying involves simultaneous effects of the thermodynamics of hot air in sample surface, and the microwaves effects in depth. The internal effect of microwaves produces mechanical and thermal phenomena, increasing the water mobility, which accelerated water transport thus reducing drying time. Talens et al. (2015a) developed a thermodynamic model that explained the mechanisms involved in mass and energy transports throughout the combined drying by hot air and microwave of orange peel. These authors reported that the samples treated by HAD+MW showed an internal swelling at 14 % moisture caused by the internal evaporation produced by the microwave energy.

In order to study the expansion effect of microwaves on orange by-products tissue, particle size distribution mas measured in dried samples after milling. Table 4 shows the volume weighted diameter ($D_{4,3}$) and the surface weighted diameter for orange peel powder samples dried by HAD and by HAD + 6 W/g. It is possible to observe how the $D_{4,3}$ of samples dried by HAD was 325 ± 8.7 mm, which is significantly lower ($p \leq 0.05$) than $D_{4,3}$ of samples dried by HAD + 6 W/g (466.5 ± 15.3 mm), which is 30 % higher. The same occurs with the surface weighted diameter $D_{3,2}$, which was 43 % higher ($p \leq 0.05$) for samples dried by HAD + 6 W/g (260.1 ± 12.7 mm), than for samples dried by HAD (146.0 ± 5.8 mm). This could be explained due to the expansion phenomena occurred during microwave drying, causing the samples to swell, increasing their particle size. Talens et al., 2015b showed a macroscopic swelling in volume variation and in micrographies of orange peel treated by HAD + MW at different power intensities. Although the volume expansion observed by these authors was in orange peel samples that were not milled, the results from the present study showed that the expansion phenomena can be observed even if dried peels are destructured by a milling process, to convert them into powder for further application as food ingredients.

Powdered samples were hydrated and the particle size was measured again (Table 4). Results showed that samples dried by HAD increased their $D_{4,3}$ by 1.76 times when hydrated, whereas samples dried by HAD + 6 W/g increase their $D_{4,3}$ by 1.37 times. $D_{3,2}$ increased 18 % in hydrated HAD samples whereas no increase in surface weighted diameter was observed for hydrated HAD + MW samples. As $D_{4,3}$ is related to large particles present in the sample.

Table 4: Particle size distribution of the orange fiber obtained from orange by-products by applying hot air (HAD) and hot air coupled with microwave drying (HAD+MW).

	HAD		HAD + 6 MW	
particle size	dry	wet	dry	wet
$D_{4,3}$ (mm)	325 ± 8.7	572.0 ± 19.2	466.5 ± 15.3	641.9 ± 19.2
$D_{3,2}$ (mm)	146.0 ± 5.8	178.6 ± 9.1	260.1 ± 12.7	246.2 ± 16.0

$D_{4,3}$, $D_{3,2}$ represent volume weighted mean diameter, surface weighted mean diameter
Data represent means and standard deviation of experiments performed in triplicate.

Figure 3 shows this particle size distribution of dry and hydrated powder samples. It is possible to observe how HAD + MW samples have higher percentage of larger particles both in dry and hydrated form.

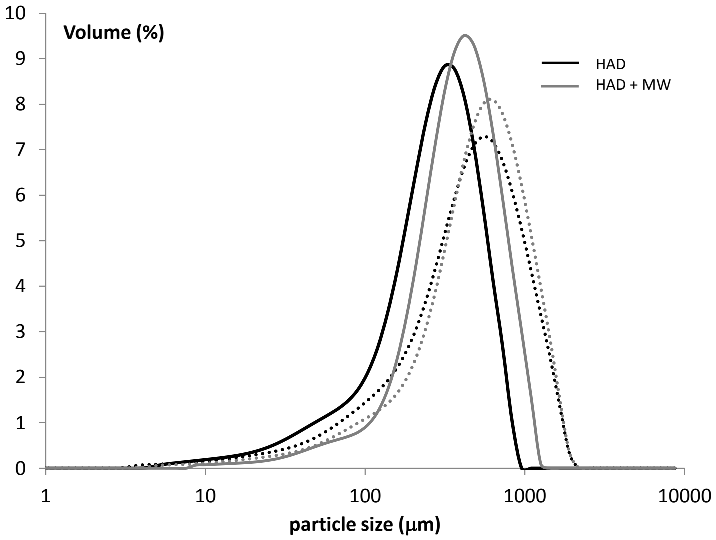


Figure 3. Particle size distribution of dry (──) and hydrated (– – –) citrus fiber obtained from citrus by-products treated by hot air drying (HAD) and hot air-microwave drying (HAD+MW).

Particle size distribution affects water retention capacity (WRC) because it is related to pore-size distribution and the number of a given size pore in each size class (Gupta, 2006). WRC is the most common parameter used in the industry to characterize the rehydration capacity of fiber and is also related to the physiological function of dietary. Table 5 shows the results obtained for the hydration properties measured. There were no significant difference on water retention capacity (12.66 and 12.23 g_{water}/g_{dm}, respectively) nor oil retention capacity between treatments (1.65 ± 0.01 and 1.73 ± 0.27 g_{water}/g_{oil}, respectively). WRC refers to the mechanisms and processes related to hygroscopicity of dried samples. ORC refers to the ability of fibers to hold oil and it is also realted to sorption properties. Talens et al., 2015b describe the rehydration process of dried orange peels (var Navel) giving physical meaning to the WRC by relating the isosteric heat of sorption, or the potential energy with which the water is held, to the internal surface. This relationship corresponds to the definition of surface tension, therefore WRC is directly related to the surface tension of the samples in such a way that if the internal surface area increases due to the expansion effect of microwave power, WRC will also increase. However, these authors measured WRC in unstructured orange samples with a cylindrical shape, whereas for this experiment, samples were milled with a sieve of 200 mm and WRC was measured in powder samples, modifying their structure and surface tension, and altering therefore the effect of HAD + MW on WRC. Furthermore, the orange varieties were also different for each research work, which could explain different effects of HAD + MW on WRC. Because fibers are also polymers sinthesized in nature, fiber content may also vary within a source. These variation affect the final ingredient composition, because commercial extraction processes are not complete isolation processes and cannot isolate the fiber itself (Nelson, 2001). Because the composition varies, functional properties such as moisture absorption, also vary.

Nevertheless, swelling capacity was significantly higher for HAD + MW samples (16.5 ± 0.7 ml/g_{dm}) than for HAD samples (14.75 ± 0.35 ml/g_{dm}). If no differences were found on WRC among fibers obtained by different treatments, but significant ($p \leq 0.05$) differences were found on swelling capacity, then the particle size is the only characteristic that differed among fibers that can explained these differences. Therefore, it can be concluded that HAD + MW caused an increase in particle size and porosity of orange powder samples which affected their swelling capacity but not their water retention capacity.

Table 5: Physical properties of the fiber obtained by hot air drying (HAD) and hot air + MW drying (HAD + MW) of orange peel.

	Orange fiber	
	HAD	HAD + MW
WRC (g_{water}/g_{dm},)	12.6 ± 0.5	12.2 ± 0.3
OHC (g_{oil}/ g_{dm})	1.6 ± 0.0	1.7 ± 0.3
SC (ml/ g_{dm})	14.7 ± 0.3^{a}	16.5 ± 0.7^{b}
Yield stress (Pa)	165.1 ± 26.0^{a}	87.8 ± 26.7^{b}
Apparent viscosity (Pa/s)	0.9 ± 0.2	0.9 ± 0.1

Data represent mean and standard deviation. ^{a,b}Values with different superscript are significantly different

Rheological characterisation of HAD and HAD + MW fibers was performed to study possible mechanical changes caused by those differences in both particle size and porosity. The flow behaviour of fiber dispersions presented non-newtonian shear-thinning behaviour, decreasing their viscosity with the application of increasing shear rates, which is in accordance with the typical behaviour of fiber suspensions (Lundberg et. al, 2014). Although the apparent viscosity resulted to show same values for both types of fiber (Table 5), the shear stress that needs to be applied to the solution before it begins to flow (Yield Stress) was considerably higher in the case of HAD-treated fiber (165 Pa) and compared to HAD + MW-treated fiber (88 Pa). This higher resistance to flow may be explained by the lower volume occupied by HAD-treated fiber (Table 4 and Table 5), when, at low shear rates, fiber molecules touch each other and further molecules force them to interpenetrate one another to form an entangled network (Cepeda and Collado, 2014). At this point where entanglement occurs, the increase of viscosity with the concentration is much steeper.

In the flow measurements, structure is easily broken by the aplication of increasing shear rates impeding to detect any influence of the porosity and higher volume on the structure. On the contrary, oscillatory measurements can determine this influence more precisely as the structure remains unbroken during most of the test. Therefore, the viscoelastic properties of both fibers were also investigated through oscillatory measurements. Both samples presented a greater storage modulus (G’) over the loss modulus (G”) confirmed by the low tanδ (G”/G’) values along most of the oscillation stress range (Figure 4). This behaviour indicates a predominant solid-like behaviour and more precisely a gel-like structure (Sendra et al., 2010).

HAD samples recorded higher G´and G” values comparing to HAD + MW samples. As explained above, the higher swelling capacity of HAD + MW fiber, caused by a greater porosity and thus, greater volume, made a less structured material, showing thereby a less stronger structure with considerable lower storage modulus values.

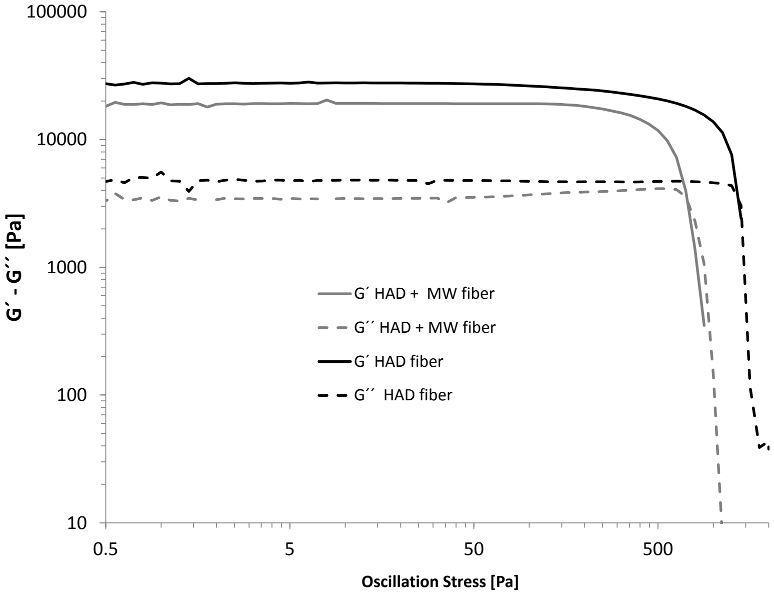


Figure 4. Representative stress sweep curves of the fiber processed by HAD and HAD + MW

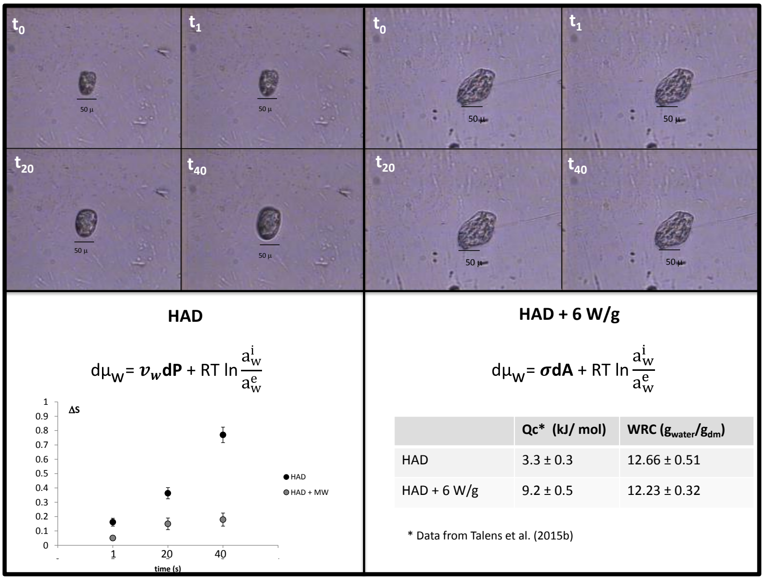
Likewise, HAD fiber showed a stronger structure. This fact can be seen at higher stresses when the structure is broken. The stress needed to collpase the system was higher for HAD samples.

In a fiber rehydration process, food in glassy state with high mechanical energy stored, from the shrinkage-swelling phenomena induced throughout drying process with a high surface tension, the gradient of the water chemical potential that causes the water inlet will come induced by the following equation:

$$d\mu_w = v_w dP + \sigma dA + RT \ln \frac{a_w^i}{a_w^e} \qquad (2)$$

Where: $d\mu_w$ is the gradient of the water chemical potential, $v_w dP$ corresponds to pressure variation, σ is the surface tension, dA is the surface variation and a_w is the water activity.

Two different drying techniques have been applied, where the shrinkage-swelling phenomena affect various terms of equation 2. HAD mainly affects the mechanical term of equation 2 due to the fact that higher mechanical energy is stored during drying and, therefore, more energy could be released during the rehydration (Figure 5a). HAD + MW mainly affects surface tension term as it is possible to observe in values of isosteric heat (Figure 56b).



$$d\mu_W = v_w dP + RT \ln \frac{a_w^i}{a_w^e}$$

$$d\mu_W = \sigma dA + RT \ln \frac{a_w^i}{a_w^e}$$

	Qc* (kJ/ mol)	WRC (g_{water}/g_{dm})
HAD	3.3 ± 0.3	12.66 ± 0.51
HAD + 6 W/g	9.2 ± 0.5	12.23 ± 0.32

* Data from Talens et al. (2015b)

(a) (b)

Figure 5. (a) Micrographies of HAD fiber particles during the rehydration process and surface variation throughout 40 s. (b) Micrographies of HAD + 6W/g during the rehydration process and table comparing Qc and WRC of orange peel dried by HAD and by HAD + MW.

Conclusions

A new fiber ingredient was obtained from orange by-products by applying two drying techniques: hot air (HAD) and hot air coupled with microwave drying (HAD + MW). An important reduction in processing time (92 %) and energy consumption (77 %) was achieved, compared to conventional hot-air drying. An increase in particle size due to an increase in porosity during drying improved fiber swelling capacity. Although viscosity of both treatments showed similar values, the higher swelling capacity of HAD + MW-treated fiber provoked a significant decrease in the viscoelasticity of the samples. The drying treatment did not affect chemical composition, WRC, ORC, pH or AOC of orange fibers. Total dietary fiber content was about 60 % with a ratio of soluble to insoluble fiber of 1:1. Colour was not affected by HAD + MW. The shrinkage-swelling phenomena occurred during drying affected the gradient of the water chemical potential. HAD mainly affects the mechanical term due to the fact that higher mechanical energy is stored during drying and, therefore, more energy could be released during the rehydration. HAD + MW mainly affects surface tension term as it is possible to observe in values of isosteric heat. Therefore, the potential use of HAD + MW as an efficient process for valorisation of citrus by-products into value-added ingredients, with optimum nutritional and technological properties has been shown.

Acknowledgements

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References

AFNOR. 1997. Association Française de Normalisation (AFNOR), 1997. Norme Française homologuée, Aliments des animaux. Détermination séquentielle des constituants pariéaux. Méthode par traitement aux détergents neutre et acide et à l'acide sulfurique. AFNOR, Paris NF V 18–122:11.

Andrade, J. M. d. M., E. V. d. Jong, and A. T. Henriques. 2014. Byproducts of orange extraction: influence of different treatments in fiber composition and physical and chemical parameters. 2014 50(3):10.

Arslan, D. and M. M. Ozcan. 2010. Study the effect of sun, oven and microwave drying on quality of onion slices. LWT-Food Sci. Technol. 43(7):1121-1127.

Baker, R. A. 1994. Potential dietary benefits of citrus pectin and fiber. Food Technology 48(11):133-&.

Bejar, A. K., N. Kechaou, and N. B. Mihoubi. 2011. Effect of Microwave Treatment On Physical and Functional Properties of Orange (Citrus Sinensis) Peel and Leaves. J Food Process Technol 2(2):1-7.

Bergese, P. 2006. Specific heat, polarization and heat conduction in microwave heating systems: A nonequilibrium thermodynamic point of view. Acta Materialia 54(7):1843-1849.

Bocco, A., M.-E. Cuvelier, H. Richard, and C. Berset. 1998. Antioxidant Activity and Phenolic Composition of Citrus Peel and Seed Extracts. J. Agric. Food Chem. 46(6):2123-2129.

Brand-Williams, W., M. E. Cuvelier, and C. Berset. 1995. Use of a free radical method to evaluate antioxidant activity. LWT - Food Science and Technology 28(1):25-30.

Cepeda, E. and I. Collado. 2014. Rheology of tomato and wheat dietary fibers in water and in suspensions of pimento puree. J. Food Eng. 134:67-73.

Demirel, Y. and S. I. Sandler. 2001. Linear-nonequilibrium thermodynamics theory for coupled heat and mass transport. International Journal of Heat and Mass Transfer 44(13):2439-2451.

Fabek, H., S. Messerschmidt, V. Brulport, and H. D. Goff. 2014. The effect of in vitro digestive processes on the viscosity of dietary fibres and their influence on glucose diffusion. Food Hydrocolloids 35(0):718-726.

Fava, F., G. Zanaroli, L. Vannini, E. Guerzoni, A. Bordoni, D. Viaggi, J. Robertson, K. Waldron, C. Bald, A. Esturo, C. Talens, I. Tueros, M. Cebrián, A. Sebők, T. Kuti, J. Broeze, M. Macias, and H.-G. Brendle. 2013. New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). New Biotechnology 30(6):647-655.

Ghanem, N., D. Mihoubi, N. Kechaou, and N. B. Mihoubi. 2012. Microwave dehydration of three citrus peel cultivars: Effect on water and oil retention capacities, color, shrinkage and total phenols content. Industrial Crops and Products 40(0):167-177.

Green, D. and R. Perry. 2007. Perry's Chemical Engineers' Handbook, Eighth Edition. McGraw-Hill Education.

Grigelmo-Miguel, N. and O. Martín-Belloso. 1998. Characterization of dietary fiber from orange juice extraction. Food Research International 31(5):355-361.

Gu, L., R. Ruan, P. Chen, W. Wilcke, and P. Addis. 2001. Structure-function relationships of Highly Refined Cellulose. Transactions of the Asae 44(6):1707-1712.

Gupta, C., Wang, D. . 2006. Water Retention in Soil. Pages 1864 - 1870 in Encyclopedia of Soil Science. R. Lal, ed. Taylor & Francis.

Howarth, N. C., E. Saltzman, and S. B. Roberts. 2001. Dietary fiber and weight regulation. Nutrition Reviews 59(5):129-139.

ISO. 1973. Determination of total fat content, ISO 1443:1973 standard. in International standards meat and meat products. International Organization for Standardization, Genève, Switzerland.

ISO. 1978. Determination of total nitrogen content, ISO 937:1978 standard. in International standards meat and meat products. International Organization for Standardization, Genève, Switzerland.

ISO. 1997. Determination of moisture content, ISO 1442:1997 standard. in International standards meat and meat products. International Organization for Standardization, Genève, Switzerland.

ISO. 1998. Determination of ash content, ISO 936:1998 standard. in International standards meat and meat products. International Organization for Standardization, Genève, Switzerland.

Kowalski, S. J., K. Rajewska, and A. Rybicki. 2005. Stresses generated during convective and microwave drying. Dry. Technol. 23(9-11):1875-1893.

Lees, R. 1968. Laboratory handbook of methods of food analysis. Leonard Hill Books, London.

Lopez, G., G. Ros, F. Rincon, M. J. Periago, C. Martinez, and J. Ortuno. 1997. Functional properties of dietary fiber. Mechanisms of actions in the gastrointestinal tract. Archivos latinoamericanos de nutricion 47(3):203-207.

Lundberg, B. 2005. Using highly expanded citrus fiber to improve the quality and nutritional properties of foods. Cereal Foods World 50(5):248-252.

Lundberg, B., X. Pan, A. White, H. Chau, and A. Hotchkiss. 2014. Rheology and composition of citrus fiber. J. Food Eng. 125(0):97-104.

Marlett, J. A., M. I. McBurney, and J. L. Slavin. 2002. Position of the American Dietetic Association: Health implications of dietary fiber. J. Am. Diet. Assoc. 102(7):993-1000.

McCleary, B. and L. Prosky. 2008. Advanced Dietary Fibre Technology. Wiley.

McPherson, K. 1982. Dietary fiber. J. Lipid Res. 23:221-242.

Nelson, A. L. 2001. Properties of high-fiber ingredients. Cereal Foods World 46(3):93-97.

Nijhuis, H. H., H. M. Torringa, S. Muresan, D. Yuksel, C. Leguijt, and W. Kloek. 1998. Approaches to improving the quality of dried fruit and vegetables. Trends Food Sci. Technol. 9(1):13-20.

Park, Y., D. J. Hunter, D. Spiegelman, L. Bergkvist, F. Berrino, P. A. van den Brandt, J. E. Buring, G. A. Colditz, J. L. Freudenheim, C. S. Fuchs, E. Giovannucci, R. A. Goldbohm, S. Graham, L. Harnack, A. M. Hartman, D. R. Jacobs, I. Kato, V. Krogh, M. F. Leitzmann, M. L. McCullough, A. B. Miller, P. Pietinen, T. E. Rohan, A. Schatzkin, W. C. Willett, A. Wolk, A. Zeleniuch-Jacquotte, S. M. M. Zhang, and S. A. Smith-Warner. 2005. Dietary fiber intake and risk of colorectal cancer - A pooled analysis of prospective cohort studies. JAMA-J. Am. Med. Assoc. 294(22):2849-2857.

Primo-Yúfera, E. and J. M. Carrasco-Dorrien. 1987. Química agrícola. 3, Alimentos. Alhambra.

Pszczola, D. 2006. Fiber gets a new image. Food Tech 60(2):43-53.

Raghavendra, S. N., N. K. Rastogi, K. Raghavarao, and R. N. Tharanathan. 2004. Dietary fiber from coconut residue: effects of different treatments and particle size on the hydration properties. European Food Research and Technology 218(6):563-567.

Regulation EU No 1169/2011. 2011. Pages 18–63 in Regulation EU No 1169/2011. Vol. L304. a. r. E. N. a. E. N. o. Regulation EU No 1169/2011 of 25 October 2011 on the provision of food information to consumers, ed. Official Journal of European Union.

Rimm, E. B., A. Ascherio, E. Giovannucci, D. Spiegelman, M. J. Stampfer, and W. C. Willett. 1996. Vegetable, fruit, and cereal fiber intake and risk of coronary heart disease among men. JAMA-J. Am. Med. Assoc. 275(6):447-451.

Santana, M. d. F. S. d., Gasparetto, Carlos Alberto. 2009. Microstructure of dietary fiber from orange albedo: a study by microscopy and physical techniques. Ciência e Tecnologia de Alimentos 29(1): 124-134.

Selvendran, R. R. 1984. The plant-cell wall as a source of dietary fiber - chemistry and structure. Am. J. Clin. Nutr. 39(2):320-337.

Sendra, E., V. Kuri, J. Fernandez-Lopez, E. Sayas-Barbera, C. Navarro, and J. A. Perez-Alvarez. 2010. Viscoelastic properties of orange fiber enriched yogurt as a function of fiber dose, size and thermal treatment. LWT-Food Sci. Technol. 43(4):708-714.

Talens, C., M. Castro-Giráldez, and P. J. Fito. 2015. A thermodynamic model for hot-air microwave drying of orange peel. J. Food Eng. in press.

Talens, C., M. Castro-Giráldez, and P. J. Fito. 2015. Effect of microwave power coupled with hot air drying on orange peel. J. Food Eng. in press.

Traffano-Schiffo, M. V., M. Castro-Giráldez, P. J. Fito, and N. Balaguer. 2014. Thermodynamic model of meat drying by infrared thermography. J. Food Eng. 128(0):103-110.

Tsami, E., M. K. Krokida, and A. E. Drouzas. 1998. Effect of drying method on the sorption characteristics of model fruit powders. J. Food Eng. 38(4):381-392.

Turbak, A. F., Snyder, F.W., Sandberg, K.R. 1983. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. Pages 815–827 in Proc. J Appl Polym Sci: Appl Polym Symp 37 (Proc. Cellul. Conf., 9th, 1982, Part 2).

Wang, L., H. Xu, F. Yuan, R. Fan, and Y. Gao. 2015. Preparation and physicochemical properties of soluble dietary fiber from orange peel assisted by steam explosion and dilute acid soaking. Food Chem. 185(0):90-98.

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Evaluación de las propiedades tecnológicas y sensoriales de un nuevo ingrediente a base de fibra de naranja como sustituto de grasa en purés de patata.

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RESUMEN

La tecnología de secado combinado aire caliente-microondas (AC+MW) puede reducir el tiempo de proceso y los costes de evaporación asociados a los procesos de obtención de fibra a partir de subproductos cítricos, resultando en un ingrediente rico en fibra dietética con propiedades tecnológicas y sensoriales adecuadas para su aplicación en la industria alimentaria. El objetivo de este trabajo ha sido evaluar las propiedades tecnológicas y sensoriales de una nueva fibra obtenida a partir de subproductos cítricos mediante secado AC+MW, aplicándola como sustituto de grasa en purés de patata.

Para ello se formularon cuatro purés de patata con un 7 % de grasa y cuatro tipos de fibra cítrica diferentes: una comercial de alta calidad, otra obtenida a partir de subproductos de naranja mediante secado por aire caliente y dos obtenidas mediante AC+MW aplicando dos potencias diferentes. Asimismo, se formuló un puré de patata con un 14 % de grasa utilizando nata y un puré control sin fibra ni nata. Las fibras se caracterizaron por su capacidad de retención de agua y aceite y por su capacidad de hinchamiento. Los purés de patata se caracterizaron reológica y sensorialmente. Se midieron sus propiedades viscoelásticas (G' y G"), y se llevó a cabo una evaluación sensorial mediante un panel formado por 7 catadores entrenados en 6 atributos sensoriales.

La textura de los purés con fibra resultó más viscosa, tanto a nivel reológico como a nivel sensorial, que la del puré elaborado con nata. Además, los purés elaborados con fibra obtenida por AC+MW presentaron una cremosidad muy similar al puré elaborado con nata y, aunque resultaron más granulosos, se consideró debido a la mayor capacidad de hinchamiento de estas fibras al rehidratarse. Como conclusión, se ha conseguido sustituir hasta un 50 % la grasa en puré de patatas utilizando una fibra obtenida a partir de subproductos de naranja, mediante un nuevo método de secado que puede suponer un ahorro de entre el 50 y 80 % del tiempo de proceso respecto a otros métodos convencionales.

Una mayor comprensión de la función de la fibra en la salud ha traído innovaciones en el desarrollo de alimentos e ingredientes con fibra añadida. Tradicionalmente el maíz, el trigo y la avena han aportado la fibra para ser usada como ingrediente en otros alimentos. Sin embargo, hay muchas otras fuentes de fibra de frutas, vegetales, legumbres y semillas que también pueden ser extraídas y agregadas a otros alimentos como sustitutos de azúcar y grasa.

La fibra dietética de los cítricos se considera de una calidad superior a otras alternativas como los cereales porque tiene una mayor proporción de fibra soluble (pectinas) y compuestos bioactivos asociados (flavonoides, polifenoles, carotenoides y vitamina C) con propiedades antioxidantes, que pueden proporcionar efectos beneficiosos adicionales para la salud (Grigelmo-Miguel y Martin-Belloso, 1999; Marin et al., 2007.

Por otro lado, la industria de zumo de naranja utiliza aproximadamente el 50 % de la fruta, mientras que el otro 50 % lo constituyen las pieles (flavedo y albedo), la pulpa y membranas (residuo del zumo), y las semillas, pudiendo alcanzar el 60 % de los subproductos totales (Fernandez-Lopez et al., 2004). Estos subproductos tienen numerosas aplicaciones que dependen de las propiedades funcionales de la materia prima así como la aplicación final buscada. Como

en la mayoría de las frutas, después de eliminar el agua de la piel, los principales componentes son carbohidratos solubles e insolubles. La fracción soluble en agua contiene azúcares y fibra soluble como la pectina; mientras que la fibra insoluble está constituida por celulosa, hemicelulosa y lignina (50-70 % de la parte insoluble).

Debido a la capacidad de retener agua de las fibras cítricas, éstas resultan efectivas para mimetizar grasa sin aportar efectos negativos en sabor, color, volumen o textura, como suele ocurrir normalmente en productos a los que se ha reducido el contenido en grasa con otros ingredientes. Cuando las fibras son utilizadas en la elaboración de alimentos, sus propiedades fisicoquímicas influyen también en las características físicas y sensoriales de éstos, especialmente cuando se usan como agentes gelificantes, espesantes y/o estabilizantes. Las propiedades funcionales de las fibras se determinan por lo general in vitro y sirven para dar una idea de su comportamiento in vivo, ya que en este medio están sometidas a un entorno fisiológico muy complejo y a una serie de mecanismos que pueden modificarla (Dervisoglu and Yazici, 2006). Las propiedades funcionales de la fibra son las responsables de los efectos fisiológicos que desarrolla y están influenciadas por la estructura de la fibra, su composición, origen y proceso de obtención.

En trabajos anteriores se ha demostrado la potencialidad de la tecnología de secado combinado aire caliente-microondas como método estabilización de subproductos cítricos (Fava et al., 2013). Esta tecnología, además de suponer un ahorro de tiempo y energía en la etapa de secado del subproducto, puede generar cambios en la estructura de las fibras que afecten favorablemente a sus propiedades tecnológicas.

Por lo tanto, el objetivo de este trabajo ha sido evaluar las propiedades tecnológicas y sensoriales de una nueva fibra obtenida a partir de subproductos cítricos mediante secado combinado aire caliente-microondas, aplicándola como ingrediente sustituto de grasa en purés de patata.

2. MATERIALES Y MÉTODOS

Los subproductos cítricos se obtuvieron a partir de pieles de naranja (variedad Navel) resultantes del proceso de extracción de zumo mediante piñas rotativas (Zumex, Valencia, España). La fibra de naranja utilizada se obtuvo mediante el siguiente proceso: picado de las pieles, escaldado a 65ºC durante 5 min, centrifugado 1000 rpm 5 min, secado y molido a un tamaño de partícula de 200 µm.

El secado de las pieles por aire caliente-microondas se realizó utilizando un equipo piloto de energía electromagnética a una frecuencia de microondas de 2450 MHz (MMP20T ,Sairem S.A., Miribel, Francia). La temperatura del aire de secado fue de 55ºC y la velocidad del aire 7 m/s. Las muestras secadas solo por aire caliente (AC) tardaron 180 min en alcanzar un contenido en agua de 10 ± 1 g agua/ 100 g peso fresco. A las muestras secadas por AC+MW se les aplicó dos potencias de microondas diferentes: 1.5 W/g para la muestra MW1 y 4 W/g para la fibra MW2, durante 90 y 30 min, respectivamente, hasta alcanzar la misma humedad que AC. La fibra cítrica comercial utilizada como referencia fue Herbacel AQ Plus (Herbstreith & Fox, Alemania). Los tiempos de secado para alcanzar la humedad deseada se determinaron en experimentos preliminares.

La capacidad de retención de agua (CRA), de aceite (CRO) y de hinchamiento (CH) de las fibras se midió mediante los métodos descrito por Lundberg et al. (2014).

El puré de patata de referencia (REF) consistía en copos de patata deshidratada (11,4%), agua (57,1%), leche semidesnatada (11, 4%) y nata con 35% de materia grasa (20,0%). Los purés con grasa sustituida se formularon sustituyendo el 100% de la nata por 1 % de fibra cítrica comercial diluida en agua (COM) y 1% fibra cítrica obtenida mediante secado por aire caliente-microondas, previamente diluida en agua (MW1 y MW2). Como control se preparó también una fórmula sin nata y sin fibra (NOFIB).

Por lo tanto, cuatro fueron las muestras de purés con fibra evaluadas: puré con 7 % de grasa y 1% de fibra cítrica comercial (COM), puré con 7% de grasa y 1 % de fibra obtenida mediante secado por aire caliente (AC) y puré con 7% de grasa y 1% de fibra obtenida mediante el nuevo proceso (MW1 y MW2).

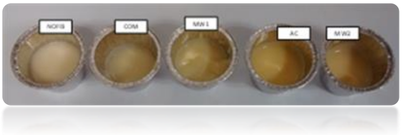


Imagen 1: Muestras evaluadas durante el análisis reológico y sensorial.

Las medidas de reología de los purés se realizaron a 40ºC utilizando un reómetro de control de fuerza AR-2000 (TA Instruments, UK) con una geometría de platos paralelos de 20 mm de diámetro y superficie rugosa, y con una separación de 2 mm. Las muestras se analizaron por triplicado. Se midió G′ y G′′. El módulo de almacenamiento (G′) y el módulo de pérdidas (G´´) es un indicador del comportamiento viscoelástico de un material. El análisis sensorial de los purés se llevó a cabo mediante un panel formado por 7 catadores entrenados aplicando un análisis descriptivo cuantitativo (QDA) de acuerdo a las normas UNE-ISO 6658:2008 y UNE 87025:1996. Se emplearon escalas no estructuradas de 10 puntos para analizar 6 atributos sensoriales: 2 a nivel visual (homogeneidad y viscosidad) y 4 en boca (granulosidad, carácter graso, cremosidad y viscosidad). Cada catador evaluó 6 muestras de puré de patata por triplicado: AC, MW2, MW4, COM, SF y el puré de referencia. La cantidad de muestra servida a cada catador fue de 40g y la temperatura a la que se realizó el análisis sensorial fue de 40±1ºC. El orden de presentación fue diferente y balanceado.

El análisis estadístico se llevó a cabo mediante el programa R-project (R versión 3.0.1.) aplicando un ANOVA de un factor para determinar la significación de las diferencias entre muestras para los parámetros analizados. Además, se ha aplicado un test de contraste (Tukey test) para establecer entre qué muestras existen dichas diferencias.

3. RESULTADOS Y DISCUSIÓN

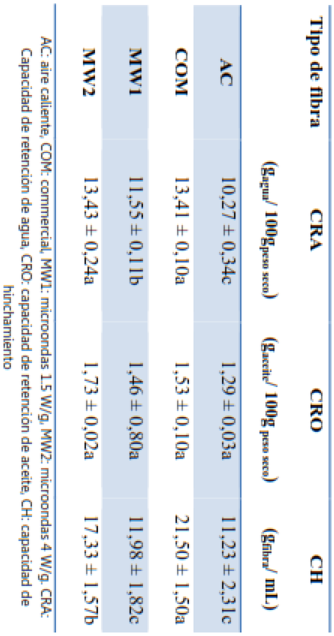
Los resultados indicaron que existían diferencias estadísticamente significativas (p<0,001) entre muestras en cuanto a viscosidad (tanto visual como en boca), granulosidad, carácter graso y cremosidad. Por otra parte, no hubo diferencias estadísticamente significativas (p>0,05) entre muestras para el atributo homogeneidad, es decir, las muestras obtenidas con los diferentes tratamientos eran homogéneas a nivel visual (Tabla 1). Las viscosidades más altas se observaron con las fibras obtenidas por AC y por MW mientras que la más baja se observó en el puré elaborado sin fibra. Así, las fibras obtenidas por AC y MW proporcionaron una viscosidad visual mayor al puré de patata que la fibra comercial y que el puré de referencia. En boca, la fibra MW presentó una viscosidad muy similar a la fibra comercial, y el mayor valor se percibió en el puré elaborado con la fibra AC. Los purés elaborados con las fibras obtenidas por microondas (MW1 y MW2) presentaron una granulosidad mayor que el resto. Además, se observó que en los purés elaborados con fibra se percibió menos cantidad de grasa en boca que en el puré de patata de referencia. No se percibieron diferencias entre las muestras con fibra y las muestras sin fibra en cuanto al carácter graso.

	Media								***Tukey test***					
Parámetros	AC	COM	MW1	MW2	SF	REF	F-valor	p-valor	*AC*	*COM*	*MW1*	*MW2*	*SF*	*REF*
Homogeneidad	8,600	8,471	8,510	8,490	8,629	8,257	0,391	$0{,}854^{ns}$	a	a	a	a	a	a
Viscosidad vis.	8,362	7,824	7,657	8,162	5,348	6,829	13,600	$0{,}000^{***}$	c	bc	bc	c	a	b
Granulosidad	2,905	3,833	3,800	3,129	2,976	2,129	7,817	$0{,}000^{***}$	ab	b	b	b	a	a
Carácter graso	1,667	1,657	1,552	1,976	1,571	3,690	10,690	$0{,}000^{***}$	a	a	a	a	a	b
Cremosidad	7,024	6,957	6,981	4,195	4,290	5,157	16,170	$0{,}000^{***}$	b	b	b	a	a	a
Viscosidad b.	7,295	6,795	6,724	6,919	4,467	5,790	13,450	$0{,}000^{***}$	c	bc	bc	bc	a	b
G’	4704,7	7024,3	5099,3	3517,0	1173,9	1770,8	33,95	$0{,}000^{***}$	bc	a	b	c	d	d
G’’	899,3	649,0	627,3	506,2	155,1	160,3	32,67	$0{,}000^{***}$	a	b	b	b	c	c

AC: aire caliente, COM: comercial, MW1: microondas 1.5 W/g, MW2: microondas 4 W/g, SF: sin fibra, REF: referencia
Valores con diferente letra son significativamente diferentes (p < 0,001)

Tabla 1. Valores medios y significación de las diferencias para cada parámetro analizado en las muestras de puré de patata.

Los purés elaborados con las fibras AC y MW1 fueron los más cremosos. Además, la cremosidad del puré elaborado con la fibra MW2 fue similar a la del puré de referencia. En cuanto al análisis reológico, G′ resultó significativamente mayor para la muestra COM, seguido de MW1, AC y MW2. Los valores más bajos de G′ se registraron en las muestras REF y SF, tal y como ocurría con la viscosidad visual y en boca. El módulo de pérdidas G′′ fue mayor para la muestra AC, seguido por COM, MW1 y MW2, mostrando la misma tendencia que la viscosidad en boca. Valores altos de elasticidad demuestran la presencia de una mayor estructura de la muestra. Sin embargo, la relación entre el módulo viscoso y el módulo elástico pueden aportar información útil para determinar las propiedades sensoriales de un producto. Tal es el caso de las muestras AC, COM y MW1, las cuales presentan una relación similar entre ambos módulos (viscoelasticidad parecida) y son a su vez portadoras de una mayor cremosidad. La CRA de las fibras MW2 y COM fueron mayores que las fibras MW1 y AC.



Tipo de fibra	**CRA** (g_{agua}/ 100$g_{peso\ seco}$)	**CRO** (g_{aceite}/ 100$g_{peso\ seco}$)	**CH** (g_{fibra}/ mL)
AC	10,27 ± 0,34c	1,29 ± 0,03a	11,23 ± 2,31c
COM	13,41 ± 0,10a	1,53 ± 0,10a	21,50 ± 1,50a
MW1	11,55 ± 0,11b	1,46 ± 0,80a	11,98 ± 1,82c
MW2	13,43 ± 0,24a	1,73 ± 0,02a	17,33 ± 1,57b

AC: aire caliente, COM: commercial, MW1: microondas 1.5 W/g, MW2: microondas 4 W/g. CRA: Capacidad de retención de agua, CRO: capacidad de retención de aceite, CH: capacidad de hinchamiento

Tabla 2. Propiedades tecnológicas medidas en las diferentes fibras

En cuanto a la CH las diferencias entre fibras fueron todas significativas. La CH de la fibra COM resultó significativamente mayor que MW2, seguida de MW1 y AC. En cuanto a CRO, no se observaron diferencias significativas entre muestras, al igual que en cremosidad y homogeneidad visual (Tabla 2).

Por último, teniendo en cuenta los tiempos de proceso para la obtención de las fibras mediante secado por AC (180 min) y secado AC+MW a dos potencias diferentes (90 y 30 min), se ha conseguido reducir el tiempo de proceso entre un 50 – 80 %, lo cual puede suponer importantes ahorros energéticos.

4. CONCLUSIONES

El contenido en grasa de purés de patata elaborados con nata fue reducido en un 50 % utilizando diferentes tipos de fibra cítrica. Todas las fibras aumentaron la viscosidad visual y en boca de los purés, así como su comportamiento viscoelástico. Las fibras obtenidas por secado combinado aire caliente-microondas (4 W/g) presentaron una capacidad de hinchamiento similar a la fibra comercial y una capacidad de retención de agua igual. Además, estas fibras se percibieron como más granulosas en boca pudiendo explicarse por el mayor aumento de volumen al rehidratarse. Tanto la fibra comercial como las fibras obtenidas por el nuevo proceso generaron una menor percepción de grasa en boca que la referencia. Finalmente, la cremosidad de los purés de patata elaborados con fibras obtenidas mediante el nuevo proceso se valoró como muy similar a la referencia. Finalmente, se ha conseguido sustituir hasta un 50 % la grasa en puré de patatas utilizando una fibra obtenida a partir de subproductos de naranja, mediante un nuevo método de secado que puede suponer un ahorro de entre el 50 y 80 % del tiempo de proceso respecto a otros métodos convencionales.

REFERENCIAS

Dervisoglu, M., Yazici, F., (2006). Note. The effect of citrus fibre on the physical, chemical and sensory properties of ice cream. Food Science and Technology International 12(2), 159-164.

Fava, F., Zanaroli, G., Vannini, L., Guerzoni, E., Bordoni, A., Viaggi, D., Robertson, J., Waldron, K., Bald, C., Esturo, A., Talens, C., Tueros, I., Cebrián, M., Sebők, A., Kuti, T., Broeze, J., Macias, M., Brendle, H.-G., (2013). New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). New Biotechnology 30(6), 647-655.

Fernandez-Lopez, J., Fernandez-Gines, J.M., Aleson-Carbonell, L., Sendra, E., Sayas-Barbera, E., Perez-Alvarez, J.A., (2004).

Application of functional citrus by-products to meat products. Trends in Food Science & Technology 15(3-4), 176-185.

Grigelmo-Miguel, N., Martin-Belloso, O., (1999). Influence of fruit dietary fibre addition on physical and sensorial properties of strawberry jams. Journal of Food Engineering 41(1), 13-21.

Lundberg, B., X. Pan, A. White, H. Chau, and A. Hotchkiss. 2014. Rheology and composition of citrus fiber. J. Food Eng. 125(0):97-104.

Marin, F.R., Soler-Rivas, C., Benavente-Garcia, O., Castillo, J., Perez-Alvarez, J.A., (2007). By-products from different citrus processes as a source of customized functional fibres. Food Chemistry 100(2), 736-741.

RESULTADOS: Artículo 4.6

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A new efficient process for the simultaneous obtention of dietary fiber and bioactive extracts from orange by-products using hot air-microwave drying

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ABSTRACT

Currently industrial citrus by-products represent a relevant environmental issue. The main aim of this work was to develop a novel time and cost-efficient process for conversion of orange by-products into three food-grade ingredients with health-related benefits was developed by applying forced air-microwave drying (MW). Total phenolics, antioxidant capacity, individual phenolic acids, flavonoids, limonin and carotenoids were monitored during blanching and colour extraction steps by analysing fresh by-products and process co-products: an aqueous extract rich in polyphenols and an ethanolic extract rich in carotenoids. After drying, the resulting fiber was characterized in terms of chemical composition, soluble and insoluble dietary fiber content and particle size. Technological properties (WRC, ORC, SC) and colour were compared to those of commercial citrus fiber. Energy and time consumption were compared with conventional forced air drying (HAD). Most polyphenols (50-65 %) and limonin (70 %) were extracted during the blanching step. 86 % of carotenoids were removed by soaking in ethanol. The orange fiber obtained had 71.9 g DF/ 100 g and antioxidant properties (205 mg TE/ Kgdm). Whiteness, WRC and ORC was similar to commercial citrus fiber. MW reduced drying time and energy consumption by up to 50 % compared to HAD.

Keywords: orange by-product, microwave drying, citrus fiber, bioactive compounds, citrus polyphenols, limonin

NOTATION

MW	microwave drying
HAD	hot air drying
AOC	antioxidant capacity
WRC	water retention capacity
DF	dietary fiber
TDF	total dietary fiber
IDF	insoluble dietary fiber
SDF	soluble dietary fiber
dm	dry matter
j	relative humidity (-)
M	mass per time in wet basis (kg s^{-1})
M'	mass per time in dry basis (kg s^{-1})
x	mass fraction (kg kg^{-1})
X	absolute moisture (kg water kg dry air $^{-1}$)
t	time (s)
h	specific enthalpy (J kg^{-1})
p_s	water saturation pressure (kPa)
C_p	heat capacity at constant pressure (W g^{-1} K^{-1})
DH	molar enthalpy (J mol^{-1})
ρ	density (kg m^{-3})
v	velocity (m s^{-1})
S	section (m^2)
E	energy (kW or kWh)
W	microwave energy (W g^{-1})
P	absolute pressure (Pa)
T	temperature (K)
R	ideal gases universal constant (J mol $^{-1}$ K^{-1})
Qc	isosteric heat

Subscripts and superscripts:

amb	ambient conditions
da	dry air
D	drying conditions
0	initial time
v	vapour
w	water
i	internal
e	external

1. Introduction

Food industry generates millions of tons per year of plant processing by-products, particularly in the fruit processing sector. The exploitation of these by-products is limited because their inadequate biological stability.

The most common and easiest route for exploitation citrus processing by-products is to use them in animal feeding (Bampidis and Robinson, 2006). For more than twenty years, the use of processing technologies to fractionate and recover potentially high value components such as dietary fiber (DF) (Aravantinos-Zafiris et al., 1994; Harris and Smith, 2006; Larrauri, 1999), carotenoids and natural antioxidants (Kris-Etherton et al., 2002; Lu and Foo, 2000; Moure et al., 2001) has been investigated. Studies have been conducted to demonstrate the physical, chemical and functional properties of dietary fiber (DF) derived from fruits such as oranges and lemons (Fernández-López et al., 2009; Figuerola et al., 2005; Marin et al., 2007; Russo et al., 2014), passion fruit (Hernández-Santos et al., 2015) and pitaya peels (Zhuang et al., 2012) highlighting their antioxidants properties.

Sensory properties such as colour, flavour and above all, bitterness of citrus by-products has limited their use in food application. Some polyphenols (flavonoids) and terpenoids such as limonin are responsible for this bitterness. Flavanones are usually present in diglycoside form, conferring the typical taste to citrus fruits (Macheix, 1990). The colour is mainly given by carotenoids and to a lesser extent by flavonoids (Braddock, 1999)

Different process for obtaining dietary fiber from orange by-products have been described by some authors (Andrade et al., 2014; Attavanich, 2003; de Moraes Crizel et al., 2013), but these methods use conventional hot air drying. In previous work carried out by Fava et al. (2013) the use of hot air-microwave technology was tested as a procedure for stabilizing citrus by-products and for further recovery of bioactive compounds and dietary fiber from the dried by-product. Results from this work showed that the use of microwaves did not only minimize processing time and microbial load, but also showed potential for obtaining a dietary fiber with neutral colour and optimum water retention capacity from the stabilized by-product.

Drying costs are one of the main costs in valorisation processes of high moisture by-products and represents a key factor in the economic feasibility of the process (Zhang et al., 2006). High temperatures or long drying times in conventional air drying may cause serious damages to product flavour, colour and nutrients, reducing bulk density and rehydration capacity of the dried product (Chen et al., 2011; Femenia et al., 2009). Microwaves have been used for food drying in order to avoid quality losses and to achieve fast and effective thermal processing (Nieto Calvache et al., 2015; Prothon et al., 2001). The use of microwaves in some processes such as drying results in a substantially reduced processing time leading to increased production capacity, as well as improved quality and shelf life of final products (Zhang et al., 2006).

Apart from drying, there are two important pre-treatments that are used for improving final product quality: blanching and extraction of undesired compounds, mainly responsible for colour and bitterness. Blanching is necessary to eliminate soluble sugars and to inactivate the polyphenol oxidases to avoid possible browning of the fiber during the drying step (Morales-Blancas et al., 2002; Peerajit et al., 2012; Wuttipalakorn et al., 2009). Different methods have been studied to reduce bitterness based on the elimination of limonin content, which is the molecule responsible for bitterness in citrus fruits. Some of these methods are: use of limonoate dehydrogenase to prevent development of limonin (Hasegawa et al., 1973), use of adsorbents such as β-cyclodextrin for removal of limonin (Konno et al., 1982) or use of ethanol (Attavanich, 2003; Ubando-Rivera et al., 2005).

High fiber ingredients exhibit many properties that influence the physiological functions of foods. However, preparation steps such as drying may modify these properties. Understanding the properties of high fiber ingredients is essential to developing new food products (Nelson, 2001). Particle size is of major importance, determining both fiber technological functionality and fiber role in the digestive tract (transit time, fermentation, faecal excretion). The shape and the size of fibers depends on degree of processing and may vary during transit in the intestine tract as result of digestion process. Water retention capacity (WRC), swelling capacity (SC) and oil retention capacity (ORC) suggest some possibilities about the use of fibres as ingredients in food products: eg., dietary fiber with high ORC allow the stabilization of high fat food products and emulsions. Dietary fibers with high WRC and SC can be used as functional ingredients to avoid syneresis and modify the viscosity and texture of some formulated low fat foods (Elleuch et al., 2011).

The aim of this work was (i) to propose a multipurpose process for the simultaneous obtention of dietary fiber and bioactive rich extracts from orange by-products, applying hot air-microwave technology as a more efficient drying process than conventional hot air; (ii) to monitor the distribution of individual polyphenols, carotenoids and limonin during blanching and ethanol soaking and (iii) to study the physico-chemical and technological properties of the dietary fiber obtained.

2. Material and Methods

Plant material

Oranges (*Citrus sinensis* (L.) Osbeck, var Washington Navel) were processed for juice extraction by a Spanish citrus juice industry (Grupo Leche Pascual, Aranda de Duero, Spain) and the residue was supplied as samples of orange by-products for this study, including flavedo, albedo, segments, juice sacs and seeds. For polyphenol analysis only, samples were lyophilized in a freeze-dryer (Labconco, freezone 4.5, Kansas, USA*)* for 24 h, powdered using a blender (IKA, Germany) and stored at 4 ºC in the dark until use.

Procedure and sample preparation

This process was developed at the pilot plant of AZTI (Spain). The methodology consisted of five main steps (Figure 1): Mincing, blanching, decolouring, drying and milling.

Orange by-products were minced to 0.5-1 cm particle size using a cutter (Stephan UMC-5, Stephan, Germany) and blanched in water (vol 1:4) at 65 ºC for 5 min. The maximum operational temperature was considered 65 ºC considering that blanching causes adverse losses in the antioxidant capacity over 70 ºC (Abu-Ghannam and Jaiswal, 2015). Afterwards, samples were centrifuged at 1000 x g for 5 min using a high performance centrifugal machinery (Comteifa, Barcelona, Spain). The aqueous extract resulting from blanching was collected and analysed for polyphenols characterization.

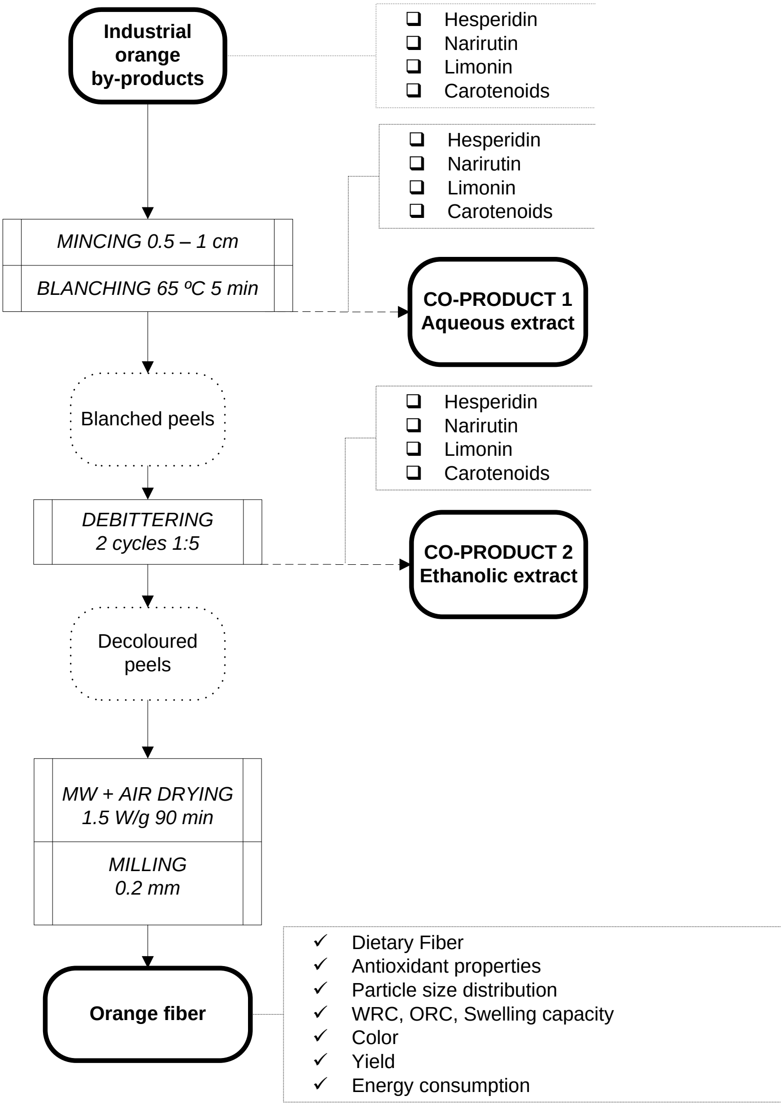

Figure 1. Flow diagram of the experimental procedure

Approximately, 500 g batches of blanched by-products were then soaked in food grade 96% ethanol (two cycles, 1:5 w/vol) under constant agitation, using a mixing/overhead stirrer RW 28 basic with propeller stirrer 4-bladed (IKA, Germany), during 1 hour for removal of compounds responsible for colour and bitterness. Finally, samples were centrifuged at 1000 g for 5 min to remove excess ethanol. Ethanol was collected for its characterization.

Decoloured samples (300 g batches) where then introduced in a pilot scale 2450 MHz electromagnetic microwave equipment (MMP20T, Sairem S.A., Miribel, France) and dried at 1.5 W/g, , air temperature and velocity, 35 ºC and 7 m/s, respectively, during 90 min (Fava et al., 2013). After drying, samples were milled using an ultracentrifuge mill (ZM 100, Retsch, Germany) with a sieve of 200 µm. At this stage, powdered samples were packed in plastic bags for characterization. The procedure described above was carried out in triplicate from the same batch of fresh material in order to avoid variability due to cultivar, seasonality and time of harvest.

Characterization methods

Chemicals and reagents

Trolox [(+/-)-6-hydroxy-2,5,7,8-tetramethyl-chroman-2-carboxilic acid], Folin Ciocalteu reagent, DPPH [2,2-diphenyl-1-picrylhydrazyl]) and Phenolic standards (gallic acid, chlorogenic acid, caffeic acid, p-coumaric acid, ferulic acid, eriocitrin, hesperidin, naringin, quercetin-3-O-glucoside and limonin) were obtained from Sigma Aldrich, (St. Louis, USA). Sodium carbonate, methanol, formic acid, acetone, n-hexane and ethanol (Panreac Quimica S.A.U., Barcelona, Spain) and Mili-Q water were also used. All chemical and reagents used in this study were of analytical grade.

Proximate analysis

Samples were analysed according to the ISO recommended standards: Moisture by 1442:1997, (ISO, 1997), ash by ISO 936:1998 (ISO, 1998), protein content by ISO 937:1978 (ISO, 1978) and fat content by ISO 1443:1973 (ISO, 1973). Total sugars were analysed by Luff–Schoorl method for reducing sugars (Lees, 1968)

The total protein content was determined by the Kjeldahl method using the Digestion Unit K-435 and a distillation unit B-324 (Buchi Labortechnik AG, Switzerland). A correction factor of 6.25 was used. Crude fat was extracted with petroleum ether using a Soxtec HT 1043 extraction unit (Foss Tecator, Denmark). The ash content was performed in a muffle furnace (Carbolite CWF 1100, Carbolite, UK) set to 550 ºC. The moisture content was determined at 105 ºC (Memmert, Germany), for approximately 18 h until constant weight. The carbohydrate content was determined by the difference.

For the fiber ingredient obtained, total, soluble, and insoluble dietary fiber was determined by the AOAC enzymatic-gravimetric method, 991.43 (1991). Neutral detergent fiber and acid detergent fiber was analyzed by the gravimetric method AOAC 973.18 (1977). Cellulose content was calculated as the difference between acid detergent fiber and acid detergent lignin. Finally, hemicellulose content was determined according to NF V 18-122 (AFNOR, 1997).

The total caloric value was calculated by adding up the calories provided by the energy-containing nutrients and considering 4 kcal/g for protein, 9 kcal/g for fat, 4 kcal/g for carbohydrate and 2 Kcal/g for fiber (2011).

Polyphenol extraction

Polyphenol extraction from orange peels was carried out adapting the procedure described by Khan et al. (2010). Dried powdered samples (1 g) were placed in a 50 mL falcon tube and 20 mL of extraction solution consisting of MeOH:H_2O:Formic acid (75:24.9:0.1; v/v/v)) was added. Then, it was sonicated in an ultrasound bath (Ultrasounds-H Bath model, P-Selecta) at 30 ºC, 25 MHz for 30 min, centrifuged at 2660 *g* for 10 min, and taken to a final volume of 25 mL with MQ water. Extracts were filtered through a 0.22 µm PVDF filter and immediately analysed within 24 h for the determination of total phenolics, phenolic acids and flavonoids by chromatography and for the antioxidant assay.

Total phenolics content

Total phenol content (TPC) was measured by Folin-Ciocalteu assay, using gallic acid as standard (2-20 mg/L) adapted from Singleton et al. (1999) to plate reader spectrophotometer (Varioskan, Thermo Scientific, USA). The reaction mixture was composed of 140 µL of orange extract obtained (previously diluted 1:50) or gallic acid standards, 30 µL of Folin–Ciocalteu reagent and 140 µL of 20 % sodium carbonate in 96-well plates. The reaction was mixed and allowed 1 h in dark. The absorbance was measured at 750 nm and TPC was expressed as mg of gallic acid equivalent per kg of dried matter (mg GAE/kg dm).

Individual polyphenols and limonin analysis by chromatography

Standard stock solutions were prepared in methanol, except for hesperidin that was dissolved with water: dimethylformamide (80:20, v/v) and stored at -20 ºC in darkness. Agilent 1100 Series liquid chromatograph (Agilent, California, USA) equipped with a degasser, a binary pump, an autosampler, a column oven and a diode array detector (DAD) coupled to a mass detector Ion Trap XCT PLUS with an electrospray interface was used for the analysis. Chromatographic separation was performed at 30 ºC on a Gemini C18 analytical column (150 mm x 2.1 mm i.d, 5 µm, Phenomenex, Torrance, Canada) with a C18 column guard cartridge. A gradient program for general polyphenol analysis was employed. The mobile phase consisted of water/0.1 % formic acid (Solvent A) and methanol/0.1 % formic acid (Solvent B). The elution conditions applied were: 0-2 min, 10 % B isocratic; 2-35 min, linear gradient 10-35 % B; 35-55 min, linear gradient 35-60 % B; 55-58 min, 60 %

B isocratic; 58-59 min, linear gradient 60-100 % B, 59-62 min, 100 % B isocratic; and finally 62-63 min, linear gradient 100-10 % for reconditioning the column. Citrus flavanones eriocitrin, hesperidin and naringin were analysed separately under the same conditions but following shorter elution chromatogram: 0-12 min, linear gradient 33-40 % B; 12-13 min, linear gradient 40-100 % B; 13-15 min, 100 % B isocratic; and finally 15-16 min, linear gradient 100-33 % for reconditioning the column. For limonin analysis, the mobile phase consisted of water/ 0.1 % formic acid (Solvent A) and acetonitrile/0.1 % formic acid (Solvent B). The elution conditions applied were: 0-5 min, linear gradient 20-35 % B; 5-18 min 35 % B isocratic; 18-19 min, 35-60 % B linear gradient; 19-22 min, 60 % B isocratic, 22-23 min, 60-100 % B linear gradient; 23-25 min 100% B isocratic and finally 25-26 min linear gradient 100-10 % for reconditioning the column. The flow rate was 0.4 mL/min and 10 µl of sample was injected. Chromatograms were monitored at 210, 254, 280 and 320 nm. Mass spectral analysis was performed in positive (for polyphenols) and negative (for limonin) ionization mode. Nitrogen was used as drying gas at a constant flow rate of 8 l/min and the temperature was set at 350 ºC. The nebulizer gas pressure was set at 40 psi and the capillary voltage at 3500 V. Polyphenols and limonin were analysed by direct injection of the orange extracts, previously diluted (1:2) in water and filtered through a 0.22 µm PVDF filter. Identification was made possible by comparison of retention times, UV-visible espectra and MS/MS data with those of the standards. Quantification was performed by reporting the measured integration areas in the calibration equation of the corresponding standards.

Antioxidant capacity

The antioxidant capacity (AOC) was measured by DPPH method using Trolox as standard (0-225 mg/L) adapted from (Brand-Williams et al., 1995) to a plate reader spectrophotometer (Varioskan, Thermo Scientific, USA). Briefly, 20µl of orange extract (without dilution) or Trolox standards were added to 280 µl of 25 mg/l DPPH solution (dissolved in methanol). The absorbance of the remaining DPPH was measured after 30 min at 515 nm. The final results were expressed as mg of Trolox equivalents (TE) per kg of orange dry matter (mg TE/kg dm)

Total carotenoids

Total carotenoids were determined spectrophotometrically by adapting the method described by Sinclair (1984).

For carotenoids extraction from solids samples, 0.1 g of sample was placed in a 15 mL falcon tube and 10 mL of acetone was added, then, sonicated in an ultrasound bath (Ultrasounds-H Bath model, P-Selecta) at ambient temperature for 30 min, centrifuged at 2660 g for 15 min. The supernatant was recovered and filtered through a 0.22 µm PTFE filter. For aqueous samples a liquid-liquid extraction with n-hexane was performed. Sample (2.4

mL) were mixed with n-hexane (2 mL) and mixed for 5 minutes in a vortex mixer. The n-hexane layer was recovered and filtered through a 0.22 µm PTFE filter. The absorbance at 450 nm was measured using a spectrophotometer (Varioskan, Thermo Scientific, USA). Concentration values were calculated through the mass extinction coefficient of beta-carotene in acetone (2542 mL/g cm). Values were expressed in ppm ßCeq. (ppm of ß-Carotene equivalent).

Particle size distribution

Analysis of the particle size distribution was carried out using a laser diffractometer Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK). The Mie theory was applied by considering a refractive index of 1.5 and absorption of 0.01. Samples were diluted in de-ionised water at 2000 rpm until an obscuration rate of 15 % was obtained. $D_{3,2}$ (surface weighted mean diameter) and $D_{4,3}$ (volume weighted mean diameter), D_{10} (the size which 10% of the particles are below), D_{50} (median size) and D_{90} (the size which 90% of the particles are below) were obtained..

In order to study the technological properties of the new fiber obtained, commercial citrus fiber (Herbacel AQ Plus Citrus Fiber, Herbstreith & Fox) was used as a reference for water and oil retention capacities, swelling capacity and colour.

Water and oil retention capacity

For water retention capacity (WRC) samples (0.5 g ± 0.0001 g) were hydrated in 20 mL of distilled water in a 50 mL falcon tube and left overnight to ensure the fiber was fully hydrated. Then, the tubes were centrifuged at 1000 × *g* for 10 min (adapted from Robertson et al., 2000). The supernatant was decanted and the tubes were carefully inverted to drain residual unbound water from the sample. The remaining pellet was dried overnight in an oven at 105 ºC and weighed to consider possible solid matter losses in the draining step. For oil retention capacity (ORC), 20 mL of sunflower oil was added to 0.5 g of sample in a 50 mL falcon tube and left overnight. The tubes were then centrifuged at 1000 × *g* for 10 min. The supernatant was decanted and the tubes were carefully inverted to drain residual oil from the sample. WRC and ORC were calculated as the amount of water or oil retained by the pellet (g/g_{dm}).

Swelling capacity

Swelling capacity (SC), defined as the ratio of the volume occupied when the sample is immersed in excess of water after equilibration to the sample weight, was measured by the method of Raghavendra et al. (2004). To 0.2 g of dry sample placed in a graduated test tube; around 10 mL of water was added to hydrate the sample for 18 h; then the final volume attained by fiber was measured and expressed as volume/g of original sample (dm).

Colour

Colour was measured following CIELab scale. L*, a* and b* parameters were measured using a Minolta CM 3500d colorimeter (Osaka, Japan), where he L* value gave information on the luminance, and the a* and b* values gave information about the colour of the sample (a: from green to red, and b: from dark blue to yellow). Whiteness was determined using the following formula: $\text{whiteness} = 100 - \sqrt{[(100 - L^*)^2 + a^{*2} + b^{*2}]}$, according to Park (1995).

Energy consumption

For the energy consumption calculations, two drying experiments were carried out in triplicate comparing conventional hot air drying at 55ºC (HAD) with hot air drying at 35 ºC coupled with microwaves (MW). HAD was carried out on the same equipment as described above without applying microwave energy. Drier dimensions were 0.66 m x 0.66 m x 0.83 m, air velocity was 7 m/s, ambient temperature was 15 ºC and relative humidity was 60 %. Mass variation was measured at different times. Samples weight at different times (from 50 to 180 min) was measured by a precision balance Mettler Toledo AB304-S (± 0.001g).

Statistical analysis

To determine statistical differences among the fiber obtained by the new process and the commercial fiber, the non-parametric Wilcoxon signed rank test was used with confidence levels of 95 % ($p \leq 0.05$) using the program Statgraphics Centurion XVI 16.1.

Results and discussion

The proximate chemical composition of the fresh by-product is shown in Table 1. Average moisture content prior to drying procedure was 81.9 ± 1.9 %. It can be seen that after water, the main component was dietary fiber (6.4 ± 1.8 %) followed by sugars (3.8 ± 2.2 %), therefore the efficient removal of water and sugar from by-products is important for their exploitation into valuable ingredients such as dietary fiber. Furthermore, the removal of colour and bitter compounds from the fiber ingredient is crucial for its application in food matrices without affecting the sensory properties of the final product.

Table 1: Fresh orange by-product and orange fiber composition in % wet matter[a].

Parameters	Fresh by-product (%)
Water	81.9 ± 1.9
Total sugars	4 ± 2
Protein	1.0 ± 0.5
Fat	<0.1
Ash	0.5 ± 0.1
TDF	6.4 ± 1.8

[a] Values represent mean of 3 replicates ± SE

Total phenolic content, antioxidant capacity, phenolic acids and flavonoids in fresh orange by-products are listed in Table 2. TPC found in raw material was 8520 mg GAE/kg$_{dm}$. If results are expressed in wet matter (1713.4 mg GAE/kg they can be compared to those obtained by Khan et al. (2010) who reported 2750 mg GAE/ kg after 30 min of ultrasound extraction from orange peel' extracts. Polyphenols identified and quantified in orange by-products were chlorogenic acid, caffeic acid, *p*-coumaric acid, ferulic acid, eriocitrin, quercetin, quercetin-rutinoside (rutin), quercetin-glucoside, narirutin and hesperidin. Ferulic acid was the most abundant phenolic acid (42 ± 2.5 mg/kg$_{dm}$). These results are in accordance with data reported by Russo et al. (2014) who detected 46 ± 0.5 mg ferulic acid/ kg lemon by-products.

Hesperidin was the main flavonoid identified (866 ± 11 mg/kg$_{dm}$). Taking into account the variability due to variety, cultivar, harvest month, etc., and expressing the results in fresh weight (190 ± 2 mg/kg), they are consistent with those found by Ramful et al. (2010). These authors examined hesperidine in different citrus fruits and reported a range between 83 ± 0.06 and 234 ± 1.73 mg/g fresh weight. Nonetheless, no naringin was detected, instead, its isomer narirutin was identified and quantified as naringin (287 mg/kg$_{dm}$).

Table 2: Total polyphenol content (TPC), antioxidant content (AOC), carotenoids, limonin, phenolic acids and flavonoids in fresh orange by-products. Results are expressed as mg/kg of dried matter of raw material (fresh orange peel)[a]. TPC is expressed in mg GAE/kg_{dm} and AOC in mg TE/kg_{dm}.

Analyte	Concentration (mg/kg_{dm})
TPC	8520 ± 17
AOC	1568 ± 10
Carotenoids	80 ± 6
Limonin	75.8 ± 9.2
Phenolic acids	
p-Cumaric acid	10 ± 4
Ferulic acid	42 ± 2
Cafeic acid	12.0 ± 1.3
Chlorogenic acid	1.4 ± 0.8
Flavonoids	
Eriocitrin	17 ± 2
Quercetin-rutinoside (rutin)	7.5 ± 1.2
Quercetin-glucoside	3.0 ± 0.4
Quercetin	27 ± 8
Naringin	ND
Narirutin	287 ± 10
Hesperidin	866 ± 11

ND: not detected. [a] Values represent mean of 3 replicates ± SE

Naringin and narirutin are flavanone glicosides of naringenin. They differ in the disaccharide residue: neohesperidose (rhamnosyl-α-1,2-glucose) for naringin and rutinoside (rhamnosyl-α-1,6-glucose) for narirutin (Tripoli et al., 2007). Neohesperidosides have a bitter taste, while rutinosides have a bland taste. Hesperidin has also a rutinoside residue, thus, both main flavonoids found in orange peels have not a bitter taste. Therefore, bitter taste was mainly due to the presence of limonin.

Preliminary experiments for the optimization of the blanching and ethanol soaking conditions were published in Fava et al. (2013). These results showed that blanching by water immersion at 65º C and colour extraction by ethanol soaking in two consecutive cycles of 1:5 (w/vol) were more effective for compounds extraction.

During the blanching step main polyphenols, flavones glycosides, hesperidin and narirutin were removed. This could be due to the fact that blanching enhances polyphenol extraction by eliminating soluble sugars, making polyphenols flavonoids, usually linked to bigger molecules such as carbohydrates and proteins, more available. The ethanol soaking step was carried out for removal of compounds responsible of colour and bitternes (carotenoids and limonin, respectively).

As a result of the process developed, two main co-products were obtained: water from blanching (aqueous extract) and ethanol from decolouring (ethanolic extract). The concentrations of TPC, AOC, carotenoids, limonin, hesperidin and narirutin in both co-products are presented in Table 3.

Regarding TPC, for each kg of fresh orange by-products, 1.63 g GAE were obtained in the aqueous extract and 0.59 g GAE in the ethanolic extract. For each kg of fresh orange by-products, AOC was 0.4 g TE in the aqueous extract and 0.1 g TE in the ethanolic extract. Blanching water contained 51 % and 65 % of the recovered hesperidin and narirutin, respectively. Approximately 70 % of limonin was extracted during the blanching step and the rest was extracted by ethanol soaking (24 %).

Table 3: Distribution of total carotenoids, limonin, hesperidin and narirutin in process co-products (water and ethanolic extracts) and in orange fiber. AOC is expressed as mg TE/kg.

mg/kg[a]	Aqueous extract	Ethanolic extract
TP	1635.3 ± 12.3	599 ± 8
Hesperidin	1442.1 ± 9.1	212 ± 12
Narirutin	377.5 ± 11.3	63 ± 4
AOC	403.2 ± 9.7	105 ± 5
Limonin	34.4 ± 2.4	12.2 ± 0.7
Carotenoids	0.6 ± 0.0	40.4 ± 5

[a] Results are expressed as mg/kg of initial fresh orange peel. Values represent mean of 3 replicates ± SE

The aqueous extract was richer in total phenolics, antioxidants, limonin, hesperidin and narirutin than the ethanolic extract, which was richer in carotenoids. About 86 % of carotenoids were extracted with ethanol and very little were extracted during blanching (1%) due to its hydrophobic nature. Also, regarding the decolouring step, whiteness value of the fiber obtained (80.0 ± 2.3) was similar to the commercial fiber (82.9 ± 1.4). No significant differences ($p \leq 0.05$) were found for whiteness between these samples, therefore it can be concluded that the decolouring step was effective.

The orange fiber obtained did not have a significant amount of bitter compounds as the flavonoids present (hesperidin and narirutin) have no bitter taste and the limonin content was significantly reduced. Furthermore, the AOC of the fresh by-product was 1568.0 ± 10.2 mg TE/ kg_{dm}, at the end of the process the AOC of the fiber obtained was 205.1 ± 0.4 mg TE/ kg_{dm} which adds more value to this ingredient as it can be used also for its antioxidant properties. The proximate composition of the orange fiber obtained is shown in Table 4. Results are similar to the TDF reported by Lundberg et al. (2014) for citrus fiber obtained from by-products of orange juice production. In that study authors reported a fiber ingredient with 73.4 % of TDF, and composed of cellulose (15.9 ± 0.0), hemicellulose (10.0 ± 0.1), soluble fibers such as pectin (42.2 ± 1.1) and other type of fibers (5. 1).

Table 4: Proximate analysis of the fiber obtained from orange by-products by applying hot air-microwave drying.

g/ 100 g fiber	$Fiber_{MW}$
Moisture	10.5 ± 1.7
Protein	6.3 ± 0.3
Lipids	2.5 ± 0.1
Ash	3.5 ± 0.2
Carbohydrates	4.5
Sugar	0.8 ± 0.1
TDF	71.9 ± 1.6
SDF	24.5 ± 1.4
IDF	48 ± 3
cellulose	16 ± 5
hemicellulose	< 0.1
lignin	25 ± 5
Others	6.2
SDF:IDF	1:2

TDF (Total Dietary Fiber); IDF (Insoluble Dietary Fiber); SDF (Soluble Dietary Fiber). Data represent means and standard deviation of experiments performed in triplicate (n=9)

The cellulose content of the fiber obtained by MW drying (15.7 ± 5.3) is very similar to the one reported by Lundberg et al. (2014). However, no hemicellulose was detected and the soluble fiber (24.5 ± 1.4) was also lower. This might be due to the differences among cultivars as the insoluble fiber components are mostly the elements that give the structure for the cell wall and the connective tissue of the plants. The ratio SDF:IDF was 1:2. It is generally accepted that the technical functionality of dietary fiber in foods is reliant on the ratio of soluble to insoluble dietary fiber. When dietary fiber is used as food ingredient it is suggested that the ratio of soluble to insoluble dietary fiber be 1:2. This ratio is more reflected in fiber from fruits and vegetables, while fiber from cereals typically contain higher levels of insoluble dietary fiber as cellulose and hemicellulose (Figuerola et al., 2005).

In the present study fiber size was determined in water and ethanol since some fibers swell in water and their particle size increase, besides alcoholic suspensions eliminate possible artifacts due to non-fiber components. The particle size distribution of the fiber obtained is presented in Table 5.

A dramatic increase of all diameters was detected when comparing sizes in ethanol and in water, surely due to swelling in water. $D_{4,3}$, D_{50} and D_{90} increased their size x 2.5 while $D_{3,2}$ and D_{10} increased twice their size. The volume-weighted average diameter ($D_{4,3}$) is sensitive to the presence of large particles, whereas the surface-weighted average diameter ($D_{3,2}$) is more sensitive to the presence of small particles, therefore, larger particles swelled more than smaller particles. In the citrus fiber obtained, more than 90 % of particle sizes were over 112.9 ± 8.7 μm when suspended in ethanol, while their size increased to 274.1 ± 4.5 μm when immersed in water (Figure 2).

Table 5. Comparison of the technological properties (SC, WRC, ORC) and colour parameters of the orange fiber obtained by hot air-microwave drying ($Fiber_{MW}$) and a commercial citrus fiber (COM).

Technological properties	$Fiber_{MW}$	COM
SC (mL/ g_{dm})	16.4 ± 1.8^{a}	21.5 ± 1.5^{b}
WRC (g water/ g_{dm})	11.5 ± 0.1^{a}	13.4 ± 0.3^{b}
ORC (g oil/ g_{dm})	1.5 ± 0.3	1.5 ± 0.2
L*	90.4 ± 0.0	89.3 ± 1.8
a*	0.9 ± 0.0	-0.2 ± 0.1
b*	17.5 ± 1.3^{a}	13.4 ± 0.3^{b}

[a,b]Values with different superscript are significantly different. Swelling capacity (SC), Water Retention Capacity (WRC), Oil Retention Capacity (ORC). Data represent means and standard deviation of experiments performed in triplicate.

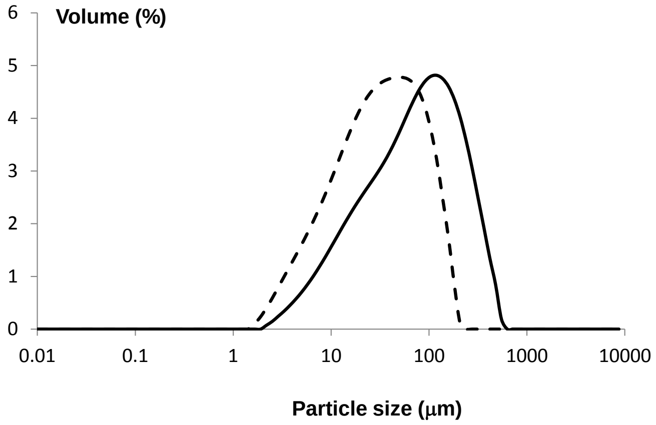

Figure 2: Particle size distribution in water (──) and in ethanol (−−−) of citrus fiber obtained by hot air-microwave drying.

In order to assess the technological functionality of the orange fiber obtained, water, oil retention and swelling capacities were analysed and compared to the commercial fiber (Table 6). WRC of the fiber obtained by MW drying (11.6 ± 1.8 g water/ g_{dm}) was slightly lower than the commercial one (13.4 ± 0.3 g water/ g_{dm}). However, this results are significantly higher than 8 g/g_{dm} reported by Braddock (1999) in orange skin and similar to 11 g water/ g_{dm} reported by Robertson et al. (2000) in citrus pulp. There were no significant differences among fibers with regards to ORC, whereas for SC, commercial fiber swelled 21.5 ± 1.5 mL/ g_{dm} and the citrus fiber obtained in this study swelled 16.4 ± 1.8 mL/ g_{dm}.

Table 6. Particle size distribution of the orange fiber obtained from orange by-products by applying hot air-microwave drying.

Particle size (μm)	Solvent	
	Ethanol	Water
$D_{4,3}$	48.5 ± 2.4	115.3 ± 1.6
$D_{3,2}$	17.4 ± 1.8	32.8 ± 2.3
D_{10}	7.0 ± 1.3	12.9 ± 1.2
D_{50}	34.2 ± 1.5	79.5 ± 1.13
D_{90}	112.9 ± 8.7	274.1 ± 4.5

$D_{4,3}$, $D_{3,2}$, D_{10}, D_{50} and D_{90} represent volume weighted mean diameter, surface weighted mean diameter and 10 %, 50 % and 90 % of all particles finer than this size, respectively. Data represent means and standard deviation of experiments performed in triplicate (n=9).

Nevertheless, swelling and water retention capacity are highly related to particle size distribution which is determined during milling. Lundberg et al.

(2014) reported for the same fiber small increases in WRC as particle size decreased, suggesting that grinding may affect matrix structure and surface area of particles, therefore, differences among the fiber ingredients studied might be due to differences on the obtention process that can be further optimized. Results discussed above already showed the potential swelling capacity of the fiber obtained.

Process yield was 75 g of fiber / kg of fresh by-products. After 90 min of MW drying the moisture content was reduced to 10.5 ± 1.7 %. Comparing to conventional drying methods such as HAD at 35 ºC, the time needed to reach the target moisture content was doubled (Table 7). MW absorption provokes internal water heating and evaporation, greatly increasing the internal pressure and concentration gradients and thus the effective water diffusion. As a consequence, shorter processing time may be required and higher product quality may be achieved (Maskan, 2000).

Table 7: Time (min) needed to reach different moisture levels (x_w) of orange by-products dried by hot air at 55 ºC (HAD) and hot air combined with microwave (MW).

x_w (g_w/ 100 g orange by-product)	$t_{process}$ (min)	
	HAD	MW
10	180	90
20	165	81
30	145	71
40	125	63
50	110	55

Energy consumption was estimated as explained in Figure 3. The total energy required for the hot air-microwave drying process described in this work was estimated as the sum of the energy required by hot air (E_{HAD}) and the energy required by microwaves (E_{MW}) per time.

E_{HAD} was calculated applying thermodynamics of humid air as explained in Green and Perry (2007). Considering the specific enthalpy (h) as the amount of heat (kJ/kg) used or released in a system at constant pressure, E_{HAD} was calculated as the difference between the enthalpy of hot air at 55ºC (h_D) and the enthalpy of ambient air at 15ºC (h_{amb}) per kg of dry air (M'). The total energy consumption of microwaves was calculated as the total microwave power applied (W) per kg of wet product (M_0).

As air is a homogeneous mixture of dry air and water vapour, the enthalpy of hot air is found taking the sum of the enthalpy of dry air and enthalpy of water vapour in the moist air. The specific enthalpy of dry air is a product of the specific heat of dry air (Cp_{da}) and the temperature of drying (T_D). The enthalpy of water vapour depends on the specific heat of water vapour at that temperature (Cp_v), the absolute moisture (X) and the latent heat of vaporization (ΔH^v). The absolute moisture (kg_w/kg_{da}) is related to the partial pressure of water vapour, which at the same time is a product of relative humidity (φ) and the vapour pressure of saturated air at that temperature (ps), the latter being dependent only on temperature. Thus, at T_{amb} and T_D it is possible to obtain the vapour pressure of saturated air at those temperatures (ps^{amb} and p_s^D).Assuming that the absolute moisture of ambient air (X_{amb}) is equal to the absolute moisture of drying air at the beginning of the drying process (X_D^0), it was possible to calculate the specific enthalpy of ambient air and drying air (h_{amb} and h_D, respectively). Finally, the mass of dry air (M') was calculated from the mass of moist air (M_D) and its absolute humidity (X_D^0). Also, M_D is a product of air density (ρ_D), air velocity (v_{air}) and the drier section (S_{Drier}). For air density estimation, at 1 atm it was possible to apply the perfect gases law, therefore, ρ_D was calculated from φ_D and p_s^D. The relative humidity of drying air (φ_D) is defined as the relationship between partial pressure of water vapour and the vapor pressure of saturated air at T_D so it was possible to calculate it as previously explained.

Figure 4 shows the energy and time required to achieve different moisture contents comparing HAD and MW. It is clear that energy consumption and time increase continuously with decreasing moisture content (Sarsavadia, 2007). At the beginning of the treatments, when high water activity produces higher dissipation of microwave energy into heat energy, this is expended in water evaporation, maintaining, in the air, the level of the internal energy (Talens et al., 2015). At the final stages of drying (between 40 and 120 min) water transport is d by mechanical energy.

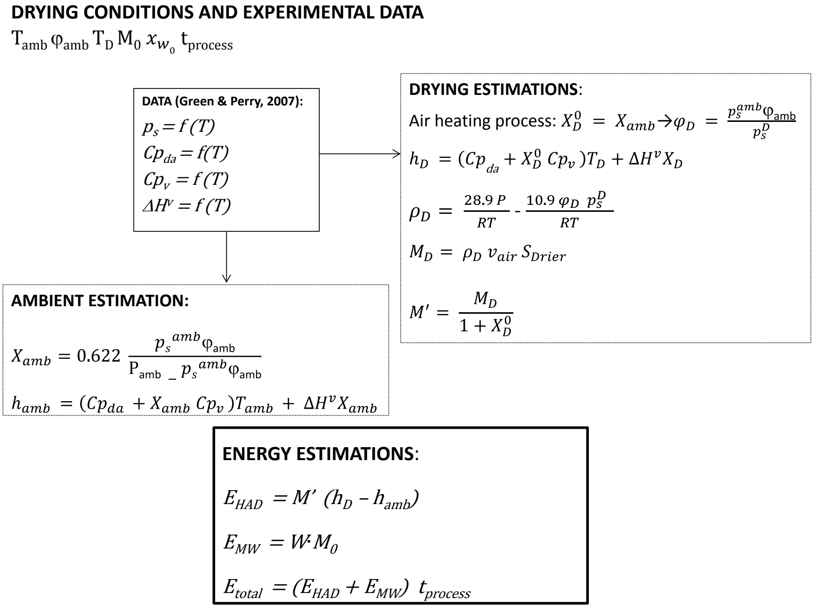

Figure 3: Drying conditions and experimental data for calculating energy consumption of two different drying processes applied to orange by-products: hit air drying (55 ºC) and hot air combined with microwave drying.

It is possible to observe how MW drying not only reduced process time by up to 50 % but also reduced energy consumption by up to 26%. These results are in accordance with Motevali et al. (2011) who evaluated energy consumption of different drying methods for pomegranate. These authors showed that the use of microwave for drying decreased drying time and energy consumption in comparison with convection drying. Also, Alibas (2007) found that the optimum energy consumption was obtained when microwave and air-drying was applied simultaneously in pumpkin slices.

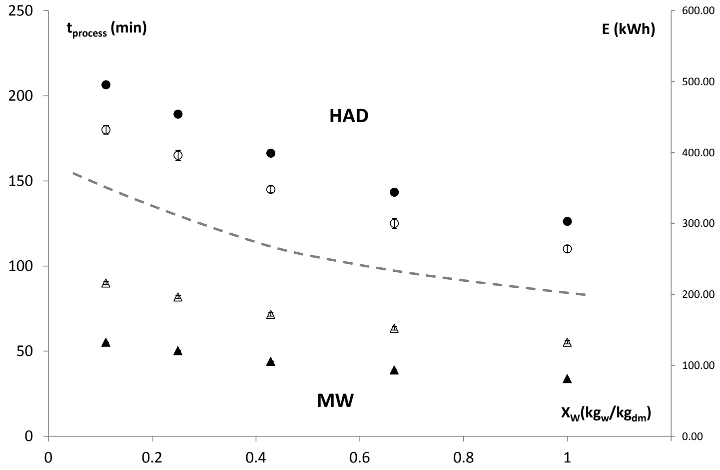

Figure 4: Time (●,▲) and energy consumption (○,△) required for drying at different moisture (x_w) using hot air drying (HAD) and hot air drying coupled with microwaves (MW).

Conclusions

An innovative multipurpose process for obtaining three functional ingredients from orange by-products was developed using hot air- microwave drying technology. An aqueous and an ethanolic bioactive extracts were obtained and characterized as rich sources of flavanones, flavanone glycosides and carotenoids typical of citrus plants. Most of these compounds were extracted during the blanching step except for carotenoids which were extracted during decolouring. A new dietary fiber ingredient with antioxidant properties has been developed. Particle size distribution showed an interesting swelling capacity when fiber was rehydrated. Colour and technological properties of the ingredient obtained were of similar quality than commercial citrus fiber. MW drying reduced process time (50%) and energy consumption (26%) when compared to hot air drying. Therefore, the process developed represented a new sustainable alternative for citrus by-products valorisation and transformation into value-added ingredients.

Acknowledgments

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References

Abu-Ghannam, N., Jaiswal, A.K., (2015). Chapter 5 - Blanching as a Treatment Process: Effect on Polyphenol and Antioxidant Capacity of Cabbage, in: Preedy, V. (Ed.), *Processing and Impact on Active Components in Food*. Academic Press, San Diego, pp. 35-43.

AFNOR, (1997). Association Française de Normalisation (AFNOR), 1997. Norme Française homologuée, Aliments des animaux. Détermination séquentielle des constituants pariéaux. Méthode par traitement aux détergents neutre et acide et à l'acide sulfurique. AFNOR, Paris NF V 18–122, 11.

Alibas, I., (2007). Microwave, air and combined microwave–air-drying parameters of pumpkin slices. LWT - Food Science and Technology 40(8), 1445-1451.

Andrade, J.M.d.M., Jong, E.V.d., Henriques, A.T., (2014). Byproducts of orange extraction: influence of different treatments in fiber composition and physical and chemical parameters. 2014 50(3), 10.

Aravantinos-Zafiris, G., Oreopoulou, V., Tzia, C., Thomopoulos, C.D., (1994). Fibre Fraction from Orange Peel Residues after Pectin Extraction. LWT - Food Science and Technology 27(5), 468-471.

Attavanich, N., Anprung, P., (2003). Dietary Fiber Powder from Citrus reticulate Blanco Peel and Its Application. Food 33, 45-55.

Bampidis, V.A., Robinson, P.H., (2006). Citrus by-products as ruminant feeds: A review. Animal Feed Science and Technology 128(3–4), 175-217.

Braddock, R.J., (1999). *Handbook of Citrus By-Products and Processing Technology*. Wiley.

Brand-Williams, W., Cuvelier, M.E., Berset, C., (1995). Use of a free radical method to evaluate antioxidant activity. LWT - Food Science and Technology 28(1), 25-30.

Chen, M.-L., Yang, D.-J., Liu, S.-C., (2011). Effects of drying temperature on the flavonoid, phenolic acid and antioxidative capacities of the methanol extract of citrus fruit (Citrus sinensis (L.) Osbeck) peels. International Journal of Food Science & Technology 46(6), 1179-1185.

de Moraes Crizel, T., Jablonski, A., de Oliveira Rios, A., Rech, R., Flôres, S.H., (2013). Dietary fiber from orange byproducts as a potential fat replacer. LWT - Food Science and Technology 53(1), 9-14.

Elleuch, M., Bedigian, D., Roiseux, O., Besbes, S., Blecker, C., Attia, H., (2011). Dietary fibre and fibre-rich by-products of food processing: Characterisation, technological functionality and commercial applications: A review. Food Chemistry 124(2), 411-421.

Fava, F., Zanaroli, G., Vannini, L., Guerzoni, E., Bordoni, A., Viaggi, D., Robertson, J., Waldron, K., Bald, C., Esturo, A., Talens, C., Tueros, I., Cebrián, M., Sebők, A., Kuti, T., Broeze, J., Macias, M., Brendle, H.-G., (2013). New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). New Biotechnology 30(6), 647-655.

Femenia, A., Sastre-Serrano, G., Simal, S., Garau, M.C., Eim, V.S., Rosselló, C., (2009). Effects of air-drying temperature on the cell walls of kiwifruit processed at different stages of ripening. LWT - Food Science and Technology 42(1), 106-112.

Fernández-López, J., Sendra-Nadal, E., Navarro, C., Sayas, E., Viuda-Martos, M., Alvarez, J.A.P., (2009). Storage stability of a high dietary fibre powder from orange by-products. International Journal of Food Science & Technology 44(4), 748-756.

Figuerola, F., Hurtado, M.L., Estevez, A.M., Chiffelle, I., Asenjo, F., (2005). Fibre concentrates from apple pomace and citrus peel as potential fibre sources for food enrichment. Food Chemistry 91(3), 395-401.

Green, D., Perry, R., (2007). *Perry's Chemical Engineers' Handbook, Eighth Edition*. McGraw-Hill Education.

Harris, P.J., Smith, B.G., (2006). Plant cell walls and cell-wall polysaccharides: structures, properties and uses in food products. International Journal of Food Science & Technology 41, 129-143.

Hasegawa, S., Brewster, L.C., Maier, V.P., (1973). Use of Limonoate Dehydrogenase of Arthrobacter-Globiformis for Prevention or Removal of Limonin Bitterness in Citrus Products. Journal of Food Science 38(7), 1153-1155.

Hernández-Santos, B., Vivar-Vera, M.d.l.Á., Rodríguez-Miranda, J., Herman-Lara, E., Torruco-Uco, J.G., Acevedo-Vendrell, O., Martínez-Sánchez, C.E., (2015). Dietary fibre and antioxidant compounds in passion fruit (Passiflora edulis f. flavicarpa) peel and depectinised peel waste. International Journal of Food Science & Technology 50(1), 268-274.

ISO, (1973). Determination of total fat content, ISO 1443:1973 standard, *International standards meat and meat products*. International Organization for Standardization, Genève, Switzerland.

ISO, (1978). Determination of total nitrogen content, ISO 937:1978 standard, *International standards meat and meat products*. International Organization for Standardization, Genève, Switzerland.

ISO, (1997). Determination of moisture content, ISO 1442:1997 standard, *International standards meat and meat products*. International Organization for Standardization, Genève, Switzerland.

ISO, (1998). Determination of ash content, ISO 936:1998 standard, *International standards meat and meat products*. International Organization for Standardization, Genève, Switzerland.

Khan, M.K., Abert-Vian, M., Fabiano-Tixier, A.-S., Dangles, O., Chemat, F., (2010). Ultrasound-assisted extraction of polyphenols (flavanone glycosides) from orange (Citrus sinensis L.) peel. Food Chemistry 119(2), 851-858.

Konno, A., Misaki, M., Toda, J., Wada, T., Yasumatsu, K., (1982). Bitterness reduction of naringin and limonin by beta-cyclodextrin. Agricultural and Biological Chemistry 46(9), 2203-2208.

Kris-Etherton, P.M., Hecker, K.D., Bonanome, A., Coval, S.M., Binkoski, A.E., Hilpert, K.F., Griel, A.E., Etherton, T.D., (2002). Bioactive compounds in foods: Their role in the prevention of cardiovascular disease and cancer. American Journal of Medicine 113, 71-88.

Larrauri, J.A., (1999). New approaches in the preparation of high dietary fibre powders from fruit by-products. Trends in Food Science & Technology 10(1), 3-8.

Lees, R., (1968). *Laboratory handbook of methods of food analysis*. Leonard Hill Books, London.

Lu, Y.R., Foo, L.Y., (2000). Antioxidant and radical scavenging activities of polyphenols from apple pomace. Food Chemistry 68(1), 81-85.

Lundberg, B., Pan, X., White, A., Chau, H., Hotchkiss, A., (2014). Rheology and composition of citrus fiber. Journal of Food Engineering 125(0), 97-104.

Macheix, J.J., Fleuriet, A., Billot, J., (1990). *Fruit Phenolics*. CRC Press, Boca Raton, FL.

Marin, F.R., Soler-Rivas, C., Benavente-Garcia, O., Castillo, J., Perez-Alvarez, J.A., (2007). By-products from different citrus processes as a source of customized functional fibres. Food Chemistry 100(2), 736-741.

Maskan, M., (2000). Microwave/air and microwave finish drying of banana. Journal of Food Engineering 44(2), 71-78.

Morales-Blancas, E.F., Chandia, V.E., Cisneros-Zevallos, L., (2002). Thermal Inactivation Kinetics of Peroxidase and Lipoxygenase from Broccoli, Green Asparagus and Carrots. Journal of Food Science 67(1), 146-154.

Motevali, A., Minaei, S., Khoshtagaza, M.H., (2011). Evaluation of energy consumption in different drying methods. Energy Conversion and Management 52(2), 1192-1199.

Moure, A., Cruz, J.M., Franco, D., Domínguez, J.M., Sineiro, J., Domínguez, H., José Núñez, M.a., Parajó, J.C., (2001). Natural antioxidants from residual sources. Food Chemistry 72(2), 145-171.

Nelson, A.L., (2001). Properties of high-fiber ingredients. Cereal Foods World 46(3), 93-97.

Nieto Calvache, J.E., Fissore, E.N., Latorre, M.E., Soria, M., De Escalada Pla, M.F., Gerschenson, L.N., (2015). Obtention of dietary fibre enriched fractions from peach bagasse using ethanol pre-treatment and microwave drying. LWT - Food Science and Technology.

Park, J.W., (1995). Surimi Gel Colors as Affected by Moisture Content and Physical Conditions. Journal of Food Science 60(1), 15-18.

Peerajit, P., Chiewchan, N., Devahastin, S., (2012). Effects of pretreatment methods on health-related functional properties of high dietary fibre powder from lime residues. Food Chemistry(0).

Prothon, F., Ahrné, L.l.M., Funebo, T., Kidman, S., Langton, M., Sjöholm, I., (2001). Effects of Combined Osmotic and Microwave Dehydration of Apple on Texture, Microstructure and Rehydration Characteristics. LWT - Food Science and Technology 34(2), 95-101.

Raghavendra, S.N., Rastogi, N.K., Raghavarao, K., Tharanathan, R.N., (2004). Dietary fiber from coconut residue: effects of different treatments and particle size on the hydration properties. European Food Research and Technology 218(6), 563-567.

Ramful, D., Bahorun, T., Bourdon, E., Tarnus, E., Aruoma, O.I., (2010). Bioactive phenolics and antioxidant propensity of flavedo extracts of Mauritian citrus fruits: Potential prophylactic ingredients for functional foods application. Toxicology 278(1), 75-87.

Regulation EU No 1169/2011, in: Regulation EU No 1169/2011 of 25 October 2011 on the provision of food information to consumers, a.r.E.N.a.E.N.o. (Ed.), *Regulation EU No 1169/2011*. Official Journal of European Union, pp. 18–63.

Robertson, J.A., de Monredon, F.D., Dysseler, P., Guillon, F., Amado, R., Thibault, J.-F., (2000). Hydration Properties of Dietary Fibre and Resistant Starch: a European Collaborative Study. LWT - Food Science and Technology 33(2), 72-79.

Russo, M., Bonaccorsi, I., Torre, G., Sarò, M., Dugo, P., Mondello, L., (2014). Underestimated sources of flavonoids, limonoids and dietary fibre: Availability in lemon's by-products. Journal of Functional Foods 9(0), 18-26.

Sarsavadia, P.N., (2007). Development of a solar-assisted dryer and evaluation of energy requirement for the drying of onion. Renewable Energy 32(15), 2529-2547.

Sinclair, W.B., (1984). *The biochemistry and physiology of the lemon and other citrus fruits*. University of California, Division of Agriculture and Natural Resources.

Singleton, V.L., Orthofer, R., Lamuela-Raventos, R.M., (1999). Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent, in: Packer, L. (Ed.), *Oxidants and Antioxidants, Pt A*, pp. 152-178.

Talens, C., Castro-Giráldez, M., Fito, P.J. A thermodynamic model for hot-air microwave drying of orange peel, 2015, Journal of Food Engineering, in press.

Tripoli, E., Guardia, M.L., Giammanco, S., Majo, D.D., Giammanco, M., (2007). Citrus flavonoids: Molecular structure, biological activity and nutritional properties: A review. Food Chemistry 104(2), 466-479.

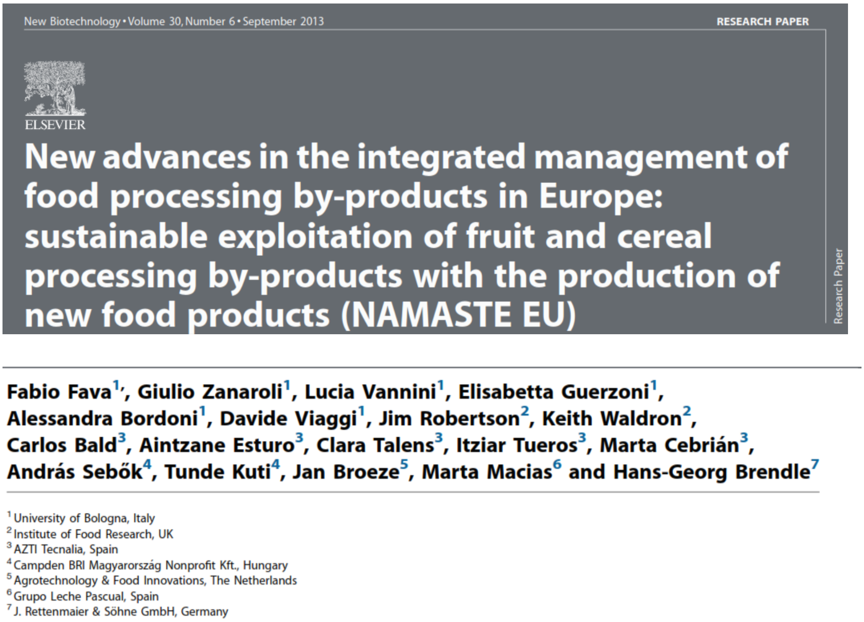
Ubando-Rivera, J., Navarro-Ocana, A., Valdivia-Lopez, M.A., (2005). Mexican lime peel: Comparative study on contents of dietary fibre and associated antioxidant activity. Food Chemistry 89(1), 57-61.

Wuttipalakorn, P., Srichumpuang, W., Chiewchan, N., (2009). Effects of Pretreatment and Drying on Composition and Bitterness of High-Dietary-Fiber Powder from Lime Residues. Drying Technology 27(1), 133-142.

Zhang, M., Tang, J., Mujumdar, A.S., Wang, S., (2006). Trends in microwave-related drying of fruits and vegetables. Trends in Food Science & Technology 17(10), 524-534.

Zhuang, Y., Zhang, Y., Sun, L., (2012). Characteristics of fibre-rich powder and antioxidant activity of pitaya (Hylocereus undatus) peels. International Journal of Food Science & Technology 47(6), 1279-1285.

RESULTADOS: Artículo 4.7



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RESEARCH PAPER

ELSEVIER

New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU)

Research Paper

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By-products generated every year by the European fruit and cereal processing industry currently exceed several million tons. They are disposed of mainly through landfills and thus are largely unexploited sources of several valuable biobased compounds potentially profitable in the formulation of novel food products. The opportunity to design novel strategies to turn them into added value products and food ingredients via novel and sustainable processes is the main target of recently EC-funded FP7 project NAMASTE-EU. NAMASTE-EU aims at developing new laboratory-scale protocols and processes for the exploitation of citrus processing by-products and wheat bran surpluses via the production of ingredients useful for the formulation of new beverage and food products. Among the main results achieved in the first two years of the project, there are the development and assessment of procedures for the selection, stabilization and the physical/biological treatment of citrus and wheat processing by-products, the obtainment and recovery of some bioactive molecules and ingredients and the development of procedures for assessing the quality of the obtained ingredients and for their exploitation in the preparation of new food products.

The food and drink industry represents a large and economically important sector in Europe. Fruit and cereal processing has increased considerably during the past 25 years mostly as a con-sequence of the fact that epidemiological studies have related an increased dietary consumption of fruits and cereal fibres with a decrease in the incidence of cancer and cardiovascular disease mortality [1,2]. Processing generates large volumes of waste and by-products (between 20 and 60%, w/w of the fruit and cereal processed) [3] with a high biochemical and chemical oxygen demand (BOD and COD, respectively), and with associated high treatment cost. A sustainable Agro-Food industry recognizes that waste prevention, minimization and valorization, rather than 'end of pipe', are the required solutions for waste management. Thus, the legislation at the European level is promoting the use of these solutions. However, strategies and technologies to secure eco-nomic and environmental solutions for an effective management of food by-product and waste have to be developed. In general, such streams are currently only partially valorized at different value-added levels (spread on land, animal feed, composting, among others), whereas the main volumes of them are managed as waste of environmental concern with relevant negative effects on the overall sustainability of the food processing industry [IAP ETP Food for Life:

http://etp.ciaa.be/documents/CIAA-ETP% 20broch_LR.pdf].

Vegetable, cereal and fruit processing by-products and waste are typically rich in proteins, sugars and lipids and contain particular aromatic and aliphatic complex compounds [4]. Thus they are cheap abundant sources of not only value-added bio-based chemicals and materials of high interest for the chemical and textile sectors, but also, in the case of by-products (which differ from waste in that they have not been widely exposed to environmental con-tamination), for the modern cosmetic, pharmaceutical and food industry [IAP ETP Food for Life: http://etp.ciaa.be/documents/ CIAA-ETP%20broch_LR.pdf]. Indeed, after specific pretreatments with physical and biological agents followed by tailored recovery procedures, they might provide specific natural antioxidants, anti-microbial agents, vitamins, among others, along with macromolecules (e.g. soluble fibres), bioactive oligosaccharides, oligopeptides, and pigments. Further, some of the compounds occurring in the hydrolyzates resulting from the by-products pretreatment can be transformed into more sophisticated molecules like flavours and fermentation products, throughout tailored biotechnological processes [5,6]. All these natural compounds can be combined in the formulation of new food products with the attempt to close the circle within large fruit and cereal food industries and/or to create new synergies between fruit/cereal processing industries and food producing industries. The final outcome would be an improvement of the overall sustainability and competitiveness of the European food industry. This is the main target of the EC-funded FP7 project NAMASTE-EU (Joint EC & DBT-India call: KBBE-2009-2-7-02: Valorization of by-products in food processing), which specifically aims at developing new protocols and processes for the sustainable exploitation of citrus by-products and wheat bran surpluses into natural ingredients for beverages, snacks along with edible fractions and fillers enriched in active molecules (vitamins, oligosaccharides, minerals, aminoacids, antioxidants) of interest for the preparation of new ingredients and food products.

2. State-of-the-art of citrus and wheat processing by-products production and valorization in Europe

The global citrus fruits production (i.e. oranges, grapefruit, lemons and limes, and some tangerines) reached almost 90 million tons (MT) in 2011/12 campaign [7]. Brazil is still the main citrus producer with around 20 MT, mainly oranges, followed by USA with nearly 11 MT and the Mediterranean area being the third major citrus producing area in the world, with 10 MT in 2011/12. About a third of global citrus fruit production goes for processing (around 27 MT in 2011/12 campaign) and more than 80% of this is for orange juice production [7]. The residue resulting from its processing is mainly constituted by peels, which are almost one-fourth of the whole fruit mass, seeds and fruit pulp remaining after juice and essential oil extraction, for an overall amount of by-product corresponding to about 50–60% of the original mass processed [8]. There is a lack of reliable information on citrus wastes generation. On the basis of the above mentioned data, the global amount of citrus by-products can be estimated in 16 MT.

From production data provided by C.L.A.M. (Liaison Committee for Mediterranean Citrus), AIZCE (Spanish Association of Indus-tries of Citrus Fruit Juices and Concentrates) and NAMASTE project participants and collaborators, European and Mediterranean citrus by-products production is over one MT per year. The disposal of the fresh peels is becoming a major problem to many factories. The major cereal crops produced in Europe are wheat and rice [9]. The European Union remains, by far, the main world producer of wheat (FAOSTAT Agricultural statistics) and accounts for over 20% of the production (about 10 MT/year [9]). France, Germany and the UK, collectively account for around 60% of the total EU production. Asia accounts for around 30% of global production, with India and China accounting for around 60% of total Asiatic output. The bulk of these grains are refined and used for food production. This generates a bran fraction (up to 25–30%, w/w of grain), currently used predominantly as animal feed or disposed of as waste.

The oldest and easiest route for exploitation of citrus by-pro-ducts and wastes and brans is to use them in animal feeding. The use of fresh citrus pulp, citrus silage, dried citrus pulp, citrus meal and fines, citrus molasses, citrus peel liquor, and citrus activated sludge as feedstuffs for feeds for ruminants recently increased [10]. More recently, pathways for obtaining essential oils, limonene, terpenes, aromatic liquids and citrus pulp pellets from citrus raw material have been developed [11]. Peels (albedo and flavedo), seeds and fruit pulp remaining after juice and essential oil extraction [12], have different applications in the domestic and inter-national markets, and include the production of chemical products, biofuels and solvents, flavours and fragrances, substances for the paint industry, cosmetics, and animal feed supplements [13,14]. Industrial citrus by-products have also been traditionally used as raw material for the production of pectin [6] often employed to increase the viscosity of liquid or semisolid foods. They are also applied as stabilizers in acid milk products and as fat mimetics. However, peels possess a large variety of bioactive compounds that might be considered as potential sources of functional components [14]. Except for ascorbic acid, citrus peels contain more bioactive compounds such as phenolic acids, flavonoids – for example, hesperidin, narirutin, naringin and eriocitrin [15] – limonoids and fibres than the juices do [16–18]. These compounds have attracted more attention due to their properties related to human health, which was ascribed to their antioxidant activities and free radical scavenging abilities [16,19]. Citrus flavonoids are powerful antioxidants against free radicals, because they act as radical-scavengers. They also have anti-microbial, anti-inflammatory and anti-atherosclerotic activity and they are chemo-preventive or anticancer agents [20]. Fibres from citrus are being considered of higher quality than those from cereal due to a better balance of soluble and insoluble dietary fibre (DF) content and, also, due to their higher water and oil holding capacities [21]. The additional advantage of citrus DF is due to their content of associated bioactive compounds (flavonoids and vita-min C) with antioxidant properties, which may exert higher health promoting effects than the dietary fibre itself [22]. Lemon possesses the highest antioxidant potential among citrus fruits and it is the most suitable fibre for dietary prevention of cardiovascular and other diseases [18]. DF is desirable not only for its nutritional aspects but also for their functional and technological properties [13,23].

Bran is composed of various tissues, such as aleurone and pericarp, and accounts for most of the micronutrient, phytochemical and fibre content of the grain. Bran is particularly rich in DF and, for rice bran, omega fatty acids and contains significant quantities of starch, protein, vitamins, and dietary minerals [24]. At the industrial level bran, and in particular wheat bran, is currently used for the production of low-value products, like composts and livestock feed, and significant amounts are disposed of in landfills as waste. Dry fractionation technologies allow bran to be separated and recovered to efficiently separate high and low value components to develop nutritionally enhanced ingredients and products [25]. Wheat bran can be used to enrich breads and breakfast cereals in fibre content, especially for the benefit of those wishing to increase their intake of DF often for alleviating constipation, but less emphasis has been given to enhancing fibre quality in foods through modification to the fibre matrix and the control of its physicochemical properties. However, cost-effective deconstruction of these by-products into their polymeric, oligomeric and individual components, through mechanical and/or (bio)chemical means could provide valuable streams for exploitation in several different applications in the food industry. The DF content of cereal bran is based mainly on its pentosan content, mainly as arabinoxylans and xylans. The presence of phenolic acids, in particular ferulic acid, esterified to arabinoxylans gives this fraction the potential to be exploited as a source of polymers and oligosaccharides with anti-oxidant properties for food use [24] and also a potential substrate for biotechnological production of vanillin [26]. Cereal bran-derived oligosaccharides may have an effect on blood lipids and are currently candidates as prebiotic agents in foods. There remains considerable scope for exploitation in this area, through modification or tailoring physicochemical properties in foods.

3. Exploitation of constituents of citrus and wheat processing by-products in new food product formulation: current status and objectives of the NAMASTE project

Citrus and wheat processing by-products have a balanced composition of soluble and insoluble DF fractions along with several prominent bioactive compounds [27]. Despite of these favourable features, such matrices have found limited applications in the formulation of new food products and in particular in the preparation of bread, biscuits and related food products [28,29]. There is a prominent interest in increasing the consumption of all foods that can supply fibre to daily food intake. Modern diets are deficient in fibre (on average Europeans and Americans alike only consume 30% of the recommended daily intake). Recently, some researchers have published the use of citrus DF for meat products: Lemon albedo (raw and cooked) was added to cooked sausages (bolognas) and dry-cured sausages [15,22], Spanish dry-fermented sausage [30], beef burgers [31] and in dairy products [32]. Despite the several studies made to recover valuable compounds from food by-products, an important still open challenge is the development of products that meet the consumers' high quality standards for safety and organoleptic characteristics. Moreover, a crucial step in the conversion of food by-products into potential new ingredients and food products is adopting technological processes that allow the production of microbiologically and chemically stable ingredients/products while minimizing bio-active, nutritional and functional properties losses.

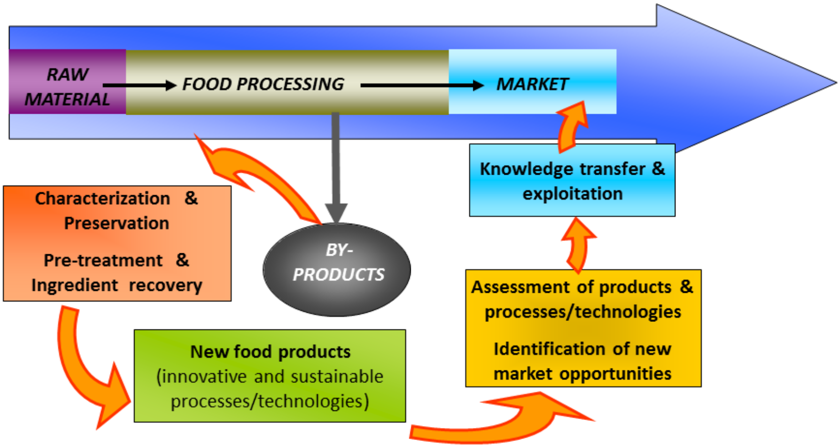

FIGURE 1. *Schematic diagram showing the main steps ensuring NAMASTE EU potential to recover fruit and cereal processing by-products into the food value chain.*

NAMASTE-EU has the technical objective to develop and assess laboratory-scale experimental protocols relying on economical and environmental sustainable processes and technologies for converting citrus and wheat processing by-products into ingredients and new food products with improved and health promoting properties. More specifically, it is addressed to develop and assess the by-product processing steps reported in Fig. 1, that is, (a) methods for the selection and characterization of the by-products to be employed consisting of integrated protocols for the assessment of quality, chemical and microbial safety of food industry by-products, (b) tailored techniques for the preservation and stabilization of by-products, (c) improved methods for the efficient recovery of DF, oligosaccharides, vitamins, antioxidant and anti-microbial agents from stabilized bran and citrus by-products consisting of tailored physical/enzymatic biomass pretreatment followed by selected recovery procedures, (d) novel or integrated methods for analysing the nutritional quality, chemical and microbiological safety of food ingredients recovered, (e) an improved and assessed, two-phase biotechnological process for the production of vanillin from ferulic acid-enriched bran hydro-lyzates; (f) innovative protocols for exploiting natural ingredients, including those obtained through fermentation, together with pretreated citrus by-products and bran in the formulation of a new beverage, fruit paste, citrus filled snacks and citrus paste-based self-stable fillers for bakery products of interest for the EU food market by means of high pressure homogenization and extrusion processes and (g) integrated and innovative methods/techniques for the assessment of nutritional quality, chemical and microbial safety of the new food products and of the environmental and economical sustainability of processes selected and employed in the project along with strategies and protocols for the evaluation of risks, economic benefits and new industrial/market opportunities in Europe for the new food products.

4. Main findings from the characterization, stabilization and exploitation of citrus processing by-products.

The characterization was performed on peels collected from three different sweet orange varieties (Citrus sinensis, varieties Lane Late, Valencia Late and Barberina) and two varieties of lemon (Citrus limon var. Fino and Verna). Centesimal compositions were deter-mined by standard official methods. Mean results for the orange varieties obtained from the cultivars in Palma del Río, Spain, expressed in % WM were: fat content 0.21 0.10, protein 1.50 0.11, moisture 77.55 2.90, total sugars 5.24 0.38, ash 0.73 0.12, pH 3.97 0.49. The highest variability was found in the fat content (51% approx.) while it did not exceed 20% in other parameters. However, fat content is low in the orange by-products. The composition of the sample of lemon by-product of the fino variety was in % WM: free sugars 1.77, fat <0.1, protein 1.06, moisture 85.04, ash 0.6 and pH 3.5; the composition of the by-product of the verna variety taken in June was similar (fat 0.13%, protein 1.41%, moisture 82.18%, ash 0.8% and pH 3.93) except for sugar content, which was higher (4.07%) probably due to the ripening degree and the characteristics of this variety. Results were similar to those expected from the literature [12,33]. All samples had a good microbiological quality (estimated by number of total viable cells, coliforms, Salmonella spp., Listeria monocytogenes, sulphite reducing clostridia, coagulase positive staphylococci, yeasts and moulds), indicating good handling and good quality of the raw material. Citrus polyphenols (TPC) were extracted from peels by a standard ultrasound-assisted liquid–liquid extraction procedure using a methanol:water:formic acid mixture and measured by Folin–Ciocalteu assay using gallic acid as standard [34]. Total poly-phenol content ranged from 0.8 to 1.3 and 1.1 to 1.8 g gallic acid equivalents (GAE)/100 g dry matter in orange and lemon peels, respectively, and 1.0 in mandarin. Values are in the range of several reported values found in the literature [12,18,33]. The samples of different orange varieties and production sites displayed total phenolics concentrations in the range of 2.58–3.25 g GAE/kg wet matter; no relationship was observed between phenol content and the variety or production site of the orange, indicating that variability in TPC was due to different ripening degrees. Seeds have also shown a significant amount of polyphenols but at lower values with respect to peels. Lemon peels of the Verna variety did not differ significantly in phenolic content from the variety Fino. Such findings were consistent with those previously reported by Marin et al. [12]. Individual polyphenol analysis in citrus by-products was performed by direct injection of filtered citrus extracts into an Agilent 1100 LC-MS/MS (liquid chromatography tandem mass spectrometry) system using commercial phenolic standards of gallic acid, chlorogenic acid, cafeic acid, p-coumaric acid, ferulic acid, eriocitrin, hesperidin, naringin, catechin, and quercetin glucoside. A reversed-phase Gemini (Phemomenex) C18 (150 2.1 mm I.D., 5 mm) column was used, while solvents for the mobile phase were water and methanol both in 0.1% formic acid. The flow rate was 0.4 mL/ min and the injection volume was 10 mL. The chromatographic separation was carried out at 308C in gradient mode for 63 min. Mass spectra were obtained on an ion trap mass spectrometer (Bruker) with ESI ion source operated in positive and negative mode. For the MS/MS analysis, manual MSn was used for fragmentation. Identification of polyphenols was made possible by comparison of retention times and mass spectra with those of the standards. Lemon seeds were the only sample that contained catechin. They also contained higher concentration of eriocitrin (356 mg/kg) than lemon peel (40 mg/kg) and orange peel (2.7 mg/kg). The highest concentration of naringin stereoisomers was found in the orange samples. Hesperidin concentrations were in the same order of magnitude in all samples, but it was detected at higher concentrations in the lemon seeds. Previous studies already mentioned the higher antioxidant capacity and total phenolics content of lemon peel [35].

Then, the best strategies for the by-products stabilization based on maintaining a low water activity and gentle heat treatments were identified through several lab scale experiments to have the safe by-products maintained for several months. Drying composes the most important cost in most valorization pathways when the water content of the material is as high as in the case of citrus by-products. Therefore, different innovative and more sustainable drying technologies were assayed. The influence of drying on the content of polyphenols of citrus by-products and in the physical–chemical properties of the obtained DFs has been investigated first, showing that the drying temperature is critical [33]. The free sugar content as well aspolyphenol oxidasesoccurring inthe matricesmayproduce a brown colour which might limit the product applications in food formulations. Therefore, an enzyme inactivation step and elimination of these free sugars have been considered. Lario et al. [22] reported the advantages deriving from blanching at 908C for 5 min before drying. Blanching of citrus by-products employed before drying provided benefits on the obtainment of DF powder. Some of the reported benefits were the enhancement of the water holding capacity, the prevention of fibre browning during the drying step and a reduced water activity of the final DF. However, hydrosoluble bioactive components like vitamins, polyphenols, pectins are leaving the material during blanching together with sugars [11]. Microwave drying technology (MW) provokes biomass internal water heating and evaporation, greatly increasing the internal pressure and concentration gradients and thus the effective water diffusion. As a consequence of this, shorter processing time may be required to achieve a higher product quality [36]. Moreover, MW favoured phenolic compound release from the microstructure of the vegetable walls thus facilitating further extraction of the same compounds [37]. Instant Controlled Pressure Drop (DIC) technology is a combined thermo-mechanical treatment that has been proven to facilitate the drying processes through the expansion effect it has on the vegetable microstructure. It has been used with success as pre-treatment in the production of dehydrated products and as previous treatment to facilitate extraction processes [38]. Finally, both MW and DIC may modify the microstructure of the vegetable material through an expansion effect that can improve the technological properties of the obtained dietary fibre. Vapour blanching and blanching by water immersion along with simple hot air heating, MW drying technology and DIC before conventional drying have been tested on the selected products and com-pared in terms of energy consumption and impacts on the quality of the resulting ingredients. All methods mentioned use low temperatures to stabilize the material. The criterion for comparing procedures was based on visual colour after drying. Reference optimal colour was assumed to be freeze-dried citrus by-product. Hot air conventional drying was performed at 50 and 658C in a convection oven. MW treatments were carried out in pilot scale microwave equipment (electromagnetic microwave generator MMP20T, Sairem S.A., Miribel, France) in batch conditions at 2450 MHz. A range of particle size (0.5–1.5 cm), sample load (10–500 g), power density (5–30 W/g), % ventilation (50–75%) were tested with blanched and not blanched samples.

Dehydration kinetics was observed up to 150 min treatment. DIC treatments were made in a laboratory-pilot scale ad hoc constructed DIC equipment (ABCAR-DIC, La Rochelle, France). Particle size (<0.2–1 cm), moisture con-tent at the moment of expansion (8–50%), pressure (1.5–6 bar) and time of processing (15–180 s) are some of the critical parameters of the DIC process that were assayed. The effect of the stabilization treatment on process efficiency, yield, product moisture content, water activity, instrumental colour, microbiology and sensory quality was assessed. DIC treatment induced darkening of the material, which increased with the temperature of the treatment. Further studies demonstrated that MW and DIC modified the microstructure of the vegetable material through an expansion of microstructure and that this in turn improves the technological properties of the obtained DFs. No reduction on total polyphenol content was observed via vapour blanching, buta phenol depletion of about 70% was observed when blanching was performed by immersion in hot water, probably due to the leaching of the soluble polyphenols, as already described by Marin et al. and Kuljarachanan et al. [12,39]. However, the vapour blanched peels showed an intense browning during the drying process, probably due to the high free sugars content of the starting material (around 20% of dried matter in the case of orange peels). MW drying did not affect the total phenolic content of the sample and slightly increased the total carotenoid content of raw by-product (which was 151 mg/kg dried matter, similar to what was observed on similar by-products by others [40]), probably due to carotenoids isomerization [41]. MW drying highly reduced the process time required to reach target moisture content (7–11%) and water activity (0.20–0.35) by 3-fold compared to hot convection drying at 658C. Microbial analysis carried out on MW treated samples showed that this pre-treatment reduced moulds and yeasts by 3 log cycles, aerobic mesophilic bacteria by 4 log cycles and sporulating mesophilic bacteria by 1 log cycle. Although it is considered a relatively expensive technology, MW drying operational costs are lower than those of other drying technologies, due to its efficiency in evaporating water. In addition it does not display remarkable adverse effects on the technological and sensoryproperties of the citrus-derivedingredients tested. Thus, at this stage, MW technology was selected as the drying method for stabilizing citrus peels.

Following MW drying, a set of experiments were carried out to eliminate bitter molecules, flavours and colour from the resulting fibres to obtain marketable products. For this purpose, classic solvent extraction (SE) and Ultrasound Assisted Extraction (USE) were compared. Ethanol at 75% and 96% was used as preferred solvent, based on preliminary trials. The efficiency of the extraction was determined during one or two extraction cycles and at solid:solvent ratio of 1:10 and 1:5. USE was more efficient than SE, with a 20–27% higher extraction. Two cycles at solid:solvent ratio 1:5 were more efficient than 1 cycle at 1:10 ratio. An additional 30– 50% of polyphenols was obtained in the second extraction cycle. Ethanol at 96% and two extraction cycles, ratio 1:5, gave the best results in terms of extraction yield and colour of the resulting fibre. USE resulted to be the best option: high reproducibility, shorter times, simple, reduced solvent consumption and low temperature, especially useful for thermolabile compounds such as polyphenols [42]. As a result, a citrus DF with a good water binding capacity over 10 g water/g fibre (AACC Method 38-12.02) with acceptable colour was obtained.

A polyphenol rich crude concentrated extract was also produced as a co-product of this debittering step. Its final total polyphenol content was 120 g GAE/kg. The flavonoids naringin and hesperidin were the major polyphenols found, which are flavanones almost exclusively from citrus, not found in other vegetables [43]. Quercetin-o-glucoside, rutin, p-coumaric acid, ferulic acid and caffeic acid were also found but at much lower concentrations. Naringin concentration was 11 g/kg and hesperidin concentration 31 g/kg. The method allows obtaining a crude polyphenol rich extract together with a citrus DF that could be used as ingredients in the formulation of food products and feed with technological and health properties. However, several experiments addressed to improve the extraction yield and efficiency and to recover the polyphenols as well as other soluble compounds that are lost in the blanching step are in progress.

Main findings from the characterization, stabilization and exploitation of wheat bran

A survey on the generation of wheat bran, associated with characterization of feedstock to be used as part of NAMASTE-EU, has shown that geographical origin and wheat type (hard/soft) have little effect on the composition of the bran; hence as a feedstock for industrial exploitation all sources of wheat bran can be considered equivalent. As a low moisture and hence reasonably stable commodity wheat bran can also be stored without the need for elaborate stabilization regimens. However, the associated resident, mainly fungal, microflora has to be considered within any pro-posed processing activity. For wheat bran, there are 2 main challenges to overcome for raw material supply. First is to confirm that low moisture (relative humidity <65%) is suitable for longer term storage of bran (over 1 year) without compromising microbial safety. Second is to confirm that pesticide residues, in a recognized food-grade product, remain within accepted limits [44] and do not become concentrated during downstream processing activities. Recent approaches with cereal bran have involved the use of processing technologies to fractionate and recover potentially high value components such as residual starch and protein, along with bioactive components such as DF natural antioxidants and functional compounds, like oligosaccharides with potential pre-biotic activity. Within NAMASTE, integrated protocols have been developed for the exploitation of wheat bran for its holistic and sustainable use to extract value-added components, from starch and protein and involving the solubilization of the fibre concentrate non-starch polysaccharide (arabinoxylan) fraction. Wheat bran composition from Standard Food Composition Tables (www.ars.usda.gov/) has a moisture content (in w/w) between 8 and 10%, protein content 13–16%, lipid 4.3–5.5% and ash 5–6%. Carbohydrate is the major component in wheat bran, with dietary fibre contributing around 40% of the bran dry weight (range 36– 45%) and with variable amounts of starch; typically around 10%. The major non-starch-polysaccharides (NSP) components are cellulose (20%) and arabinoxylans (60%).

The protocols developed to selectively degrade bran involve the treatment of bran and selected milling fractions to remove starch and protein and yield a DF concentrate (Fig. 2).

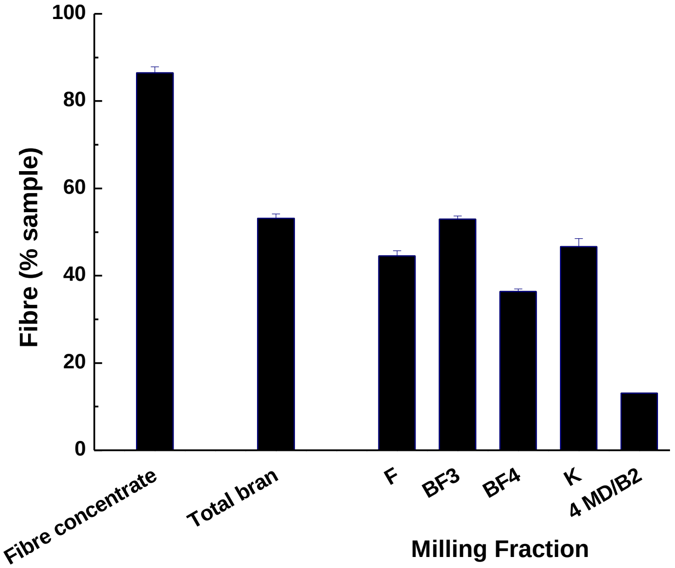

FIGURE 2. DF content in wheat bran and selected milling fractions. Samples were obtained from an industrial Roller Mill by intercepting the flow of partially milled grain, at points designated F, BF3, BF4, K and 4MD/B2 from within the mill sifters scheme. The sifters are arranged to separate flour and bran fractions, through partial recirculation and resifting of flow streams to recover the flour during the milling process. The bran-enriched/flour-depleted fractions, designated as F, BF3, BF4, K and 4MD/B2, have been identified as their sampling location from within the mill sifters.

The fibre concentrate provides the substrate for enzymatic treatments to solubilize component polysaccharides. The amount of fibre concentrate recovered varies with milling fraction source, but all fractions are similar in composition, being enriched in arabinoxylans and cellulose.Milling fractions provide the opportunity to control or increase the substrate concentration available for subsequent enzymatic treatments, for example, using xylanase activity to release oligosaccharides. The fibre concentrate from the original total bran (45% recovery) is over 85% DF asdeterminedbydirect analysis [45]. Starch and protein digests arising from the isolation of the fibre concentrate can be recovered for further use. Because the protocols used involve food-grade enzyme preparations obtained from producer companies (e.g. Novozymes, Denmark, and Biocatalysts Ltd., UK), the food-grade Hazard Analysis & Critical Control Points (HACCP) standards of the raw bran can be maintained during processing.

The water-insoluble residue DF concentrate has been used as a substrate suitable for the enzymatic release of water soluble cereal fibre-based oligosaccharides with prebiotic activity [46,47]. Selective use of xylanase activity yieldsa profile of oligosaccharideswhich remains stable during prolonged incubation (>6 h). Enzymatic treatment protocols based on xylanase activity to degrade arabinoxylans can release approximately 25% of the fibre concentrate as water soluble polysaccharides and oligosaccharides (Fig. 3). However, the yield of solubilized material varies between milling fractions, suggesting that differences in arabinoxylan structure and in susceptibility to enzyme attack are also important determinants of bran matrix solubilization.

The extent of digestion also varies with enzyme source, enzyme cocktails like Depol 740L (Biocatalysts Ltd., Cardiff, UK) tending to lead to a greater extent of digestion com-pared to single recombinant xylanases, like Pentopan (Novozymes, Denmark) (Fig. 3).

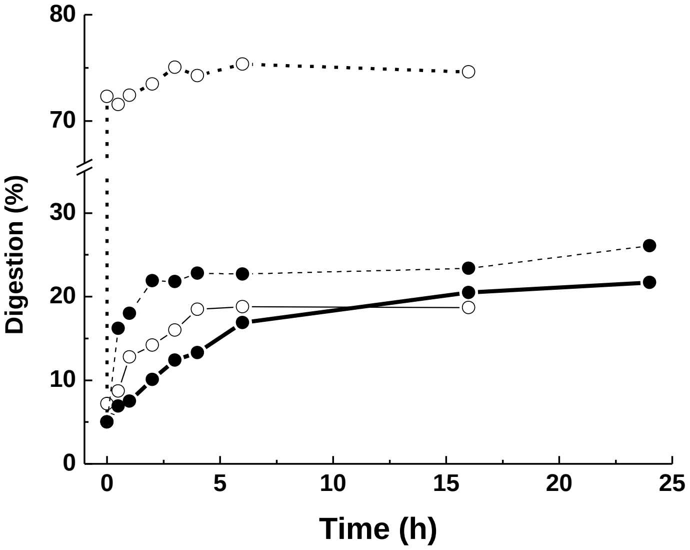

Figure 3: Enzymatic digestion of arabinoxylan (AX) and wheat bran fibre concentrate: ---○---, AX sol (Pentopan); ---○---, AX insol (Pentopan); ▬●▬, bran (Pentopan); —●—, bran (Depol). AX was supplied by Megazyme (Ireland) as wheat flour low viscosity AX (sol) and wheat flour insoluble AX. Pentopan (Novozymes) is a recombinant xylanase and Depol 740L a polysaccharidase enzyme cocktail with feruloyl esterase activity. Enzymes were standardized for use at 7.5 U xylanase activity/g substrate and incubated in deionized water (pH 6) at 508C. Enzyme activity was stopped by boiling 15 min.

This suggests that arabinoxylan structural features are important in controlling the extent of digestion but, from the behaviour of a water soluble and water insoluble arabinoxylan, that other architectural features also influence digestibility and hence oligosaccharide yield. The similarity in digestion between water insoluble arabinoxylan and wheat bran fibre suggests that architectural features are crucial in deciding enzyme accessibility for digestion .Physical methods, for example, Instant Controlled Pressure Drop (DIC) and Steam Explosion, can be used to disrupt the bran matrix, the objective being to enhance enzymatic solubilization but without significant effects on arabinoxylan structure and loss of ferulic acid through the treatment conditions.

Extraction of enzyme-solubilized fractions in 80% ethanol indicates that material solubilized through xylanase treatment is around 75% oligosaccharides, similar to other reported recoveries [48].

The oligosaccharides released are collectively termed FAXX. The presence of ferulic acid benefits the anti-oxidant properties and makes FAXX prospectively more desirable and valuable as an ingredient for incorporation into foods for health promotion. Prebiotic properties are evaluated through in vitro fermentation and assay using fluorescence in situ hybridization probes (FISH) [49]. The residue remaining after enzymatic treatment remains available as a fibre concentrate or can be channelled for biofuel use, thereby accounting and exploiting all the raw material, as envisaged in the protocol developed. The protocols developed are currently being used to evaluate the proposed technical and economical viability of producing prebiotic oligosaccharides. These will be evaluated in comparison with existing protocols and also to take account of the safety and quality of the resulting ingredients and food products being elaborated. Large-scale production of bioactive agents, like oligosaccharides, from bran should reduce the costs involved in producing similar oligomer profiles through microbial fermentation and extraction of such oligomers from bran will add considerably to its economic value.

Ferulic acid is abundant in wheat bran, where it acts as a cross-linking agent among carbohydrates in the wall, being linked to sugar residues through ester links.

It is not only an effective in vitro antioxidant but also a promising substrate for the production of biovanillin, which is one of the most important aromatic flavour compounds used in the food and cosmetic industries [50]. It could be released via enzymatic hydrolysis of the cell wall components combined with the action of esterases. However, due to the extremely complicated structure of the cell wall, a combination of physical methods, aiming at disrupting the bran matrix, with an array of enzymes with varied function might be necessary. To this purpose, several protocols based on thermal pre-treatment of whole bran followed by the use of different enzyme combinations have been tested. Limited release of ferulic acid has been obtained, the highest amount being released from the arabinoxylan fraction after treatment with the xylanase Pentopan and a feruloyl esterase (0.9 g ferulic acid release/kg whole bran). Different matrix physical pre-treatments will be employed to increase the matrix accessibility to enzymes and, in turn, ferulic acid release. After release from bran, ferulic acid has been converted into biovanillin. According to the European regulation on flavours (EC N8 1334/ 2008), vanillin obtained from material of natural origin (vegetable, animal or microbiological sources) using physical, enzymatic and microbiological processes can be labelled as 'natural vanillin'. This has led to the investigation of biotechnological routes to obtain this flavour from natural substrates such as ferulic acid in particular from bran processing by-products [50]. Pseudomonas spp. have been proposed for the production of vanillin from ferulic acid. The possibility of producing vanillin from ferulic acid via P. fluorescens strain BF13 was investigated under resting cell conditions after inactivation of vanillin dehydrogenase gene (vdh) asso-ciated with concurrent expression of structural genes for feruloyl-CoA synthetase (fcs) and hydratase/aldolase (ech) from a low-copy plasmid under the control of native Pfer promoter. Since the physiological state of cells remarkably influences the expression of the ferulic acid catabolic pathway in wild type BF13 strain [51], the optimal culture conditions to obtain cells capable of efficiently performing the bioconversion were investigated. In particular, the most active cells (vanillin molar yield 63.4% after 3 h of bioconversion of 5 mM ferulic acid at 308C, pH 7.0) were obtained with metabolic induction of the biomass with 2.5 mM ferulic acid after 4.5 hours of growth at pH 6.8 and by harvesting them 1 hour after the addition of the inducer. The bioconversion step has been then optimized in terms of buffer pH, cell concentration and ferulic acid concentration by evaluating the vanillin molar yield, bioconversion selectivity and ferulic acid conversion. pH had a modest effect on the bioconversion in the range 6.5–7.5, the highest vanillin molar yield (82.8 0.9%), bioconversion selectivity (87.5 1.2%) and ferulic acid conversion (94.6 0.8%) being obtained at pH 7.0 with 6 g (wet weight) cells/L. Because of the occurrence of substrate inhibition phenomena, the highest vanillin productivity (0.61 mmol L ^{1} h ^{1}) is obtained using initial ferulic acid 5 mM, while its highest final concentration (8.2 mM) is obtained after 17 h of incubation using ferulic acid 10.0 mM (productivity 0.48 mmol L ^{1} h ^{1}). Vanillin molar yield and selectivity compar-able to those observed with food-grade ferulic acid were obtained using wheat bran enzymatic hydrolyzates containing 1 mM spiked ferulic acid, only when reducing sugars were removed from bran hydrolysate via purification on ISOLUTE ENV$^+$ column. This indicates that reducing sugars adversely affect the bioconversion efficiency of ferulic acid in bran hydrolysate, probably as they act as carbon source for the microorganism, thus favouring growth and production of nonspecific oxidoreductases responsible for vanillin oxidation. In conclusion, the developed process produced up to 8.41 mM vanillin, which is the highest final titer of vanillin produced by a Pseudomonas strain to date, and opens new perspectives in the use of bacterial biocatalysts for biotechnological production of vanillin from agro-industrial wastes which contain ferulic acid [52].

5. Food products envisaged in the project

Ingredients obtained from fruit and cereal by-products might have great potential and market opportunities in the modern society where the consumption of ‘ready-to-eat’ products with health promoting properties is increasing. The possibility of using the ingredients mentioned above to produce at laboratory scale new food products, including fruit juice beverages and snacks, self-stable fillers for bakery products, fibre-enriched bakery products, has been investigated. The preliminary results obtained showed that several self-stable fillers, differing in sensory and textural characteristics, can be obtained from citrus by-product and bran constituents via a proper and calibrated modulation of compositive, processing and storage conditions. In particular, the use of a cold technology, that is, high pressure homogenization, allowed both the inactivation of the natural microflora and target spoilage microorganisms (Saccharomyces cerevisiae and Zygosaccharomyces bailii) and the modulation of the microstructural and rheological properties such as viscosity and creaminess. The resulting products were characterized by pleasant aroma and sensory properties and a shelf-life of about 1 month. Several tests are in progress for the incorporation of the ingredients obtained from the citrus peels in functional beverages. Other ingredients, like DFs, the phenolic fraction, natural vanillin, are currently combined to give rise to new food products – such as satiating juice, fibre rich instant desert, crunchy citrus filled snack. Tests are in progress on these products for assessing their quality and safety.

6. Evaluation of industrial relevance, environmental and economic sustainability of the products and processes resulting from the project

The Strategic Research Agenda of the European Technology Plat-form

Food for Life (SRA ETP 'Food for Life', http://etp.ciaa.be/documents/CIAA-ETP%20broch_LR.pdf) has defined sustainable food production as one of the most important challenges that will be faced by the European food industry, and thus it has become a major area of interest in Europe [53]. Sustainable food production stands at the intersection of several growing needs. Primarily the needs of consumers for improved food security and safety, as well as more sophisticated needs. Secondly the quest for economic sustainability of food production, based on cost reduction and increased product differentiation and ability to meet consumers' needs. Third, the growing concern for reversing the over exploitation of natural resources, waste generation, and the contribution to climate change.

The approach taken by NAMASTE-EU includes an analysis of economic, social and environmental sustainability of the pro-posed ingredients and related food products. The evaluation problem is addressed through a mixed-method approach, with different layers of precision. It is well known from the literature and industrial practice that early evaluation of new technologies/ products is a particularly difficult task. This is particularly true for food ingredients, as their success depends on the acceptability of final products for consumers. Normally industries expect a high occurrence of failures of new product ideas.

The project uses primarily qualitative interviews to experts/ business players to understand the crucial issues in industrial exploitation of the new products. In addition, a more detailed evaluation of key sustainability dimensions is performed through specific risk analysis, environmental analysis, economics analysis and the evaluation of market potentialities.

The risk assessment of the processes and technologies will be performed to confirm that they conform to existing and proposed legislation on sanitary and health risks, including food safety. The environmental assessment of the new processes and technologies will be carried out through environmental indicators, that will be adapted to the needs of the project, including water use, energy use, energy efficiency rates, and waste reutilization ratios. The economic analysis will focus on the estimation of potential costs and benefits of industrial adoption of the developed technologies and products. Energy costs/saving will be a key step in the economic analysis. As mentioned above, this ‘micro/engineering’ assessment could be weakly related to the actual market performance of the developed technology. Market analysis will then relate to the crucial issue of consumers’ acceptability and willingness to pay for the new products/ingredients, which is related to the growing complexity of consumers' preferences and segmentation, as well as the effect of appropriate information campaigns [54]. This will be performed through conjoint analysis (CA). CA is a stated preference technique that uses hypothetical scenarios, com-posed of attribute levels, to estimate individuals' utilities (value) for products or services. It is already used since more than a decade for new foods, but to the best knowledge of the authors, specific applications to the by-products addressed by the project are not available. CA will be used in the NAMASTE EU project to define the optimum combination of the features of the final products for the market success from the consumers' point of view and will help to reach the real target group and communicate the advantages of the products to the consumers.

The information generated above will be used for the elaboration of Processing Protocols (PPCI) for the industrial valorization of developed processes.

7. Conclusion

Novel or improved protocols for the selection, characterization and stabilization of citrus and wheat processing by-products and common physical/chemical and biological procedures for obtaining from them bioactive molecules, DFs, prebiotics, fruit paste, biovanillin, as well as new food products have been developed and assessed. Some interdisciplinary procedures for the assessment of the quality, chemical and microbial safety of developed new ingredients and food products have also been set up. The environmental and economical sustainability of the processes are assessed based on a consistent strategy for the analysis of risks, environmental performances, economic cost/benefits and new market opportunities for the new foods and the developed technologies, leading to industrial implementation protocols. The project outcomes expected are the: (a) development of economic-ally and environmentally sustainable strategies for the industrial valorization of fruit and cereal processing industry by-products; (b) generation of a knowledge-based and combined vision in the area of environmentally sound food production technologies and (c) potential of setting up new joint ventures and, on a longer term, of better accessing new and major food markets as a result of the increased collaboration between Industries joining NAMASTE EU or associated with its action.

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References

[1] Rimm EB, Katan MB, Ascherio A, Stampfer MJ, Willett WC. Relation between intake and risk of coronary heart disease in male health professionals. Annals of Internal Medicine 1996;125:384–9.

[2] Doll R. An overview of the epidemiological evidence linking dite and cancer. Proceedings of the National Academy of Sciences of the United States of America 1990;49:119–31.

[3] Awarenet. Handbook for the prevention and minimisation of waste and valor- isation of by-products in European agro-food industries; 2004, Deposito legal: BI-223-04.

[4] Federici F, Fava F, Kalogerakis K, Mantzavinos D. Valorization of agro-industrial by-products, effluents and wastes: concept, opportunities and the case of olive oil sector. Journal of Chemical Technology and Biotechnology 2009;84: 895–900.

[5] Wyman CE. Potential synergies and challenges in refining cellulosic biomass to fuels, chemicals, and power. Biotechnology Progress 2003;19:254–62.

[6] Laufenberg G, Kunz B, Nystroem M. Transformation of vegetable waste into value added products: (A) the upgrading concept; (B) practical implementations. Bioresource Technology 2003;87:167–98.

[7] United States Department for Agriculture, USDA. Foreign agricultural service; July 2012, http://usda01.library.cornell.edu/usda/fas/citruswm//2010s/2012/citruswm-07-26-2012.pdf in http://usda.mannlib.cornell.edu/MannUsda/view-DocumentInfo.do?documentID=1774.

[8] Braddock RJ. Handbook of citrus by-products and processing technology. New York: John Wiley & Sons, Inc.; 1999: 117–33.

[9] De Bont J, Koolloos C, den Ridder J. Co-product from wheat and corn as second generation feedstocks in Europe. Nedalco; 2007, http://www.bbibiofuels.com/ few/2007/FEW07/FEW07-GS-De_Bont.pdf.

[10] Bampidis VA, Robinson PH. Citrus by-products as ruminant feeds: A review. Animal Feed Science and Technology 2006;128:175–217.

[11] Braddock RJ. By-products of citrus fruits. Food Technology 1995;49:74–7.

[12] Marin FR, Soler-Rivas C, Benavente-Garcı´a O, Castillo J, Pe´rez-Alvarez JA. By- products from different citrus processes as a source of customized functional fibres. Food Chemistry 2007;100:736–41.

[13] Moure A, Cruz JM, Franco D, Domı´nguez JM, Sineiro J, Domínguez H, et al. Natural antioxidants from residual sources. Food Chemistry 2001;72: 145–71.

[14] Schieber A, Stintzing FC, Carle R. By-products of plant food processing as a source of functional compounds. Recent Developments and Trends in Food Science Technology 2001;12:401–13.

[15] Fernádez-López J, Fernández-Ginés JM, Aleson-Carbonell L, Sendra E, Sayas- Barbera´ E, Pe´rez-Alvarez JA. Application of functional citrus by-products to meat products. Trends in Food Science & Technology 2004;15:176–85.

[16] Bocco A, Cuvelier M, Richard H, Berset C. Antioxidant activity and phenolic composition of citrus peel and seed extracts. Journal of Agricultural and Food Chemistry 1998;46:2123–9.

[17] Manthey JA, Grohmann K. Phenols in citrus peel by-products, concentrations of hydroxycinnamates and polymethoxylated

flavones in citrus peel molasses. Journal of Agricultural and Food Chemistry 2001;49:3268–73.

[18] Gorinstein S, Martin-Belloso O, Park YS, Haruenkit R, Lojek A, Ciz M, et al. Comparison of some biochemical characteristics of different citrus fruits. Food Chemistry 2001;74:309–15.

[19] Imeh U, Khokhar S. Distribution of conjugated and free phenols in fruits: antioxidant activity and cultivar variations. Journal of Agricultural and Food Chemistry 2002;50:6301–6.

[20] Tripoli E, Guardia ML, Giammanco S, Di Majo D, Giammanco M. Citrus flavonoids: molecular structure, biological activity and nutritional properties: a review. Food Chemistry 2007;104:466–79.

[21] Larrauri JA. New approaches in the preparation of high dietary fibre powders from fruit by-products. Trends in Food Science & Technology 1999;10:3–8.

[22] Lario Y, Sendra E, Garcı´a-Pe´rez J, Fuentes C, Sayas-Barbera´ E, Ferna´ndez-Lo´pez J, et al. Preparation of high dietary fibre powder from lemon juice by-products. Innovative Food Science & Emerging Technologies 2004;5:113–7.

[23] Thebaudin JY, Lefebvre AC, Harrington M, Bourgeois CM. Dietary fibres: nutri- tional and technological interest. Trends in Food Science and Technology 1997;8:41–8.

[24] Okarter N, Liu RH. Health benefits of whole grain phytochemicals. Critical Reviews in Food Science and Nutrition 2010;50:193–208.

[25] Hemery Y, Rouau X, Lullien-Pellerin V, Barron C, Abecassis J. Dry processes to develop wheat fractions and products with enhanced nutritional quality. Jour- nal of Cereal Science 2007;46:327–47.

[26] Di Gioia D, Sciubba L, Setti L, Luziatelli F, Ruzzi M, Zanichelli D, et al. Production of biovanillin from wheat bran. Enzyme and Microbial Technology 2007; 41:498–505.

[27] Ajila CM, Leelavathi K, Prasada Rao UJS. Improvement of dietary fibre content and antioxidant properties in soft dough biscuits with the incorporation of mango peel powder. Journal of Cereal Science 2008;48:319–26.

[28] Sudha ML, Vetrimani R, Leelavathi K. Influence of fibre from different cereals on the rheological characteristics of wheat flour dough and on biscuit quality. Food Chemistry 2007;100:1365–70.

[29] Nassar AG, AbdEl-Hamied AA, El-Naggar EA. Effect of citrus by-products flour incorporation on chemical, rheological and organolepic characteristics of bis- cuits. World Journal of Agricultural Science 2008;4:612–6.

[30] Fernández-López J, Fernández-Ginés JM, Aleson-Carbonell L, Sendra E, Sayas-

[31] Barbera E, Perez-Alvarez JA. Application of functional citrus by-products to meat products. Trends in Food Science and Technology 2004;15:176–85.

[32] Aleson-Carbonell L, Fernaˊndez-Loˊpez J, Peˊrez-Alvarez JA, Kuri V. Characteristics of beef burger as influenced by various types of lemon albedo. Innovative Food Science and Emerging Technologies 2005;6:247–55.

[33] Sendra E, Kuri V, Fernaˊndez-Loˊpez J, Sayas-Barbera E, Navarro C, Peˊrez-Alvarez JA. Viscoelastic properties of orange fiber enriched yogurt as a function of fiber dose, size and thermal treatment. LWT – Food Science and Technology 2010;43:708–14.

[34] Garau MC, Simal S, Rosselloˊ C, Femenia A. Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. Food Chemistry 2007;104:1014–24.

[35] Singleton VL, Orthofer R, Lamuela-Raventoˊs RM. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin–Ciocalteu reagent. Methods in Enzymology 1999;299:152–78.

[36] Gonzaˊlez-Molina E, Domıˊnguez-Perles R, Moreno DA, Garcıˊa-Viguera C. Natural bioactive compounds of citrus limon for food and health. Journal of Pharma- ceutical and Biomedical Analysis 2010;51:327–45.

[37] Igual M, Contreras C, Martıˊnez-Navarrete N. Non-conventional techniques to obtain grapefruit jam. Innovative Food Science and Emerging Technologies 2010;11:335–41.

[38] Rezzoug SA, Maache-Rezzoug Z, Sannier F, Allaf K. A thermo-mechanical pre- processing for pectin isolation from orange peel

with optimisation by response surface methodology. International Journal of Food Engineering 2008;4:10.

[39] Kuljarachanan T, Devahastin S, Chiewchan N. Evolution of antioxidant com- pounds in lime residues during drying. Food Chemistry 2009;113:944–9.

[40] Ladaniya M. Citrus fruit: biology, technology and evaluation. San Diego, CA: Elsevier Inc.; 2008.

[41] Meléndez-Martı´nez AJ, Vicario IM, Heredia FJ. Review: analysis of carotenoids in orange juice. Journal of Food Composition and Analysis 2007;20:638–49.

[42] Khan MK, Abert-Vian M, Fabiano-Tixier A-S, Dangles O, Chemat F. Ultrasound- assisted extraction of polyphenols (flavanone glycosides) from orange (Citrus sinensis L.) peel. Food Chemistry 2010;119:851–8.

[43] Erlund I. Review of the flavonoids quercetin, hesperetin, and naringenin, diet- ary sources, bioactivities, bioavailability, and epidemiology. Nutrition Research 2004;24:851–74.

[44] WHO Guidelines for predicting dietary intake of pesticide residues (revised). Prepared by the Global Environment Monitoring System – Food Contam- ination Monitoring and Assessment Programme (GEMS/Food) in collabora- tion with the Codex Committee on Pesticide Residues Programme of Food Safety and Food Aid World Health Organization; 1997, 35 WHO/FSF/FOS/ 97.7.

[45] Lee SC, Prosky L, DeVries JW. Determination of total, soluble, and insoluble, dietary fiber in foods – enzymatic gravimetric method, MES-TRIS buffer: colla- borative study. Journal – Association of Official Analytical Chemists 1992;75:395–416.

[46] Cloetens L, Broekaert WF, Delaedt Y, Ollevier F, Courtin CM, Delcour JA, et al. Tolerance of arabinoxylan-oligosaccharides and their prebiotic activity in healthy subjects: a randomised, placebo-controlled cross-overstudy. The British Journal of Nutrition 2010;103:703–13.

[47] Maki KC, Gibson GR, Dickmann RS, Kendall CW, Chen CY, Costabile A, et al. Digestive and physiologic effects of a wheat bran extract, arabino-xylan-oligo- saccharide, in breakfast cereal. Nutrition 2012;11–12:1115–21.

[48] Swennen K, Courtin CM, Lindemans GCJE, Delcour JA. Large-scale production and characterisation of wheat bran arabinoxylooligosaccharides. Journal of the Science of Food and Agriculture 2006;86:1722–31.

[49] Oguntoyinbo FA, Tourlomousis P, Gasson MJ, Narbad A. Analysis of bacterial communities of traditional fermented West African cereal foods using culture independent methods. International Journal Food Microbiology 2010;145: 205–10.

[50] Walton NJ, Narbad A, Faulds GC, Williamson G. Novel approaches to the biosynthesis of vanillin. Current Opinion in Biotechnology 2000;11:490–6.

[51] Barghini P, Montebove F, Ruzzi M, Schiesser A. Optimal conditions for biocon- version of ferulic acid into vanillic acid by Pseudomonas fluorescens BF13 cells. Applied Microbiology and Biotechnology 1998;49:309–14.

[52] Di Gioia D, Luziatelli F, Negroni A, Ficca AG, Fava F, Ruzzi M. Metabolic engineering of Pseudomonas fluorescens for the production of vanillin from ferulic acid. Journal of Biotechnology 2011;156:309–16.

[53] Saravia-Matus SL, Gomez, Paloma S, Mary S. Economics of food security: selected issues. Bio-Based and Applied Economics 2012;1:65–80.

[54] Verain MCD, Bartels J, Dagevos H, Sijtsema SJ, Onwezen MC, Antonides G. Segments of sustainable food consumers: a literature review. International Journal of Consumer Studies 2012;36:123–32.

V

CONCLUSIONES

- A thermodynamic model was developed to explain the mechanisms involved in mass and energy transports throughout the combined drying by microwave coupled with hot air (HAD + MW). A continuous shrinkage in HAD samples was produced by the internal liquid water losses, but the samples treated by HAD + MW showed an internal swelling caused by the internal evaporation produced by the microwave energy. Depending on the predominant mechanisms (HAD shrinkage and MW swelling) samples suffer volumetric contractions or expansions. This model allows optimizing the traditional hot air drying of orange peels by coupling microwaves.

- A desorption isotherm of orange peel dried by different treatments (HAD + MW) was developed and it was shown that GAB model can be used to predict moisture from a_w measurements. Macro and microstructural transformations have been described by water interactions with the tissue. Shrinkage/swelling phenomena have been observed depending on the MW power and on the nature of the tissue.

- It was possible to develop a dielectric isotherm technique adapting the GAB model to predict the water activity in HAD + MW dried orange peel by using ε' at 20 GHz. The physical meaning of the dielectric isotherm parameters (ε_0' and C_d) was studied. The value of ε_0' at 20 GHz (γ-dispersion) represents the induction effect of the minimum quantity of adsorbed water or the monomolecular moisture layer. The parameter C_d is related with the isosteric heat or the adsorption energy of the monomolecular moisture layer, as well as the C parameter of the GAB model. The application of MW power produced an increase of the isosteric heat improving the surface tension of samples and, thus, the hygroscopicity, explaining the reduction of ε_0' . A strong correlation was found between the isosteric heat of sorption and water retention capacity (WRC) of dried orange peel. Therefore, the increase in WRC with microwave power was explained by giving physical meaning to this parameter.

- A new orange fiber ingredient was obtained from orange peel by HAD + MW. An important reduction in processing time (92 %) and energy consumption (77 %) was achieved compared to hot air drying. An increase in particle size due to an increase in porosity during drying improved fiber swelling capacity. Although viscosity of both treatments showed similar values, the higher swelling capacity of HAD + MW-treated fiber provoked a significant decrease in the viscoelasticity of the samples. The drying treatment did not affect chemical composition, WRC, ORC, pH or antioxidant capacity of orange fibers. Total dietary fiber content was about 60 % with a ratio of soluble to insoluble fiber of 1:1. Color was not affected by HAD + MW. Therefore, the potential use of HAD + MW as an efficient process for valorization of orange by-products into value-added ingredients, with optimum nutritional and technological properties has been shown.

CONCLUSIONES

- The fat content of potato puree made with cream was reduced by replacing 100 % of cream with different types of citrus fiber. All fibers increased viscosity of purees, as well as their viscoelastic behavior. The fibers obtained by HAD + MW presented a swelling capacity and WRC similar to commercial fiber. Trained panelists perceived these purees as more granular in the mouth which can be explained by the greater increase in volume of the rehydrated fibers. Both, commercial fiber and fibers obtained by the new process, generated a lower perception of fat in the mouth than the reference with cream. Finally, the creaminess of potato purees made from fibers obtained through the new process was assessed as very similar to the reference.

- An innovative multipurpose process for obtaining three functional ingredients from industrial orange by-products was developed using hot air-microwave drying technology. An aqueous and an ethanolic bioactive extracts were obtained and characterized as rich sources of flavanones, flavanone glycosides and carotenoids typical of citrus plants. Most of these compounds were extracted during the blanching step except for carotenoids which were extracted during debittering. A new debittered dietary fiber ingredient with antioxidant properties was produced. Particle size distribution showed an interesting swelling capacity when fiber was rehydrated. Color and technological properties of the ingredient obtained were of similar quality than commercial citrus fiber. MW drying reduced process time (50%) and energy consumption (26%) when compared to hot air drying.

Therefore, the process developed represented a new sustainable alternative for citrus by-products valorization and transformation into value-added ingredients such as dietary fiber.

Image 5: A new dietary fiber obtention process from orange by-products by applying hot air-microwave drying, as the main result of the thesis.

VI

BIBLIOGRAFÍA

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AACC, American Association of Cereal Chemists, 2001. The definition of dietary fiber. Report of the Dietary Fiber Definition Committee to the Board of Directors of the American Association of Cereal Chemists. . Cereal Foods World 46(3):112-126.

Alimentarius, C. 2008. Report of the 30th Session of the Codex Committee on Nutrition and Foods for Special Dietary Uses. Vol. ALINORM 09/32/26, Cape Town, South Africa, 3–7 November, 2008.

Alimentarius, C. 2009. Report of the 31st Session of the Codex Committee on Nutrition and Foods for Special Dietary Uses. Vol. ALINORM 10/33/26, Düsseldorf, Germany, 2–6 November, 2009.

Anderson, A. and M. A. Eastwood. 1987. Flow characteristics and the water-retention properties of wheat bran. Journal of the Science of Food and Agriculture 39(2):185-194.

Aravantinos-Zafiris, G., V. Oreopoulou, C. Tzia, and C. D. Thomopoulos. 1994. Fibre Fraction from Orange Peel Residues after Pectin Extraction. LWT - Food Science and Technology 27(5):468-471.

Arballo, J. R., L. A. Campanone, and R. H. Mascheroni. 2010. Modeling of Microwave Drying of Fruits. Dry. Technol. 28(10):1178-1184.

Ariahu, C. C., S. A. Kaze, and C. D. Achem. 2006. Moisture sorption characteristics of tropical fresh water crayfish (Procambarus clarkii). J. Food Eng. 75(3):355-363.

Aviara, N. A. and O. O. Ajibola. 2002. Thermodynamics of moisture sorption in melon seed and cassava. J. Food Eng. 55(2):107-113.

Awarenet. 2004. Handbook for the prevention and minimisation of waste and valorization of by-products in European agro-food industries. Deposito legal: BI-223-04.

Bampidis, V. A. and P. H. Robinson. 2006. Citrus by-products as ruminant feeds: A review. Animal Feed Science and Technology 128(3–4):175-217.

Barbosa-Cánovas, G. V., A. J. Fontana, S. J. Schmidt, and T. P. Labuza. 2008. Water Activity in Foods: Fundamentals and Applications. Wiley.

Bejar, A. K., N. Kechaou, and N. B. Mihoubi. 2011. Effect of Microwave Treatment On Physical and Functional Properties of Orange (Citrus Sinensis) Peel and Leaves. J Food Process Technol 2(2):1-7.

Bingham, S. A., N. E. Day, and R. Luben. 2003. Dietary fibre in food and protection against colorectal cancer in the European Prospective

Investigation into Cancer and Nutrition (EPIC): an observational study (vol 361, pg 1496, 2003). Lancet 362(9388):1000-1000.

Bocco, A., M.-E. Cuvelier, H. Richard, and C. Berset. 1998. Antioxidant Activity and Phenolic Composition of Citrus Peel and Seed Extracts. J. Agric. Food Chem. 46(6):2123-2129.

Braddock, R. J. 1999. Handbook of Citrus By-Products and Processing Technology. Wiley.

Castells, X. E. 2012. Reciclaje de residuos industriales: Residuos solidos urbanos y fangos de depuradora. Editorial Díaz de Santos, S.A.

Castro-Giráldez, M. 2010. Estudio de los espectros dieléctricos para el control de calidad de alimentos. in Instituto de Ingeniería de Alimentos para el Desarrollo Vol. Thesis. Universidad Politécnica de Valencia.

Castro-Giráldez, M., N. Balaguer, E. Hinarejos, and P. J. Fito. 2014. Thermodynamic approach of meat freezing process. Innov. Food Sci. Emerg. Technol. 23(0):138-145.

Castro-Giráldez, M., P. J. Fito, M. Dalla Rosa, and P. Fito. 2011a. Application of microwaves dielectric spectroscopy for controlling osmotic dehydration of kiwifruit (Actinidia deliciosa cv Hayward). Innov. Food Sci. Emerg. Technol. 12(4):623-627.

Castro-Giráldez, M., P. J. Fito, and P. Fito. 2010. Application of microwaves dielectric spectroscopy for controlling pork meat (Longissimus dorsi) salting process. J. Food Eng. 97(4):484-490.

Castro-Giráldez, M., P. J. Fito, and P. Fito. 2011b. Application of microwaves dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic apple tissue. J. Food Eng. 104(2):227-233.

Comas e Boff, C., T. d. M. Crizel, R. R. de Araujo, A. d. O. Rios, and S. H. Flores. 2013. Development of chocolate ice cream using orange peel fiber as fat replacer. Ciencia Rural 43(10):1892-1897.

Communities, C. o. E. 2008. Commission Directive 2008/100/EC of 28 October 2008 amending Council Directive 90/496/EEC on nutrition labelling for foodstuffs as regards recommended daily allowances, energy conversion factors and definitions. Pages 9–13 in L 285. O. J. o. t. E. Union, ed.

Contreras, C., M. E. Martín-Esparza, A. Chiralt, and N. Martínez-Navarrete. 2008. Influence of microwave application on convective drying: Effects on drying kinetics, and optical and mechanical properties of apple and strawberry. J. Food Eng. 88(1):55-64.

Crizel, T. d. M., R. R. de Araujo, A. d. O. Rios, R. Rech, and S. H. Flores. 2014. Orange fiber as a novel fat replacer in lemon ice cream. Food Science and Technology 34(2):332-340.

Chatsisvili, N. T., I. Amvrosiadis, and V. Kiosseoglou. 2012. Physicochemical properties of a dressing-type o/w emulsion as influenced by orange pulp fiber incorporation. LWT - Food Science and Technology 46(1):335-340.

Chenoll, C. 2008. Relaciones agua-solutos-matriz insoluble en algunos sitemas alimentarios. in Instituto de Ingeniería de Alimentos para el Desarrollo Vol. Thesis. Universidad Politécnica de Valencia.

Chou, S. K. and K. J. Chua. 2001. New hybrid drying technologies for heat sensitive foodstuffs. Trends Food Sci. Technol. 12(10):359-369.

de Menezes, E. W., E. B. Giuntini, M. C. T. Dan, F. A. H. Sardá, and F. M. Lajolo. 2013. Codex dietary fibre definition – Justification for inclusion of carbohydrates from 3 to 9 degrees of polymerisation. Food Chem. 140(3):581-585.

de Moraes Crizel, T., A. Jablonski, A. de Oliveira Rios, R. Rech, and S. H. Flôres. 2013. Dietary fiber from orange byproducts as a potential fat replacer. LWT - Food Science and Technology 53(1):9-14.

Demirel, Y. 2013. Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical, Chemical and Biological Systems. Elsevier Science.

DeVries, J. W. 2010. Validation official methodology commensurate with dietary fibre research and definitions. Pages 29–48 in Dietary fibre: New frontiers for food and health. J. J. J. W. van der Kamp, B. McCleary and D.Topping ed. Wageningen Academic Publishers., Wageningen, The Netherlands.

Doll, S. R. 1990. Are we winning the fight against cancer? An epidemiological assessment: EACR—Mühlbock memorial lecture. European Journal of Cancer and Clinical Oncology 26(4):500-508.

EFSA. 2010. Panel on Dietetic Products Nutrition, and Allergies (NDA). Scientific Opinion

on dietary Reference Values for carbohydrates and dietary fibre. EFSA journal 8(3):77.

ENIDE. 2011. Encuesta Nacional de Ingesta Dietética Española.

Ensminger, E., J. E. Oldfield, and W. W. Heinemann. 1990. Feeds & nutrition: formerly Feeds & nutrition, complete. Ensminger Pub. Co.

Erle, U. 2005. Drying using microwave processing. Pages 142-152 in The Microwave Processing of Foods. H. Schubert and M. Regier, ed. Woodhead Publishing, Cambridge, UK.

FAOSTAT. 2015. Food and Agriculture Organization of the United Nations. Statistics Division.

Fava, F., G. Zanaroli, L. Vannini, E. Guerzoni, A. Bordoni, D. Viaggi, J. Robertson, K. Waldron, C. Bald, A. Esturo, C. Talens, I. Tueros, M. Cebrián, A. Sebők, T. Kuti, J. Broeze, M. Macias, and H.-G. Brendle. 2013. New advances in the integrated management of food processing by-products in Europe: sustainable exploitation of fruit and cereal processing by-products with the production of new food products (NAMASTE EU). New Biotechnology 30(6):647-655.

Fernandez-Lopez, J., J. M. Fernandez-Gines, L. Aleson-Carbonell, E. Sendra, E. Sayas-Barbera, and J. A. Perez-Alvarez. 2004. Application of functional citrus by-products to meat products. Trends Food Sci. Technol. 15(3-4):176-185.

Figuerola, F., M. L. Hurtado, A. M. Estevez, I. Chiffelle, and F. Asenjo. 2005. Fibre concentrates from apple pomace and citrus peel as potential fibre sources for food enrichment. Food Chem. 91(3):395-401.

Fito Suñer, P.J. 2002. Desarrollo de un nuevo sistema de aplicación de recubrimientos en cítricos. Tesis Doctoral, Universidad Politécnica de Valencia, Departamento de Tecnología de Alimentos.

Fuchs, C. S., E. L. Giovannucci, G. A. Colditz, D. J. Hunter, M. J. Stampfer, B. Rosner, F. E. Speizer, and W. C. Willett. 1999. Dietary fiber and the risk of colorectal cancer and adenoma in women. N. Engl. J. Med. 340(3):169-176.

Funebo, T. and T. Ohlsson. 1998. Microwave-assisted air dehydration of apple and mushroom. J. Food Eng. 38(3):353-367.

Geankoplis, C. J. 1993. Transport Processes and Unit Operations. PTR Prentice Hall.

Ghanem, N., D. Mihoubi, N. Kechaou, and N. B. Mihoubi. 2012. Microwave dehydration of three citrus peel cultivars: Effect on water and oil retention capacities, color, shrinkage and total phenols content. Industrial Crops and Products 40(0):167-177.

Gorinstein, S., O. Martí n-Belloso, Y.-S. Park, R. Haruenkit, A. Lojek, M. Ĉí ž, A. Caspi, I. Libman, and S. Trakhtenberg. 2001. Comparison of some biochemical characteristics of different citrus fruits. Food Chem. 74(3):309-315.

Green, D. and R. Perry. 2007. Perry's Chemical Engineers' Handbook, Eighth Edition. McGraw-Hill Education.

Gu, L., R. Ruan, P. Chen, W. Wilcke, and P. Addis. 2001. Structure-function relationships of Highly Refined Cellulose. Transactions of the Asae 44(6):1707-1712.

Guardiola Bárcena, J. L. 1998. Componentes nutritivos de la naranja. Pages 143-162. in Naranja y Salud. Fundación Valencia de Estudios avanzados y Consellería de Agricultura, Pesca y Alimentación, Valencia.

Heredia Moreno, A. 2003. Fibra alimentaria. Consejo Superior de Investigaciones Científicas.

Howarth, N. C., E. Saltzman, and S. B. Roberts. 2001. Dietary fiber and weight regulation. Nutrition Reviews 59(5):129-139.

Howe, G. R., E. Benito, R. Castelleto, J. Cornee, J. Esteve, R. P. Gallagher, J. M. Iscovich, D. A. Jiao, R. Kaaks, G. A. Kune, S. Kune, K. A. Labbe, H. P. Lee, M. Lee, A. B. Miller, R. K. Peters, J. D. Potter, E. Riboli, M. L. Slattery, D. Trichopoulos, A. Tuyns, A. Tzonou, A. S. Whittemore, A. H. Wuwilliams, and S. Zheng. 1992. Dietary-intake of fiber and decreased risk of cancers of the colon and rectum - evidence from the combined analysis of 13 case-control studies. J. Natl. Cancer Inst. 84(24):1887-1896.

Imeh, U. and S. Khokhar. 2002. Distribution of Conjugated and Free Phenols in Fruits: Antioxidant Activity and Cultivar Variations. J. Agric. Food Chem. 50(22):6301-6306.

Kent, M., A. Peymann, C. Gabriel, and A. Knight. 2002. Determination of added water in pork products using microwave dielectric spectroscopy. Food Control 13(3):143-149.

Kiranoudis, C. T., Z. B. Maroulis, E. Tsami, and D. Marinoskouris. 1993. Equilibrium moisture-content and heat of desorption of some vegetables. J. Food Eng. 20(1):55-74.

Kohajdova, Z., J. Karovicova, M. Jurasova, and K. Kukurova. 2011. Application of citrus dietary fibre preparations in biscuit production. Journal of Food and Nutrition Research 50(3):182-190.

Labuza, T. P., Altunakar, B. 2007. Water Activity Prediction and Moisture Sorption Isotherms. in Water Activity in Foods: Fundamentals and Applications. Vol. 109-154. G. V. Barbosa-Cánovas, A. J. Fontana, S. J. Schmidt, and T. P. Labuza, ed. IFT Press and Blackwell Publishing, Iowa, USA.

Ladanyia, M. and M. Ladaniya. 2010. Citrus Fruit: Biology, Technology and Evaluation. Elsevier Science.

Lario, Y., E. Sendra, J. García-Pérez, C. Fuentes, E. Sayas-Barberá, J. Fernández-López, and J. A. Pérez-Alvarez. 2004. Preparation of high dietary fiber powder from lemon juice by-products. Innov. Food Sci. Emerg. Technol. 5(1):113-117.

Larrauri, J. A. 1999. New approaches in the preparation of high dietary fibre powders from fruit by-products. Trends Food Sci. Technol. 10(1):3-8.

Laufenberg, G., B. Kunz, and M. Nystroem. 2003. Transformation of vegetable waste into value added products: (A) the upgrading concept; (B) practical implementation. Bioresour. Technol. 87(2):167-198.

Lévy, E. 1992. Diccionario Akal de Física. Ediciones Akal.

Lundberg, B. 2005. Using highly expanded citrus fiber to improve the quality and nutritional properties of foods. Cereal Foods World 50(5):248-252.

Lundberg, B., X. Pan, A. White, H. Chau, and A. Hotchkiss. 2014. Rheology and composition of citrus fiber. J. Food Eng. 125(0):97-104.

Manthey, J. A. and K. Grohmann. 2001. Phenols in Citrus Peel Byproducts. Concentrations of Hydroxycinnamates and Polymethoxylated Flavones in Citrus Peel Molasses. J. Agric. Food Chem. 49(7):3268-3273.

Marin, F. R., C. Soler-Rivas, O. Benavente-Garcia, J. Castillo, and J. A. Perez-Alvarez. 2007. By-products from different citrus processes as a source of customized functional fibres. Food Chem. 100(2):736-741.

Markx, G. H. and C. L. Davey. 1999. The dielectric properties of biological cells at radiofrequencies: applications in biotechnology. Enzyme and Microbial Technology 25(3–5):161-171.

Marlett, J. A., M. I. McBurney, and J. L. Slavin. 2002. Position of the American Dietetic Association: Health implications of dietary fiber. J. Am. Diet. Assoc. 102(7):993-1000.

McCleary, B. V. 2010. Development of an integrated total dietary fiber method consistent with the Codex Alimentarius definition. Cereal Foods World 55(1):24–28.

McCleary, B. V., J. W. DeVries, J. I. Rader, G. Cohen, L. Prosky, D. C. Mugford, M. Champ, and K. Okuma. 2010. Determination of total dietary fiber (CODEX Definition) by enzymatic-gravimetric method and liquid chromatography: Collaborative study. Journal of AOAC International 93(1):221-233.

McCready, R. M. 1977. Carbohydrates: Composition, distribution, significance. In Citrus Science and Technology. Pages 74–109. Vol. vol. I. P. E. S. a. M. K. V. S. Nagy, ed. AVI Publishing, Inc, Westport, CT.

McKee, L. H. and T. A. Latner. 2000. Underutilized sources of dietary fiber: A review. Plant Food Hum. Nutr. 55(4):285-304.

Medicine, I. o. 2001. Dietary Reference Intakes: Proposed Definition of Dietary Fiber. The National Academies Press, Washington, DC.

Nafisi-Movaghar, K., L. L. Druz, and C. P. Victoria. 2013. Conversion Of Citrus Peels Into Fiber, Juice, Naringin, And Oil. Google Patents.

Nicolis, G. and I. Prigogine. 1977. Self-organization in nonequilibrium systems: from dissipative structures to order through fluctuations. Wiley.

O'Shea, N., C. Rößle, E. Arendt, and E. Gallagher. 2015. Modelling the effects of orange pomace using response surface design for gluten-free bread baking. Food Chem. 166(0):223-230.

Okino-Delgado, C. H. and L. F. Fleuri. 2014. Obtaining lipases from byproducts of orange juice processing. Food Chem. 163(0):103-107.

Onsager, L. 1931. Reciprocal relations in irreversible processes. I. Physical Review 37(4):405-426.

Orsat, V., V. Raghavan, and V. Meda. 2005. 6 - Microwave technology for food processing: an overview. Pages 105-118 in The Microwave Processing of Foods. H. Schubert and M. Regier, ed. Woodhead Publishing.

Park, Y., D. J. Hunter, D. Spiegelman, L. Bergkvist, F. Berrino, P. A. van den Brandt, J. E. Buring, G. A. Colditz, J. L. Freudenheim, C. S. Fuchs, E. Giovannucci, R. A. Goldbohm, S. Graham, L. Harnack, A. M. Hartman, D. R. Jacobs, I. Kato, V. Krogh, M. F. Leitzmann, M. L. McCullough, A. B. Miller, P. Pietinen, T. E. Rohan, A. Schatzkin, W. C. Willett, A. Wolk, A. Zeleniuch-Jacquotte, S. M. M. Zhang, and S. A. Smith-Warner. 2005. Dietary fiber intake and risk of colorectal cancer - A pooled analysis of prospective cohort studies. JAMA-J. Am. Med. Assoc. 294(22):2849-2857.

Perrigue, M. M., P. Monsivais, and A. Drewnowski. 2009. Added Soluble Fiber Enhances the Satiating Power of Low-Energy-Density Liquid Yogurts. J. Am. Diet. Assoc. 109(11):1862-1868.

Pezzutti, A. and G. H. Crapiste. 1997. Sorptional equilibrium and drying characteristics of garlic. J. Food Eng. 31(1):113-123.

Pietinen, P., E. B. Rimm, P. Korhonen, A. M. Hartman, W. C. Willett, D. Albanes, and J. Virtamo. 1996. Intake of dietary fiber and risk of coronary heart disease in a cohort of Finnish men - The alpha-tocopherol, beta-carotene cancer prevention study. Circulation 94(11):2720-2727.

Pszczola, D. 2006. Fiber gets a new image. Food Tech 60(2):43-53.

Rahman, S. 2009. Food Properties Handbook, Second Edition. CRC Press.

Rakesh, V. and A. K. Datta. 2011. Microwave puffing: Determination of optimal conditions using a coupled multiphase porous media – Large deformation model. J. Food Eng. 107(2):152-163.

Rimm, E. B., A. Ascherio, E. Giovannucci, D. Spiegelman, M. J. Stampfer, and W. C. Willett. 1996. Vegetable, fruit, and cereal fiber intake and risk of coronary heart disease among men. JAMA-J. Am. Med. Assoc. 275(6):447-451.

Romero-Lopez, M. R., P. Osorio-Diaz, L. A. Bello-Perez, J. Tovar, and A. Bernardino-Nicanor. 2011. Fiber Concentrate from Orange (Citrus sinensis L.) Bagase: Characterization and Application as Bakery Product Ingredient. International Journal of Molecular Sciences 12(4):2174-2186.

Russo, M., I. Bonaccorsi, G. Torre, M. Sarò, P. Dugo, and L. Mondello. 2014. Underestimated sources of flavonoids, limonoids and dietary fibre: Availability in lemon's by-products. Journal of Functional Foods 9(0):18-26.

Salmeron, J., A. Ascherio, E. B. Rimm, G. A. Colditz, D. Spiegelman, D. J. Jenkins, M. J. Stampfer, A. L. Wing, and W. C. Willett. 1997. Dietary fiber, glycemic load, and risk of NIDDM in men. Diabetes Care 20(4):545-550.

Santana, M. d. F. S. d., Gasparetto, Carlos Alberto. 2009. Microstructure of dietary fiber from orange albedo: a study by microscopy and physical techniques. Ciência e Tecnologia de Alimentos 29(1): 124-134.

Schatzkin, A., E. Lanza, D. Corle, P. Lance, F. Iber, B. Caan, M. Shike, J. Weissfeld, R. Burt, M. R. Cooper, J. W. Kikendall, J. Cahill, L. Freedman, J. Marshall, R. E. Schoen, M. Slattery, and G. Polyp Prevention Trial Study. 2000. Lack of effect of a low-fat, high-fiber diet on the recurrence of colorectal adenomas. N. Engl. J. Med. 342(16):1149-1155.

Schieber, A., F. C. Stintzing, and R. Carle. 2001. By-products of plant food processing as a source of functional compounds - recent developments. Trends Food Sci. Technol. 12(11):401-+.

Schulze, M. B., S. M. Liu, E. B. Rimm, J. E. Manson, W. C. Willett, and F. B. Hu. 2004. Glycemic index, glycemic load, and dietary fiber intake and incidence of type 2 diabetes in younger and middle-aged women. Am. J. Clin. Nutr. 80(2):348-356.

SENC. 2001. Consenso de la Sociedad Española de Nutrición Comunitaria. Sociedad Española de Nutrición Comunitaria.

Sendra, E., V. Kuri, J. Fernandez-Lopez, E. Sayas-Barbera, C. Navarro, and J. A. Perez-Alvarez. 2010. Viscoelastic properties of orange fiber enriched yogurt as a function of fiber dose, size and thermal treatment. LWT-Food Sci. Technol. 43(4):708-714.

Sinclair, W. B. 1984. The biochemistry and physiology of the lemon and other citrus fruits. University of California, Division of Agriculture and Natural Resources.

Sosa-Morales, M. E., L. Valerio-Junco, A. López-Malo, and H. S. García. 2010. Dielectric properties of foods: Reported data in the 21st Century and their potential applications. LWT - Food Science and Technology 43(8):1169-1179.

Soysal, Y., S. Öztekin, and Ö. Eren. 2006. Microwave Drying of Parsley: Modelling, Kinetics, and Energy Aspects. Biosystems Engineering 93(4):403-413.

Spiegel-Roy, P. and E. E. Goldschmidt. 1996. The Biology of Citrus. Cambridge University Press.

Tan, K.-Y. and F. Seow-Choen. 2007. Fiber and colorectal diseases: Separating fact from fiction. World Journal of Gastroenterology 13(31):4161-4167.

Traffano-Schiffo, M. V., M. Castro-Giráldez, P. J. Fito, and N. Balaguer. 2014. Thermodynamic model of meat drying by infrarred thermography. J. Food Eng. 128(0):103-110.

Tripodo, M. M., F. Lanuzza, G. Micali, R. Coppolino, and F. Nucita. 2004. Citrus waste recovery: a new environmentally friendly procedure to obtain animal feed. Bioresour. Technol. 91(2):111-115.

Tripoli, E., M. L. Guardia, S. Giammanco, D. D. Majo, and M. Giammanco. 2007. Citrus flavonoids: Molecular structure, biological activity and nutritional properties: A review. Food Chem. 104(2):466-479.

Trumbo, P., S. Schlicker, A. A. Yates, and M. Poos. 2002. Dietary reference intakes for energy, carbohydrate, fiber, fat, fatty acids, cholesterol, protein and amino acids. J. Am. Diet. Assoc. 102(11):1621-1630.

Tulasidas, T. N. 1994. Combined Convective and Microwave Drying of Grapes. Thesis (Ph.D.)--McGill University.

Turbak, A. F., Snyder, F.W., Sandberg, K.R. 1983. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. Pages 815–827 in Proc. J Appl Polym Sci: Appl Polym Symp 37 (Proc. Cellul. Conf., 9th, 1982, Part 2)

USDA. 2014. Citrus: World Markets and Trade.

Viuda-Martos, M., Y. Ruiz-Navajas, J. Fernández-López, and J. A. Pérez-Álvarez. 2010. Effect of orange dietary fibre, oregano essential oil and packaging conditions on shelf-life of bologna sausages. Food Control 21(4):436-443.

Weickert, M. O., M. Mohlig, C. Schofl, A. M. Arafat, B. Otto, H. Viehoff, C. Koebnick, A. Kohl, J. Spranger, and A. F. H. Pfeiffer. 2006. Cereal fiber improves whole-body insulin sensitivity in overweight and obese women. Diabetes Care 29(4):775-780.

Wolk, A., J. E. Manson, M. J. Stampfer, G. A. Colditz, F. B. Hu, F. E. Speizer, C. H. Hennekens, and W. C. Willett. 1999. Long-term intake of dietary fiber and decreased risk of coronary heart disease among women. JAMA-J. Am. Med. Assoc. 281(21):1998-2004.

Wu, H., Z. Tao, G. Chen, H. Deng, G. Xu, and S. Ding. 2004. Conjugate heat and mass transfer process within porous media with dielectric cores in microwave freeze drying. Chemical Engineering Science 59(14):2921-2928.

Zhang, M., J. Tang, A. S. Mujumdar, and S. Wang. 2006. Trends in microwave-related drying of fruits and vegetables. Trends Food Sci. Technol. 17(10):524-534.

Zivanovic, S., R. W. Buescher, and K. S. Kim. 2000. Textural changes in mushrooms (Agaricus bisporus) associated with tissue ultrastructure and composition. J. Food Sci. 65(8):1404-1408.

ANEXOS

Participación en proyectos de investigación y congresos internacionales

Artículos científicos resultado de proyectos de colaboración:

1. From waste products to raw material for the development of new foods.

   Waste and Resource Management, ICE Proceedings, 2014, 1-9

Artículos en congresos internacionales:

1. Thermodynamic model of microwave drying of citrus peel with different treatments

   Inside Food Symposium, 9-12 Abril 2013, Leuven (Belgium)

2. Análisis de la producción de fibra a partir de subproductos cítricos mediante propiedades dieléctricas – **PRESENTACIÓN ORAL**

   CIBIA 9, Congreso Iberoamericano de Ingeniería de Alimentos, 13-16 Enero 2014, Valencia.

3. Thermodynamic Modeling of Orange Peel Dried by Hot air-Microwave - **PRESENTACIÓN ORAL**

   IMPI 49 Symposium, 16-18 June 2015, San Diego, (USA).

Waste and Resource Management

From waste products to raw materials for the development of new foods
Gómez, López, Esturo *et al.*

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From waste products to raw materials for the development of new foods

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This paper reports on a study into using waste products from the food industry as raw materials for food manufacture. The Value project funded by the European Regional Development Fund compiled information on the generation of waste products from the vegetable processing industry, together with their treatment and recovery. Best available technologies for using the waste for food manufacture were identified. Diagnoses on current waste generation, management, legislation and technologies were used to conduct pilot studies. Waste products were chosen for their recovery potential, importance and the needs of the food industry. This paper focuses on the extraction of high-value-added products from food waste, which can be used as natural additives in food manufacture to provide fibre content and antioxidant properties.

1. Introduction

The 'Value' project has the aim to provide technological solutions by contributing to reducing the current problem of low level waste treatment in the food industry within Europe. Some points were detected through weaknesses listed in a SWOT analysis (i.e. analysis of the competitive situation - strengths, weaknesses, opportunities, threats) conducted in the SUDOE Programme (Transnational Cooperation Operational Programme 'Southwest Europe 2007–2013' – a programme funded by the European Regional Development Fund (ERDF)). One of those points is the low level of waste treatment compared to other European countries. This situation is more severe in certain regions where there is a high concentration of food industry enterprises, such as France, Portugal and Spain, where food industry is represented by the 17%. In order to analyse the current situation and to identify needs in the field of waste management and the potential for exploitation of by- products, the Value project has involved small to medium-sized enterprises (SMEs) in the SUDOE territories (Spain, France and Portugal) that are representative of the vegetable processing industry.

The fruit and vegetable processing industry generates an amount of wastes between 5 and 50% of the raw material; currently part of these wastes go to landfill, generating consequent problems. Another important part of these wastes is intended for use as animal feed. At the same time, there is a growing concern within the vegetable processing industry in relation to providing solutions to their waste problems while avoiding additional costs. In this respect, the information available regarding the generation, treatment and recovery of waste from the vegetable processing industry has been compiled, and the best available technologies (BAT) currently available have also been identified for treatment and waste recovery, in order to obtain components of interest for the food industry.

The most interesting sectors or products to evaluate were selected according to their potential recovery and impact on the whole industry. A pilot extraction scheme was also conducted involving the recovery and utilisation of high-value-added products from residues provided by the participating companies. Subsequent results were transferred to the sector, as suggested alternatives for the use of these products, in various workshops that had been planned for the dissemination of the results obtained through the course of the project.

Those high-value-added products that arise as vegetable by-products are mainly fibres and antioxidant compounds. In recent years, society has undergone a change in its eating habits, mainly focused on leading a healthier life. This change has been reflected in an increased consumption of associated dietary products, which has resulted in the expansion of the dietary fibre market and the creation of new products with high dietary fibre content.

The success of such dietary products is based on the great health benefits of a diet rich in fibre. The properties of dietary fibre vary widely; they can be broken down into two types – soluble fibre and insoluble fibre.

(a) Soluble fibre is composed of components that capture much water and are able to form viscous gels. It is highly fermentable by intestinal microorganisms, so it produces a lot of gas in the intestine. Being highly fermentable it favours the creation of bacterial flora, which comprise one third of faecal volume; therefore, this kind of fibre also increases stool bulk and gives a softer consistency. In addition the fibre can reduce and slow down the absorption of fats and sugars in food, which helps to regulate cholesterol levels and blood glucose.

(b) Insoluble fibre is composed of substances that retain little water and swell slightly. Components of this type are poorly fermentable; in fact, they can resist the action of microorganisms in the intestine. The main effect of such fibre on the body is to cleanse: this kind of fibre acts as a natural brush. Consequently, such fibre makes the stool easier to pass along the gut and prevents constipation.

2. Materials and methods

2.1 Selection of by-products

In the first phase, some by-products were selected to be characterised. The selected by-products were those in which the vegetable processing industries from Extremadura, Murcia and La Rioja (some of the most important production regions in Spain) had an interest. These by-products were from the processing of tomato, broccoli, cauliflower, cardoon, artichoke, carrot and mushroom (see Figure 1 and Table 1).

Figure 1. Cardoon by-products at canning industry

2.2 Characterisation

Through characterisation of the by-products selected, knowledge was acquired regarding their potential use in food applications.

The selection was based on soluble and insoluble fibre content of the by-product (991.43, AOAC (1991)), as well as the potential regarding dietary fibre extraction to obtain a dietary fibre that was neutral in colour and taste, and had good technological properties for food use, in particular water holding capacity (WHC, see Robertson et al. (2000)) and oil holding capacity (OHC).

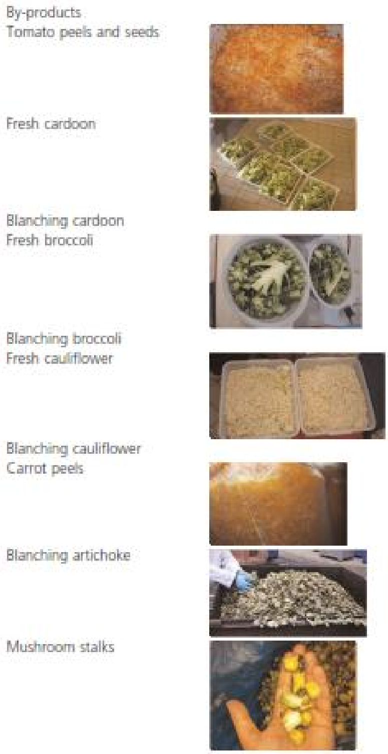

Table 1. Vegetables by-products generated in the vegetable processing industry

The WHC/OHC of a fibre is a measure of its ability to immobilise water/oil within its matrix. Such water/oil will influence the metabolic activity of fibre within the gut, and it is a property closely related to the final food product consistency. The colour was also measured using the CIELab scale with a colorimeter (Minolta CM 3500d, Osaka, Japan).

As a co-product of the dietary fibre extraction, a crude extract was obtained that was formed principally by polyphenols and carotenoids – natural antioxidants with potential applications in food, cosmetics and/or pharmaceuticals. Therefore, the by-products' polyphenols contents were analysed by the Folin– Ciocalteu method (Singleton et al., 1999), also the carotenoids contents (Ranganna, 1997), as well as total antioxidant capacity. by DPPH method (inhibitory activity of 2,2-diphenyl-1-picryl- hydrazyl), using Trolox as standard (Brand-Williams et al.,1995).

2.3 Cardoon fibre extraction and drying process

The major component of cardoon is water (around 80%); however, this plant has a high content of dietary fibre (especially insoluble fibre, but also with a significant proportion of soluble fibre). During the cardoon canning/freezing process, in the conditioning and cleaning operations, the external leaves of the plant are eliminated; these represent 75% of the raw material and are the woodiest part of the plant. The resulting by-product at those stages therefore offers a very attractive source of fibre, with potential as an ingredient in food formulations such as bread, cereals, cereal bars, bisuits, cakes, pastries, yoghurt and other dairy products, sauces, powdered dietary products, or dietary supplements, among others.

By doing preliminary tests it was found that the cardoon fibre WHC was greater than that of artichoke fibre. Therefore, the pilot study for fibre extraction was focused on the cardoon by-product as a raw material and potential source of fibre with the desirable technological properties that were being sought

In the second phase of the pilot study, extraction tests were performed combining two extraction processes: the conventional process of solid–liquid solvent extraction and ultrasound-assisted extraction (UAE) (Khan et al., 2010). Ethanol was the solvent used and the variables assayed were the solvent concentration: 75% and 96%, and solid:solvent ratio: 1:5 and 1:10, respectively. Two different drying technologies were also studied: the conventional method by forced air drying and drying assisted by microwave (MW). Two drying temperatures were assayed: 65°C, and 80°C in the case of conventional drying.

MW drying was performed in conditions previously established in a pilot electromagnetic microwave generator (MMP20T, Sairem S.A., Miribel, France). The flow chart of the operational procedure is represented in Figure 2.

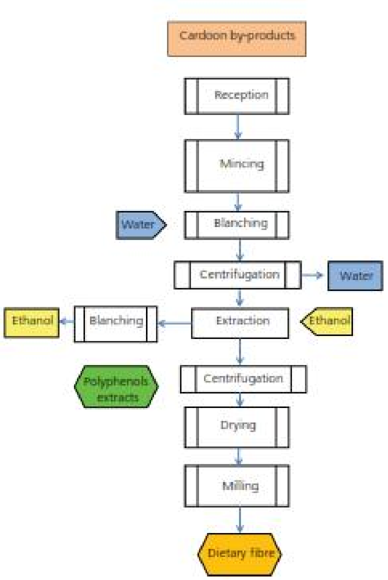

Figure 2. Flow diagram of fibre extraction

The results were evaluated in terms of colour and technological properties, basically the water retention capacity (WRC) of the resulting fibre.

2.4 Product formulation

To complete the pilot experience, the cardoon fibre extracted and dried was added into the formulation of baked products and sauces, as a texturising agent or for dietary fibre intake. The dosage of fibre in bread was calculated in order to be able to claim on the label of the product that 'source of fibre' and 'fibre' was at least 30% compared to a reference product. It was actually possible to achieve at least 2% increase in the amount of fibre in the final product.

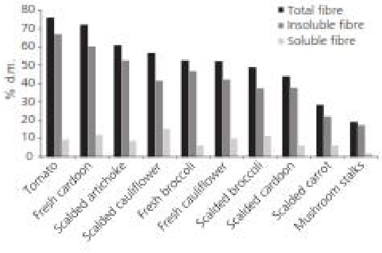

Figure 3. Total fibre content, soluble and insoluble by-products analysed (d.m.: dry matter)

Taking into account that the bread had between 3 and 5% of fibre content, the increase was thus 40–60%. Cardoon fibre likewise had fibre proportions of 0,4%, 0,5% and 0,6% added to a tomato sauce as a thickener, and this was compared to the currently used thickener. In this case, the resulting sauce product was evaluated for colour and consistency. The consistency was measured by a Bostwick consistometer that quantified the distance (cm) travelled of a known amount of sample (g) in 30 s, at an average temperature of 25 ± 1°C.

Similarly, the polyphenol extract obtained as a co-product from fibre blanching was incorporated into various cosmetic formulations by counting, with the collaboration of a cosmetic company, Sirius Bio.

3. Results

3.1 Characterisation

The by-products characterisation revealed that cauliflower and broccoli have an interesting content of soluble fibre (Figure 3); however, their disadvantage comes from the sensory point of view, owing to the sulfur components that give its characteristic aroma when it is cooked (like broccoli, for example) or the colour intensity of broccoli. Moreover, their water content, as in the case of cardoon, involves a higher cost of energy used in drying.

Carrot by-products could be an important source of carotenoids, but they have a low fibre content. Because of the high sugar content, the by-products could be considered in the energy recovery path once extraction of carotenoids has been completed. Another factor to consider is the volume generated.

Results show that artichoke represents a good source of polyphenols (Figure 4). However, cardoon was finally selected for the pilot trial owing to its higher fibre content and its colour characteristics that made it more suitable for producing a marketable fibre, which was neutral in colour and flavour. It is important to note that, during the blanching operation of by-products (which is carried out to ensure the products are stabilised in respect of oxidation and microbiology delay), there is a

significant loss of soluble material.

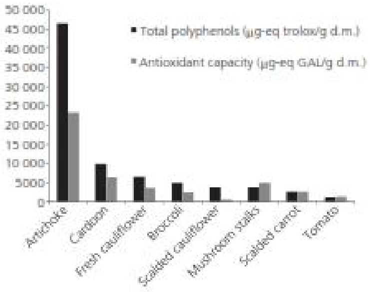

Figure 4. Total polyphenols and antioxidant capacity of different by-products characterised (d.m.: dry matter)

In order to obtain a fibre with the desired characteristics (i.e. neutral in colour and flavour), artichoke and cardoon represented the best option because of their low content of carotenoids. Tomato by-products have a high fibre content; however, their carotenoid content can provide sensory characteristics that would limit their applications.

3.2 Cardoon fibre extraction

Once the focus had been directed onto fibre extraction using cardoon by-products, different extraction and drying methods were attempted in order to obtain fibres with the desired characteristics. The fibres obtained were compared with other fibres commonly used in commercial food production, in order to compare the colour and WHC (Figure 5).

The results indicate that UAE is an interesting method to explore industrially. At the same time, it can be said that there is an improvement in the drying of samples that have been extracted by ultrasound, because of reducing drying time. The drying process seems to be what most influences the technological properties of the fibres obtained. High temperatures seem to affect the WHC higher temperatures seem to affect the WHC.

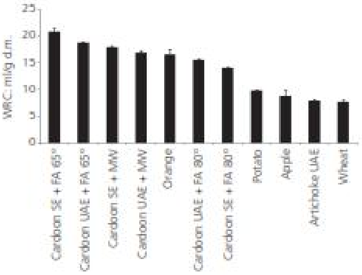

Figure 5. Water-holding capacity of cardoon fibre obtained by combinations of

different extraction and drying methods. Comparison with other commercial fibres (SE, classic solvent extraction)

The results of the colour measurements and visual appearance of the samples are presented in Figures 6–8: The best combination of processes in terms of colour seems to be UAE with forced air conventional drying at 80˚C. It has been seen that drying at 80˚C gives a better result in terms of colour than drying at 65˚C, probably due to the shorter duration of drying. Therefore, a combination of UAE with forced air drying at 65˚C could be the best option.

The fibre obtained from cardoon differs from those that are currently on the market, in terms of its higher relative content of soluble fibre, higher WHC and its increase in volume. These features mean that it is a product with a wide range of potential applications as an ingredient in feed formulation with technological and/or dietary purposes.

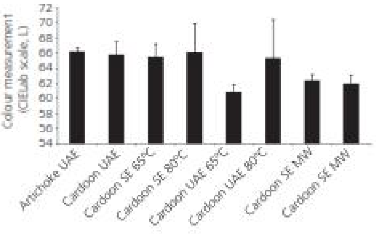

Figure 6. Colour measurements (CIELab scale, L) of the fibre samples obtained combining different extraction and drying methods (SE: classic solvent extraction, UAE: ultrasound assisted extraction, MW: microwave drying, FA: forced air conventional drying. Reference drying method was vacuum drying at low temperature 40–45 ˚C)

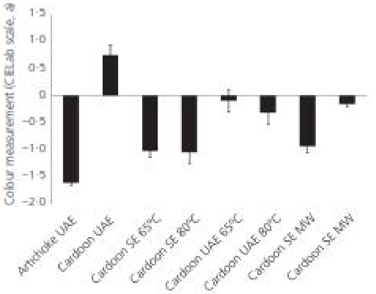

Figure 7. Colour measurements (CIELab scale, a) of the fibre samples obtained combining different extraction and drying methods (reference drying method was vacuum drying at low temperature 40–45 ˚C)

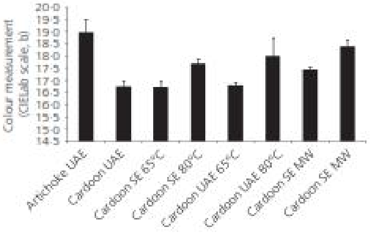

Figure 8. Colour measurements (CIELab scale, b) of the fibre samples obtained combining different extraction and drying methods (reference drying method was vacuum drying at low temperature 40–45 ˚C)

3.3 Product formulation

The sensorial and consistency tests results indicate that cardoon fibre can be applied in bakery products, although they could be greatly improved by changing the formulation in order to improve 'sponginess' texture. The bread samples where cardoon fibre was used developed less mass, leaving the crumb firmness more compact (Figure 9). Sensorial features were acceptable, although colour could be improved. The overall result could be improved by using slightly less fibre, using a stronger flour or by using bread improvers.

Figure 9. Examples of cardoon fibre application tested: bread

The addition of cardoon fibre to tomato sauce is interesting in that the product presents characteristics, in terms of consistency and colour, that are similar to conventional tomato sauce with commercial fibre incorporated (see Table 2 and Figure 10).

Polyphenol extracts of cardoon were incorporated into a cosmetic formulation elaborated by Sirius Bio, where cardoon extract showed a good integration and homogeneity in the final product (Figure 11). The next step would be to study the availability and stability of polyphenol compounds incorporated into the cosmetic product over time, as well as its assimilation, through a clinical trial.

4.1 Cardoon fibre and polyphenols extraction

Most cardoon polyphenols are lostin the leachate after the blanching stage. At industrial scale, this polyphenol loss could be minimised by concentrating the liquid on extraction. Comparing the two methods of extraction, it could be the case that ultrasound assistance enables the saturation rate to be reached in less time than for conventional extraction; thus ultrasound facilitates and improves the extraction, and therefore presents an interesting methodology to explore industrially.

Fibre content: %	Commercial fibre, 0·4%	Cardoon fibre, 0·4%	Cardoon fibre, 0·5%	Cardoon fibre, 0·6%
Consistency: cm	7·50	8·00	7·50	6·80
Colour:				
Colour L	23·96	23·56	23·67	23·59
Colour a	27·71	26·12	25·63	25·70
Colour b	13·28	13·09	13·00	13·17

Table 2. Colour measurements (CIELab scale) and consistency of the tomato sauces samples with cardoon fibre

Figure 10. Tomato sauces samples with different contents of cardoon fibre (FC): (a) commercial fibre (STA); (b) 0.4%; (c) 0.5%; (d) 0.6%

Figure 11. Body milks elaborated by cardoon polyphenol extracts (Sirius Bio)

4. Conclusion

Ultrasound-assisted extraction can besaid to enable the samples to be better dried and in less time, possibly because of modification of the tissue so that humidity can be evacuated easily. The drying process seems to be what most influences the technological properties of the fibres obtained; higher temperatures seem to affect the WHC.

The cardoon fibre extracted by conventional maceration presents he best WHC, followed by the fibre extracted using ultrasound.

Therefore, a combination of UAE with forced air drying at 65°C could be the best option, as long as the performance is improved at the extraction stage.

The fibre obtained from cardoon by-products differs from those currently available in the market in respect of its high content of insoluble fibre, its high WHC and increase in volume, which together make it a product with a wide range of possible applications as an ingredient in the formulation of dietary foods.

The properties and application possibilities presented by cardoon fibre and extracted polyphenol compounds have attracted significant attention from companies – both proces- sors that generate by-products and future users of those new ingredients for enriched products development.

4.2 Applications and further research programme

The results indicate that cardoon fibre can be applied in bakery-type products, although they could be greatly improved by changing the formulation as described earlier.

The addition of cardoon fibre into tomato sauce is interesting because the product behaviour has the same characteristics in terms of consistency and colour as conventional tomato sauce with commercial fibre incorporated. The added value brought by the use of cardoon fibre, from the technological and functional point of view, is

- good performance in processing
- good stability and appearance owing to the fibre’s WHC properties
- flavour, colour and texture that is satisfactory to consumers.

The meat industry is another potential user of fibres with high WHC. For this application, the fibre must be as neutral as possible in terms of colour and flavour. Further studies are required to make improvements in this regard.

Further analyses and studies of extraction ratio performance improvement would be required, by using multiple extraction cycles, for example, which could make it possible to obtain a fibre with a suitable colour.

Thanks to the cooperation between companies under the Value project framework it has been possible to continue with the assessment of new ingredients extracted from by-products in different food matrixes. The website of the project (www.proyectovalue.eu) makes available the diagnoses regarding the current generation and management of plant residues and the revision of existing legislation.

The research continues through the Provalue project, which extends the field of application to other food subsectors such as the meat, fishing, olive and wine industries.

Acknowledgements

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UE / EU - FEDER / ERDF

Figure 13. European Regional Development Fund (ERDF) logo

Thanks to the work carried out by the Value Consortium it has been possible to develop and to obtain promising results for the food

industry. The Consortium is composed of seven members, through which all regions of SUDOE in Spain, France and Portugal are represented.

The project coordinator is the Association for Research, Development and Innovation in Food of La Rioja (AIDIA), which participates with the technological centre specialised in marine and food research, AZTI-Tecnalia, located in the Basque country; the Spanish Federation of Food Industries and Beverage (FIAB); the CENER Foundation, a centre specialised in renewable energy and located in Navarra; APESA, a partnership for environment and security in Aquitaine; the CRT-CATAR transfer centre for agricultural resources in Toulouse; and CVR WASTE technical centre for waste recovery in Guimaraes (Portugal). All partners share a common commitment to improve the environment and in particular to improve the management and recovery of waste.

Figure 12. SUDOE Interreg programme logo

The opinions presented in this document represent only the Value project partners and they are not in any way the official opinion of the management bodies of the Territorial Cooperation Programme European Southwest Space (SUDOE) (see Figures 12 and 13 for related logos).

REFERENCES

AOAC (Association of Analytical Communities) (1991) 991.43: Determination of soluble, insoluble, and total dietary fiber in foods and food products. AOAC International, Gaithersburg, MD, USA.

Brand-Williams W, Cuvelier ME and Berset C (1995) Use of a free radical method to evaluate antioxidant activity. Lebensmittel-Wissenschaft und Technologie – Food Science and Technology 28: 25–30.

Khan MK, Abert-Vian M, Fabiano-Tixier AS et al. (2010) Ultrasound-assisted extraction of polyphenols (flavanone glycosides) from orange (Citrus sinensis L.) peel. Food Chemistry 119(2): 851–858.

Ranganna S (1997) Manual of Analysis of Fruit and Vegetable Products, 9th edn. Tata McGraw Hill, New Delhi, India.

Robertson JA, de Monredon FD, Dysseler P et al. (2000) Hydration properties of dietary fibre and resistant starch: a European collaborative study. Food Science and Technology 33(2): 72–79.

Singleton VL, Orthofer R and Lamuela-Raventos RM (1999) Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. Methods in enzymology 299(C): 152–178.

Thermodynamic model of microwave drying of citrus peel with different treatments

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ABSTRACT

The microwave drying operation includes mechanisms associated with the hot air drying and microwave heating. The coupling of both techniques produces cross-flow of heat and mass unquantifiable and difficult to explain using traditional methodologies. The application of thermodynamics in the microstructure of the product permits to describe and quantify the real phenomena in heating and dehydration which occur in the tissue. One of the critical steps for off-flavours extraction and fiber conformation of orange by-product is the drying operation. The effect of different microwave power densities (0 W/g, 2 W/g, 4 W/g and 6 W/g) combined with 55ºC air drying on drying kinetics, dielectric properties and microstructure of orange peel has been studied. Mass variation, water activity and dielectric properties were measured at time points 0 min, 5 min, 15 min, 40 min, 60 min and 120 min for each drying experiment. The effect of power density on absolute humidity, drying curves, desorption isotherms and dielectric loss factor at 15 GHz was analysed. Results showed that higher microwave power levels resulted in higher amounts of water evaporated in the same time and faster drying rates. However, desorption isotherms did not show differences among power density while microstructure microscopy showed the opposite. Dielectric loss factor allowed the determination of the critical water activity at which liquid phase disappeared suggesting that microwave energy could be an advantage until the critical water activity is reached.

1 Introduction

A correct quantification of microstructural transformations, produced during the microwave drying process may allow the design of suitable structures for extraction processes off-flavors. The citrus juice industry produces a great amount of waste that needs an innovation and development to become products. There is a continuous demand to develop innovative approaches for the valorization of citrus by-products; transforming them into healthy food ingredients by applying environmentally and economically sustainable processes. Citrus waste are a potential source of different bioactive compounds such as dietary fiber and natural anitoxidants among others, and also potential sources of flavours and food colorants.

Furthermore, in previous work it was observed that microwave drying of citrus peels could potentially reduce evaporation costs, resulting in a stabilized product for further conversion into dietary fiber with optimal microbial, sensory and technological properties.

2 Material and Methods

2.1 *Sample preparation*

Navel oranges were bought from a local supermarket and peeled at 5 mm thickness. Orange peels were cut in 20 mm cylinders with a core borer. The average moisture content of fresh samples was determined by drying in a vacuum oven at 60ºC until constant weight was reached (AOAC method 934.06, 2000). Water content (x_w) of fresh peel samples was 0.750 ± 0.001g/g sample.

2.2 *Drying operation*

Samples were subjected to air drying (AD) and microwave assisted air drying (AD+MW), using a modified household microwave oven, where air temperature, air velocity and microwave power could be controlled (Fig. 1). The air velocity was controlled using a digital hot wire anemometer TESTO 425 (precision ± 0,03 m/s). Considering previous results the drying temperature and the optimal air velocity inside the cavity were kept at 55ºC and 2.5 m/s, respectively. The microwave power level used was selected such that samples did not burn during drying.

Orange peel samples were placed flavedo side up on the drier grid to favour mass transfer. Four drying experiments were carried out in triplicate (0 W/g, 2 W/g, 4 W/g and 6 W/g). For each experiment, 5 min and 15 min dried samples were obtained uncontinuously (2 independent trials). For timepoints 40 min, 60 min and 120 min, one unique experiment was carried out by placing 9 samples and removing the corresponding samples at each timepoint. Mass, water activity and dielectric spectrum was analyzed for each fresh and dried samples.

At each timepoint, mass variation was determined by using a Mettler Toledo Balance (± 0.0001 g) (Mettler-Toledo Inc., Schwarzenbach, Switzerland) and water activity was measured with a dew point hygrometer Aqualab series 3 TE (Decagon Devices Inc., Washington, USA). Each sample treated was reposed at 25ºC for 1 h, on Decagon containers, closed with parafilm, in order to eliminate the concentration profiles in samples.

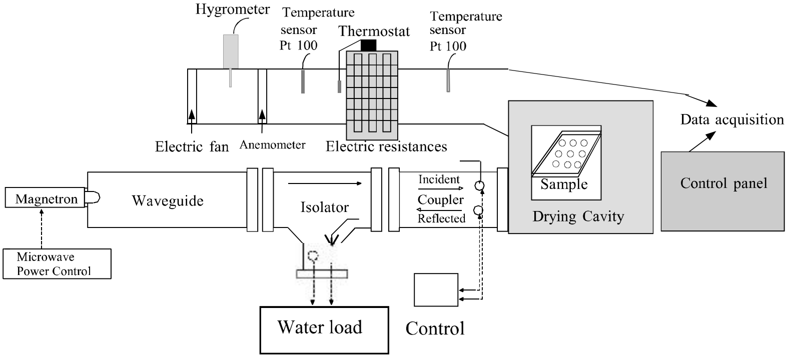


Fig. 1 Schematic description de of the laboratory equipment used to dry samples

2.3 *Dielectric properties*

The system used to measure dielectric properties consists on an Agilent 85070E Open-ended Coaxial Probe connected to an Agilent E8362B Vector Network Analyzer. The software of the Network Analyzer calculates the dielectric constant and loss factor as a reflected signal function. For these measurements the probe was fixed to a stainless steel support, and an elevation platform brings the sample near the probe.

The system was calibrated by using three different types of loads: air, short-circuit and 25ºC Milli-Q water. Once the calibration was made, 25ºC Milli-Q water was measured again to check calibration suitability.

3 Results

3.1 *Drying kinetics*

Mass variation and a_w (Table 1) were determined at each timepoint before and after the drying treatment.

Table 1 Initial and final water activity values (a_w) obtained after 5 min, 15 min, 40 min, 60 min and 120 min of orange peel drying under different conditions

Drying cond.	a_{wo}	a_{w5}	a_{w15}	a_{w40}	a_{w60}	a_{w120}
AD + 0 W/g	0.981 ± 0.002	0.950± 0.007	0.930± 0.007	0.814± 0.030	0.314± 0.156	0.163± 0.023
AD + 2 W/g	0.972± 0.001	0.965± 0.081	0.905± 0.026	0.583± 0.045	0.210± 0.021	0.209± 0.023
AD + 4W/g	0.975± 0.003	0.965± 0.005	0.946± 0.006	0.409± 0.187	0.121± 0.011	0.083± 0.004
AD + 6 W/g	0.970± 0.001	0.946± 0.005	0.898± 0.007	0.203± 0.180	0.099± 0.000	0.130± 0.0125

Moisture content (x_w, kg_w/ kg_T) was obtained from mass losses along the drying process by using the corresponding mass balances, by a initial value of 0.754±0.0012.

After 15 min drying with hot air at 55ºC the absolute humidity was 1.71 kg_w/ kg_{dm} whereas when drying was carried out with hot air assisted with 6 W/g of microwave energy the absolute humidity after 15 min was 1.27 kg_w/ kg_{da}. Also, after 120 min drying with hot air absolute humidity was 0.38 kg_w/ kg_{da}, but when using 6 W/g of microwave energy during the same time, absolute humidity decreased to 0.12 kg_w/ kg_{dm}.

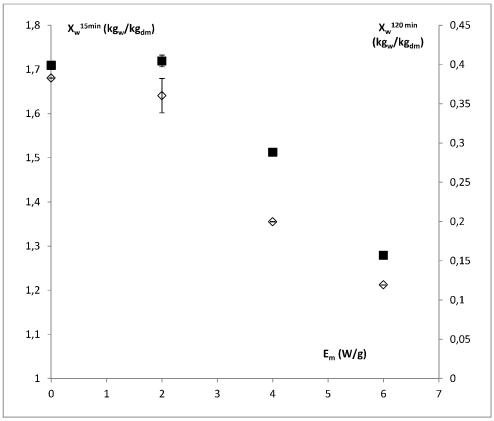


Fig. 2 Effect of microwave energy absorbed by absolute humidity (X_w) at 15 min (■) and 120 min (◊) during orange peel drying.

Figure 2 shows how the microwave energy, with high penetration increases the drying effect of the hot air. Figure 3 showed that the drying rate during the first 15 min of drying only with hot air was 0.124 ± 0.005 Kg w/ min achieving an absolute humidity of 2.69 ± 0.01 Kg w/ Kg d.m. However, when using hot air combined with 6 W/ g the drying rate was 0.175 ± 0.005 Kg w/ min and the relative humidity after the first 5 min was 2.56 ± 0.01 Kg w/ Kg d.m.

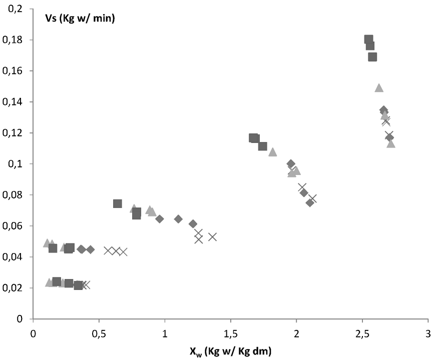


Fig. 3 Drying curve of orange peel dried by: hot air (AD, ■), AD + 2 W/g (◆), AD + 4 W/g (▲), AD + 6 W/g (◆)

In figure 3 is possible to observe the drying rate curve in falling rate stage, were the samples dried with additional microwave energy increase the water loss. This effect is explained in the driving forces of this drying stage, in fall rate stage the driving forces are the internal transport of water, the microwave energy has high penetration increasing the mobility of the water dropped in the tissue. Therefore, the effect of microwave is not applied in heating sample is applied in motion or mechanical energy.

However, the desorption isotherms showed that the relationship between absolute humidity and water activity (see Figure 4) was not affected by the drying treatments. Although microstructural differences showed a pore expansion on orange tissue pores. The isotherm support the idea that the microwave energy affect only in the water internal transport.

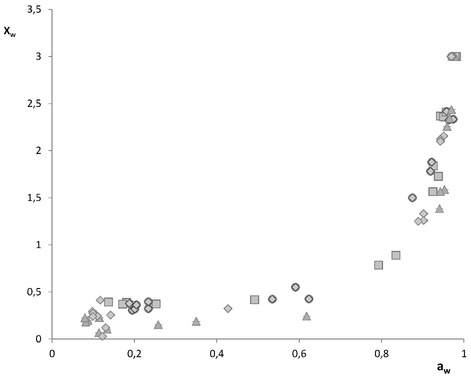


Fig. 4 Desorption isotherms of orange peel dried by hot air (AD ■), AD + 2 W/g (◆), AD+ 4 W/g (▲), AD + 6 W/g (◆)

3.2 Dielectric properties

Dielectric properties showed that at water relaxation frequency (15 GHz), microwave signal decreases while there is water in liquid phase. Once the critical a_{wc} is reached (0.6 for albedo and 0.8 for flavedo), liquid phase disappears and the loss factor is nule.

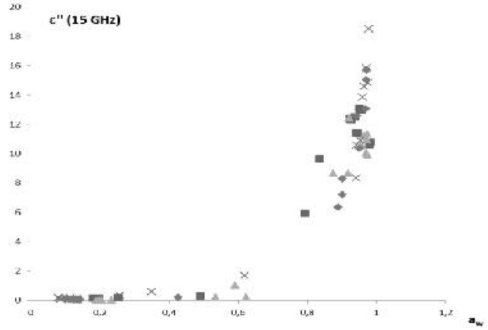


Fig. 5 Relationship between loss factor e'' (15 GHz) and water activity of orange flavedo dried by hot air (AC ■), AC + 2 W/g (▲), AC + 4 W/g (✕), AC + 6 W/g (◆)

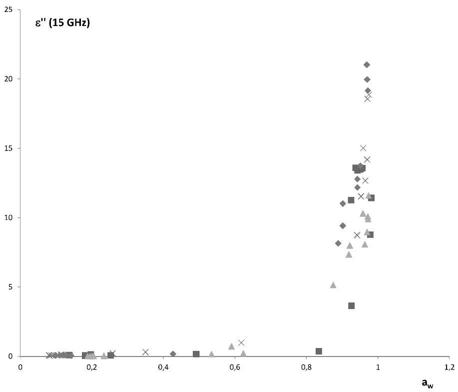
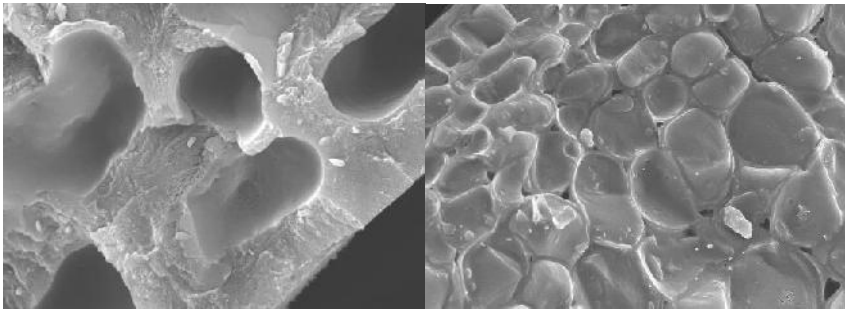


Fig. 6 Relationship between loss factor ε'' (15 GHz) and water activity of orange albedo dried by hot air (AC ■), AC + 2 W/g (▲), AC + 4 W/g (✕), AC + 6 W/g (◆)



(a) (b)

Fig. 7 Images captured by Cryo-SEM microscopy showing the microstructure of fresh (a) and dried (b) orange flavedo using combination of hot air (55ºC) assisted by 2 W/g microwave energy

4 Conclusions

Higher microwave power levels increased the amount of water diffused through the orange peel tissue for the same drying time. Drying rate was faster when combining hot air and microwave energy than only with hot air, showing that microwave energy helps heating the liquid phase and accelerates evaporation. However, the amount of water adsorbed it is not influenced by the drying treatment although changes on tissue microstructure are observed. The measurement of dielectric properties allows determination of critical aw representing a practical control value to decide when microwave energy has no more effect in accelerating water evaporation.

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References

Al-Harahsheh, M., Al-Muhtaseb, A. a. H., & Magee, T. R. A., 2009. Microwave drying kinetics of tomato pomace: Effect of osmotic dehydration. Chemical Engineering and Processing: Process Intensification, 48(1), 524-531.

Castro-Giráldez, M., Fito, P.J., Fito, P., 2011. Application of microwave dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic Apple tissue." Journal of Food Engineering 104, 227-233.

Contreras, C., Martín-Esparza, M.E., Chirat, A., Martínez-Navarrete, N., 2008. Influence of microwave application on convective drying: Effects on drying kinetics, and optical and mechanical properties of apple and strawberry. Journal of Food Engineering 88, 55-64.

Garau, M. C., Simal, S., Roselló, C., Femenia, A., 2007. Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. Food Chemistry 104(3), 1014-1024.

Huang, L.-l., Zhang, M., Wang, L.-p., Mujumdar, A. S., & Sun, D., 2012. Influence of combination drying methods on composition, texture, aroma and microstructure of apple slices. LWT - Food Science and Technology 47, 183-188.

ANÁLISIS DE LA PRODUCCIÓN DE FIBRA A PARTIR DE SUBPRODUCTOS CÍTRICOS MEDIANTE PROPIEDADES DIELÉCTRICAS

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INTRODUCCIÓN

La industria de zumos produce un gran cantidad de subproductos actualmente aún poco valorizados. Existe una creciente demanda para el desarrollo de estrategias innovadoras que permitan revalorizar estos subproductos cítricos, transformándolos en ingredientes alimentarios con propiedades beneficiosas para la salud, mediante el empleo de procesos económica y ambientalmente sostenibles.

Los subproductos cítricos son una fuente potencial de diferentes compuestos bioactivos tales como fibra dietética y antioxidantes naturales, entre otros; además de aromas y colorantes alimentarios (Garau et al, 2007).

Los costes de secado limitan la mayoría de las rutas propuestas para su valorización. En trabajos anteriores se ha observado que el secado por microondas de subproductos vegetales (pulpa de tomate, gajos de manzana, piel de naranja, etc) podía reducir potencialmente los costes de vaporización, resultando en un producto estable para su posterior conversión en fibra dietética, con una calidad microbiológica, sensorial y tecnológica adecuada (Al- Harahsheh et al, 2009; Huang et al, 2012). Una correcta cuantificación de las transformaciones microestructurales, producidas durante el proceso de secado por microondas, puede facilitar el diseño de estructuras que faciliten la extracción de aromas no deseados en etapas posteriores al secado.

MATERIALES Y MÉTODOS

Preparación de muestras

Naranjas de la variedad Navel se adquirieron en un supermercado local (Valencia). Se pelaron con un espesor de 5 mm y, posteriormente, las pieles se cortaron en cilindros de 20 mm con un descorazonador. El contenido medio en humedad de las muestras frescas se determinó mediante secado a vacío a 60ºC hasta alcanzar peso constante (AOAC method

934.06, 2000). El contenido en humedad (xw) de las muestras frescas fue de 0,750 ± 0,001g/g.

Operación de secado

Las muestras se sometieron a secado por aire forzado (AD) y secado por microondas combinado con aire caliente (AD+MW), utilizando un microondas domésticos modificado, donde la temperatura del aire, la velocidad del aire y la potencia de microondas pueden controlarse (Fig. 1).

La velocidad del aire se controló utilizando un anemómetro térmico TESTO 425 (precisión ± 0,03 m/s). Considerando resultados previos, la temperatura de secado y la velocidad de secado óptima en el interior de la cavidad se mantuvieron a 55ºC y 2,5 m/s, respectivamente. La potencia de microondas utilizada se seleccionó de manera que las muestras no se quemaran durante el secado.

Las muestras de pieles de naranja se situaron en la rejilla con el flavedo orientado hacia arriba del secadero para facilitar el transporte de masa. Se llevaron a cabo cuatro experimentos de secado en triplicado (0 W/g, 2 W/g, 4 W/g y 6 W/g). Para cada experimento se obtuvieron muestras a los 5 min y a los 15 min en discontinuo (2 experimentos independientes). Para los tiempos 40 min, 60 min y 120 min, se llevó a cabo un único experimento secando las 9 muestras inicialmente y retirando la muestra correspondiente a cada tiempo. Las variaciones de masa y actividad de agua se analizaron a cada tiempo, tanto para las muestras frescas como para las secas. Las variaciones de masa se determinaron mediante un balanza Mettler Toledo Balance (± 0.0001 g) (Mettler-Toledo Inc., Schwarzenbach, Switzerland) y la actividad de agua se midió con un higrómetro de punto de rocío Aqualab series 3 TE (Decagon Devices Inc., Washington, USA).

Cada muestra se dejó reposar a 25ºC durante 1 h en cápsulas de Decagon selladas con parafilm, con el objetivo de eliminar los perfiles de concentración de las muestras.

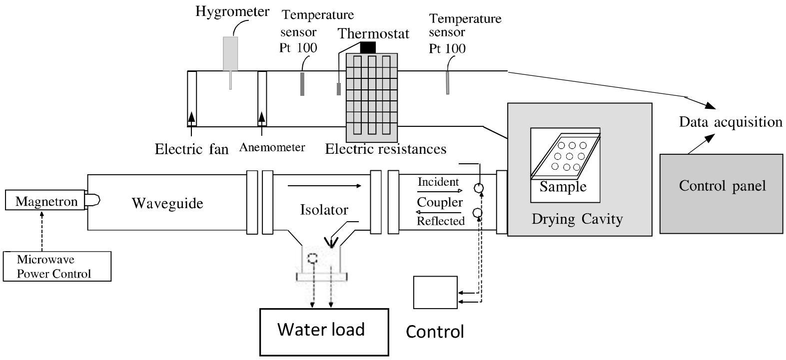

Figura 1 Descripción esquemática del equipo utilizado en el laboratorio para secar las muestras
(adaptación de Contreras et al, 2008)

RESULTADOS Y DISCUSIÓN

Cinética de secado

La variación de masa y la a_w se determinaron para cada tiempo antes y después del tratamiento de secado (Tabla 1).

Tabla 1 Valores de a_w iniciales y finales obtenidos después del secado de piel de naranja a diferentes condiciones para los tiempos 5 min, 15 min, 40 min, 60 min y 120 min.

Condiciones de secado	a_{wo}	a_{w5}	a_{w15}	a_{w40}	a_{w60}	a_{w120}
AD + 0 W/g	0,981 ± 0,002	0,950± 0,007	0,930± 0,007	0,814± 0,030	0,314± 0,156	0,163± 0,023
AD + 2 W/g	0,972± 0,001	0,965± 0,081	0,905± 0,026	0,583± 0,045	0,210± 0,021	0,209± 0,023
AD + 4W/g	0,975± 0,003	0,965± 0,005	0,946± 0,006	0,409± 0,187	0,121± 0,011	0,083± 0,004
AD + 6 W/g	0,970± 0,001	0,946± 0,005	0,898± 0,007	0,203± 0,180	0,099± 0,000	0,130± 0,0125

La humedad de la piel de naranja (x_w, kg_w/ kg_T) se calculó partir de las pérdidas de peso a lo largo del proceso de secado aplicando los diferentes balances de masas, y considerando un valor inicial de 0.754±0,0012 kg_w/ kg_T.

La Figura 2 muestra como la energía microondas, al tener mayor penetración, aumenta el efecto de secado del aire caliente. Después de 15 min de secado con aire caliente a 55ºC, la humedad absoluta fue de 1,71 kg_w/ kg_{dm} mientras que cuando el secado se realizó por aire caliente en combinación con 6 W/g de energía microondas, la humedad absoluta después de 15 min fue de 1,27 kg_w/ kg_{dm}. Igualmente, tras 120 min de secado con aire caliente, la humedad absoluta fue de 0,38 kg_w/ kg_{dm}, pero cuando se combinó con 6 W/g de energía microondas la humedad absoluta descendió a 0,12 kg_w/ kg_{dm}.

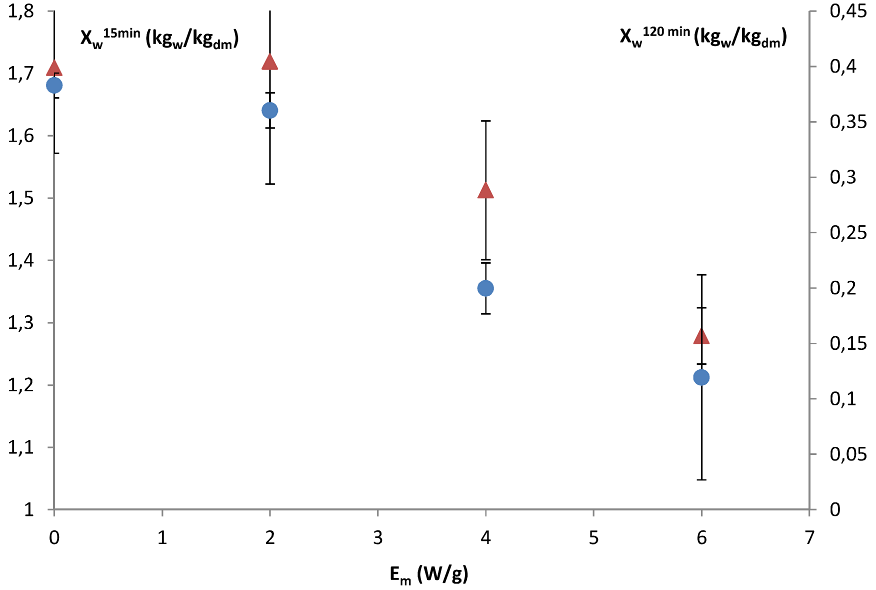

Figura 2 Efecto de la energía absorbida en la humedad absoluta (X_w) a los 15 min (▲) y a los 120 min (•) durante el secado de piel de naranja a diferentes densidades de potencia (E_m).

Además, la Figura 3 muestra como la velocidad de secado durante los primeros 5 min de secado con aire caliente fue de 0,124 ± 0,005 Kg_w/min, alcanzando una humedad absoluta de 2,69 ± 0,01 Kg_w/ Kg_{dm}. No obstante, cuando el secado se realizó utilizando aire caliente en combinación con 6 W/g de energía microondas, la velocidad de secado aumentó a 0,175 ± 0,005 Kg_w/min siendo la humedad absoluta después de los primeros 5 min de 2,56 ± 0.01 Kg_w/ Kg_{dm}.

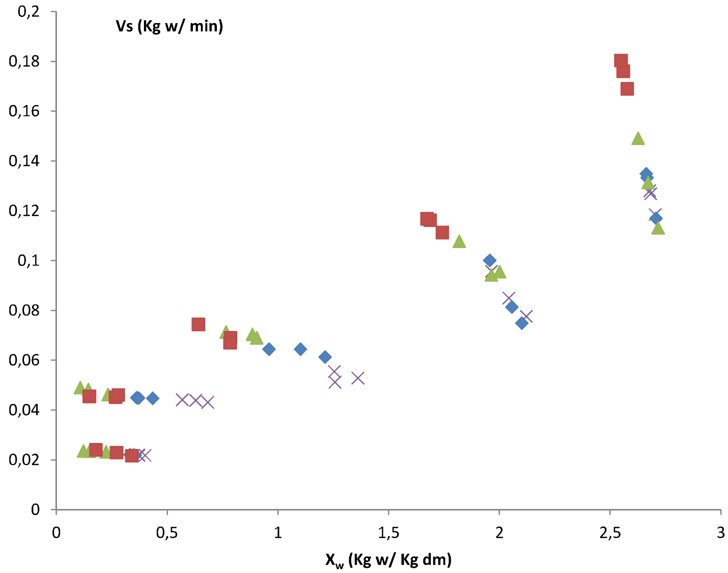

Figura 3 Curva de secado de la piel de naranja secada por aire caliente AD (×), AD + 2 W/g (◆), AD + 4 W/g (▲), AD + 6 W/g (■)

En la figura 3 se observa la curva de secado en el periodo de velocidad de secado decreciente, donde las muestras secadas con aporte de energía microondas adicional aumentan la velocidad de pérdida de agua. Este efecto se explica por la combinación de las fuerzas impulsoras en esta fase de la curva de secado: en la fase decreciente la fuerza impulsora es el transporte interno del agua, la energía microondas penetra en el tejido aumentando la movilidad del agua por su interior. Por tanto, la energía microondas no se emplea en calentar la muestra si no en movilizar el agua.

No obstante, las isotermas de desorción (Fig. 4) muestran como la relación entre la humedad absoluta y la actividad del agua no está afectada por los tratamientos de secado, a pesar de que las diferencias microestructurales demuestran una expansión de los poros del tejido de las pieles de naranja (Figura 5). Las isotermas respaldan la ida de que la energía microondas afecta solo al transporte interno del agua.

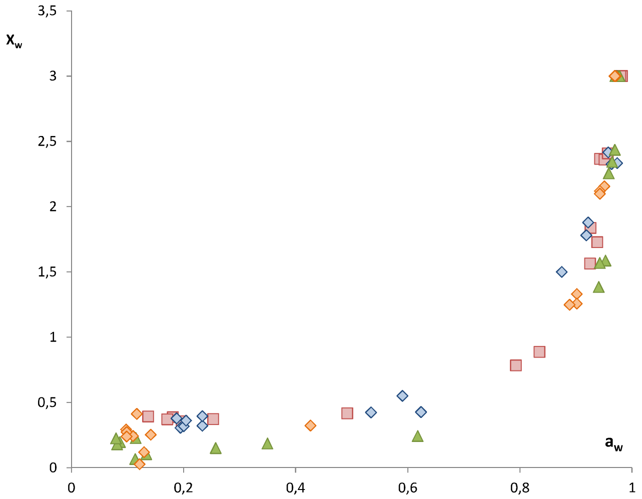

Figura 4 Isotermas de desorción de pieles de naranja secadas por aire caliente AD (■), AD + 2 W/g (◆), AD+ 4 W/g (▲), AD + 6 W/g (◆) .

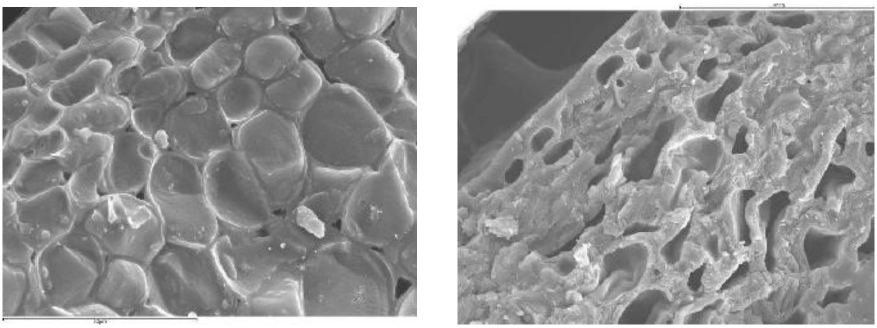
(a) (b)

Figura 5 Imágenes capturadas por cryo-SEM (5.000 aumentos) mostrando la microestructura de piel de naranja fresca (a) y deshidratada (b) utilizando aire caliente (55ºC) en combinación con 2 W/g de energía microondas.

CONCLUSIONES

Potencias altas de microondas aumentan la cantidad de agua que difunde a través del tejido de la piel para el mismo tiempo de secado.

La velocidad de secado fue más rápida cuando se combinó aire caliente y energía microondas que solo con aire caliente, mostrando que la energía microondas contribuye al transporte interno del agua.

BIBLIOGRAFÍA

Al-Harahsheh, M., Al-Muhtaseb, A. a. H., & Magee, T. R. A., 2009. Microwave drying kinetics of tomato pomace: Effect of osmotic dehydration. Chemical Engineering and Processing: Process Intensification, 48(1), 524-531.

Contreras, C., Martín-Esparza, M.E., Chirat, A., Martínez-Navarrete, N., 2008. Influence of microwave application on convective drying: Effects on drying kinetics, and optical and mechanical properties of apple and strawberry. Journal of Food Engineering 88, 55-64.

Garau, M. C., Simal, S., Roselló, C., Femenia, A., 2007. Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. Food Chemistry 104(3), 1014-1024.

Huang, L.-l., Zhang, M., Wang, L.-p., Mujumdar, A. S., & Sun, D., 2012. Influence of combination drying methods on composition, texture, aroma and microstructure of apple slices. LWT - Food Science and Technology 47, 183-188.

Thermodynamic Modeling of Orange Peel Dried by Hot air-Microwave.

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Keywords: orange peel, microwave, drying, thermodynamics, dielectrics, microstructure.

INTRODUCTION

Dielectric properties are necessary to quantify the overall heating produced when any food product is exposed to microwave energy. The aim of this work was to develop a thermodynamic-electric model for understanding internal heating, water transport mechanisms, drying kinetics and microstructure changes occurring during hot-air microwave drying of orange peels.

METHODOLOGY

Orange peel samples were dried with a specially designed hot air-microwave drying oven (HAD + MW) at 55°C combined with different MW powers. Samples were removed at different times over 120 min. Dielectric properties were measured with an Agilent 85070E open-ended coaxial probe connected to an Agilent E8362B Vector Network Analyzer.

RESULTS

The total distribution of energy was calculated as $\mathrm{E_T} = \mathrm{E_{HAD}} + \mathrm{E_{MW}}$; where $\mathrm{E_{HAD}}$ is the energy supplied by the hot air and $\mathrm{E_{MW}}$ is the energy supplied by microwaves. The microwave energy absorbed and transformed into heat energy was calculated as $\mathrm{E_{MW}} = \mathrm{E_{abs}} \cdot \mathrm{r_{MW}}$; where $\mathrm{E_{abs}}$ is the overall energy absorbed and $\mathrm{r_{MW}} = \frac{\varepsilon''}{\varepsilon' + \varepsilon''}$, is the microwave energy dissipation ratio (Figure 1c).

In Figure 1a it was possible to observe in a psychometric chart the beginning of drying at the initial value of the water activity ($a_w^0 \approx 0.97$) and finishing at the line of drying conditions. Samples treated by HAD + MW showed high levels of enthalpy at the beginning of the treatments, when high water activity produces higher dissipation of microwave energy. In order to estimate the surface temperature, an iteration system was developed as shown in Figure 1d and temperature evolution was plotted in Figure 1b.

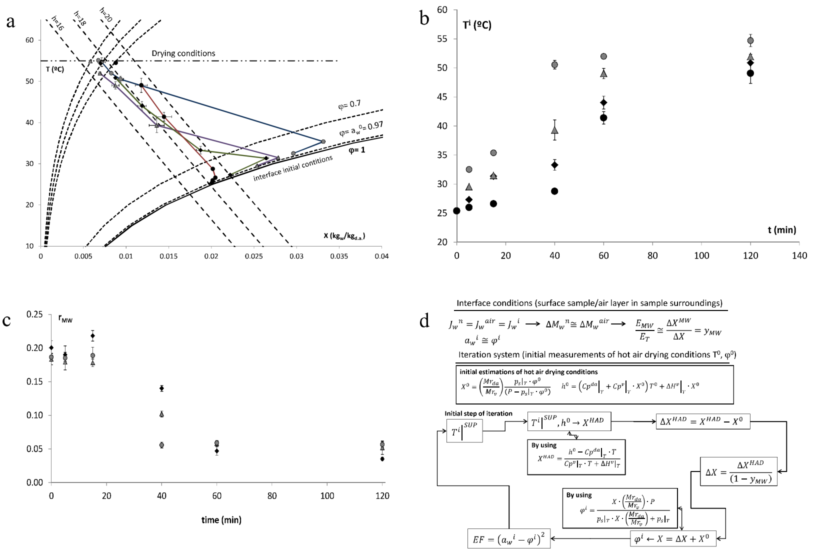

Figure 1. ● HAD, ◆ HAD+2 W/g, ▲ HAD+4 W/g, ● HAD+6 W/g; 1a (Evolution of interface air conditions throughout the drying process); 1b (Interface temperature evolution); 1c (MW energy dissipation ratio (r_{MW}); d (Iteration scheme).

DISCUSSION

In samples treated by HAD+MW, the mechanisms of surface evaporation and microwave dissipation by penetration were coupled. The result of coupled behaviors produces internal evaporation and therefore induces an internal swelling (volumetric sample expansion). Depending on the predominant mechanisms (HAD shrinkage and MW swelling) samples suffer volumetric expansions or contractions. HAD+MW treatment reduced drying time changing the structural properties and reducing the energy expended.

CONCLUSION

This model allows optimizing the traditional hot air drying by coupling microwaves as a novel time-efficient process for citrus by-products valorization.

REFERENCES

[1] M. C. Garau, S. Simal, C. Rosselló and A. Femenia, Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products. *Food Chem., 2007*, *104*, pp. 1014-1024.

[2] H. Feng, Y. Yin and J. Tang, Microwave Drying of Food and Agricultural Materials: Basics and Heat and Mass Transfer Modeling. *Food Engineering Reviews, 2012*, *4*, pp.89-106.

Presentación de posters en congresos internacionales:

1. Effect of microwave and instant controlled pressure drop technologies on physico-chemical properties of stabilized citrus processing by-products.

   EFFoST Annual Meeting, 9-11 November 2011, Berlin

2. Polyphenolic extract from orange by-products as a source of natural antioxidants

   6th Paris Polyphenols 2012: Clinical Evidences – *Polyphenols Valorization from Waste: Solutions & Strategies, 7-8 June 2012, Paris*

3. Valorización de subproductos de la industria de transformados de vegetales del SUDOE.

   11 *Congreso Nacional de Medioambiente, CONAMA, 26-30 Noviembre 2012, Madrid*

4. Thermodynamic model of microwave drying of citrus peel with different treatments

   Inside Food Symposium, 9-12 Abril 2013, Leuven (Belgium)

5. Effect of microwave drying on rheological and sensory properties of citrus fiber used for texturizing low fat potato purees.

   Eurosense 2014: 6th European Conference on Sensory and Consumer Research, 7-10 Septiembre, Copenhagen.

Effect of microwave and instant controlled pressure drop technologies on physico-chemical properties of stabilized citrus processing by-products.

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INTRODUCTION

The **European** and **Indian** food industries generate many millions of tons per year of plant **processing by-products**, particularly in the fruit and cereal processing sectors. The exploitation and disposal of these by-products is compromised through their **inadequate biological stability** (i.e. their propensity for microbiological spoilage and oxidation, as well as, proliferation of pathogenic agents). Hence, their current valorization is limited (e.g. use in animal feed and composting). However, such food processing by-products can be considered sources **of valuable food ingredients** to be exploited in the production of **new foods and feeds**.

Such by-products contain high amounts of proteins, sugars and **bioactive compounds** of high interest for the modern food industry. Indeed, after specific pretreatments with physical and biological agents followed by tailored recovery procedures they might provide natural antioxidants (Meléndez-Martínez et al, 2008), antimicrobial agents, vitamins, etc, along with macromolecules like dietary fiber (Larrauri et al, 1999) of wide interest for new food formulations .

A number of **innovative technologies** are currently used in obtaining food ingredients and in food processing (Garau et al, 2007; Rezzoug et al, 2008). The development of technological and economically viable approaches to convert such matrices into appropriate ingredients would allow to reduce the volume of by-products disposed and the production of **higher-value foodstuffs**, with remarkable positive effects on the sustainability and economic competitiveness of the European

AIM

The main objective was to study the effect of microwave drying technology (MW) and instant controlled pressure drop technology (DIC) prior to drying on the physico-chemical properties of stabilized citrus by-products from the juice industry.

MATERIAL AND METHODS

LEMON by-product (Verna) was provided by Citromil S.A., Murcia (Spain) and **ORANGE** by-product (mix of Valencia Late and Lane Late varieties) was provided by Grupo Leche Pascual (GLP), S.A.U., Burgos (Spain).

Initially, 500 g batches of **LEMON** peels were blanched in water (90 ºC, 5 min) and dried using four different technologies:

Table 1. Experimental set-up for stabilization of lemon by-products

TECHNOLOGY	EXPERIMENTAL VARIABLES		RESPONSE VARIABLES
FC	Temperature	65ºc	drying time final moisture content water activity yield water binding capacity (WBC) flavor odor instrumental color
MW	Power density	1.5 w/g 2 w/g	
DIC (+FC or +MW)	Moisture content	35% 50%	
	Pressure-time combination	2.2 bar-180s 4 bar-90s	

Subsequently, 500 g batches of **ORANGE** by-product were stabilized using MW drying at the optimum drying conditions observed for lemon by-products. Microbial and sensory analysis were carried out on these samples in order to asses the effectiveness of the selected treatment. In addition, total polyphenol content was measured at different process steps.

REFERENCES

1. Garau, M. C., S. Simal, et al. (2007). "Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products." Food Chemistry 104(3): 1014-1024.
2. Larrauri, J. A. (1999). "New approaches in the preparation of high dietary fibre powders from fruit by-products." Trends in Food Science & Technology 10(1): 3-8.
3. Meléndez-Martínez A J., Vicario I M., Heredia FJ. (2007) Review: Analysis of carotenoids in orange juice. Journal of Food Composition and Analysis 20: 638–649.
4. Rezzoug, Sid-Ahmed; Maache-Rezzoug, Zoulikha; Sannier, Frédéric; and Allaf, Karim (2008). "A Thermo-mechanical Pre-processing for Pectin Isolation from Orange Peel with Optimisation by Response Surface Methodology". International Journal of Food Engineering 4(1) Article 10.

Figure 1. 500g batches of lemon by-product were dried at a frequency of 2450 MHz in an electromagnetic MW generator (Miribel, France) at a power density of 1.5 watt/g for 60 min.

Figure 2. Laboratory-pilot scale DIC equipment. 25-35g of product were processed prior to FC or MW.

RESULTS

Results for lemon by-product showed that MW reduced by 3-fold the drying time required to reach target moisture content (7-12%) and water activity (0.30-0.50) compared to FC. MW significantly reduced flavor and odor intensity and improved colour. WBC was acceptable and similar for all treatments (WBC > 10 g water/ g dry matter).

DIC treatments prior to drying resulted in darker colour, probably due to the temperature increase during the treatment and a lower initial moisture content. Drying time was not improved by DIC treatment.

Polyphenols content showed the highest decrease after blanching. No significant decrease was observed due to MW treatment.

Table 2. Total polyphenol content (TPC) in orange by-products after different pre-treatments

TPC (ppm DM)	Raw	Blanched	Blanched + MW dried
	9,950 ± 121	2,140 ± 60	2,948 ± 464

Microbial analysis carried out on stabilized orange by-product obtained by MW treatment (MC = 7.5%) showed that moulds and yeasts were reduced by 3 log cycles; aerobic mesophilic count was reduced by 4 log cycles and sporulated mesophilic count was reduced by 1 log cycle.

Figure 3. Preliminary blanching of orange by-products avoided poliphenols oxidation and browning

Figure 4. MW drying did not negatively affect color of stabilized orange by-products

CONCLUSIONS

An innovative process for stabilizing citrus processing by-products has been proposed using MW technology. Although MW drying is considerably an expensive technology to acquire, its operational costs are lower than other drying technologies due to its efficiency evaporating water (Kg/h). Although DIC processing did not improve total drying time, visual expansion was observed showing a potential application for future improvement of water binding capacity.

A potential food ingredient with optimal microbial quality, acceptable sensory and technological properties that made it suitable for its use as a dietary fiber source for food formulations, has been obtained.

Acknowledgements

This work is part of NAMASTE project and is financed by the 7th Framework Programme (Grant Agreement Number 245267) which is also a collaborative project in coordination with DBT (India).

6th Paris Polyphenols 2012: Clinical Evidences 2012 - Polyphenols Valorisation from Waste: Solutions & Strategies

POLYPHENOLIC EXTRACT FROM ORANGE BY-PRODUCTS AS A SOURCE OF NATURAL ANTIOXIDANTS

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INTRODUCTION



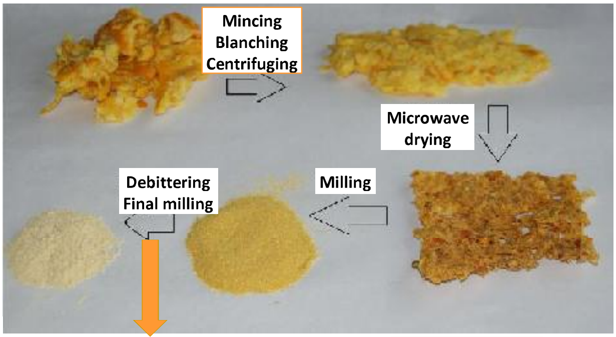
The European and Indian food industries generate millions of tons of plant processing by-products, particularly in the fruit and cereal processing sectors. The exploitation and disposal of these by-products is compromised through their inadequate biological stability (i.e. their propensy for microbiological spoilage and oxidation, as well as, proliferation of pathogenic agents). Hence, their current valorization is limited. Citrus processing by-products are usually valorized as animal feed, as a source of pectins, terpenes or for bioethanol production. Previous studies have also been done to obtain dietary fiber [1] or natural antioxidants, due to their high concentration of polyphenols [2, 3]. Orange by-products have been selected for this study because nearly 85 per cent of the total citrus for processing comes from oranges.

The **objective** of this research was to obtain and characterize polyphenol rich crude extracts from orange processing by-products in the same process than citrus fiber extraction for their further application as food ingredients in healthy foods.

MATERIAL & METHODS

FIBER AND POLYPHENOL EXTRACTION PROCEDURE:

Orange by-product (mix of Valencia Late and Lane Late varieties was provided by Grupo Leche Pascual (GLP), S.A.U., Burgos (Spain).



Mincing
Blanching
Centrifuging

Microwave drying

Milling

Debittering
Final milling

POLYPHENOL ETHANOLIC EXTRACT

Ethanol evaporation

POLYPHENOL CRUDE EXTRACT

POLYPHENOL CARACTERISATION:

Total polyphenol

Folin-Ciocalteau

140 µL of diluted orange extract or gallic acid standards, 30 µL of Folin–Ciocalteu reagent and 140 µL of 20% sodium carbonate were mixed in 96-well plates. The absorbance was measured at 750 nm after 1 h and TPC was expressed as gallic acid equivalent (GAE)/L.

Antioxidant Capacity

DPPH method

0,1 ml of diluted orange extract or Trolox standards were added to 3,9 ml of 25 mg/L DPPH solution (dissolved in methanol). The absorbance of the remaining DPPH• was measured after 1h at 515 nm against methanol blank. The final results were expressed as (mmol Trolox/L).

Bioactive Compounds Analysis

LC-MS/MS

Ultrasound assisted extraction: mixture ethanol:water:formic acid (75: 24:1) .

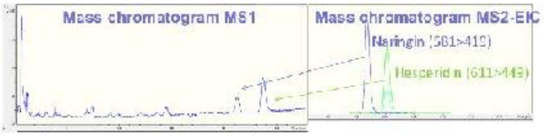
Chromatographic separation: Gemini C18 analytical column (250mm×4.6mm, 5 µm, Phenomenex, USA) with a C18 column guard cartridge at 30 ºC. Gradient elution was performed with water/0.1% formic acid (A) and acetonitrile/0.1% formic acid (B) at a constant flow rate of 0.4ml/min. In 10 µL of sample were injected. An increasing linear gradient was used in 29 min: 0 min, 20%B; 25min, 40%B; 26min, 100%B; 28min, 100%B; 29min, 20%B.

The mass spectral analysis*:* was performed in negative electrospray ionization mode. The capillary and orifice voltages were set at -3000 v and -50 v respectively. The nebulizer gas was set at 40 psi. The nitrogen auxiliary was adjusted to a constant flow rate of 8ml/min. The capillary temperature was set at 350 º C.

The identification of orange polyphenols was based on the comparison of retention time of standards, product ion spectra and UV-vis spectra.

RESULTS

- ✓ The yield of the process was 60 g of fiber and 13 g of crude concentrated per kg of fresh peels.
- ✓ Polyphenol recovery in the crude concentrated extract was 58%.
- ✓ Total phenolic content was 2,2 g Gallic equivalents/kg in orange peels and 120 g Gallic equivalents/kg in the crude concentrated extract.
- ✓ Antioxidant capacity was 1,42 g Trolox equivalents/kg in orange peels.
- ✓ Major polyphenols found in in orange peels and crude extract were flavonoids Naringin (11 mg/g) and hesperidin (31 mg/g). Quercetin-o-glucoside, rutin, p-coumaric acid, ferulic acid and cafeic acid were also found in much lower concentrations.



CONCLUSIONS

- ✓ An innovative process for obtaining orange fiber has been developed using the microwave technology during the drying step.
- ✓ A co-product of the fiber production, a crude polyphenol rich extract has been obtained.
- ✓ Naringin and hesperidin are the major polyphenols found in orange peel etanolic extract. These flavonoids are natural antioxidants and are related with specific health effects such as cancer, lipid metabolism, bone protection.
- ✓ Both products, fiber and polyphenolic extract, could be used as ingredients for the formulation of food products with technological and healthy properties.

References:

[1] Lario, Y., Sendra, E., García-Pérez, J., Fuentes, C., Sayas-Barberá, E., Fernández-López, J. et al. (2004). Preparation of high dietary fiber powder from lemon juice by-products. *Innovative Food Science and Emerging Technologies*, **5**: 113–117.
[2] Li, B.B., Smith, B., Hossain, Md. M. (2006). Extraction of phenolics from citrus peels: I. Solvent extraction method. *Separation and Purification Technology* **48**(2): 182-188.
[3] Khan, M. K., Abert-Vian, M., Fabiano-Tixier, A.S., Dangles O., Chemat, F., (2010). Ultrasound-assisted extraction of polyphenols (flavanone glycosides) from orange (*Citrus sinensis L.*) peel. *Food Chemistry* **119**(2): 851-858.
[4] http://namaste-eu-india.org/

Acknowledgements:

This work is part of NAMASTE project and is financed by the 7th Framework Programme (Grant Agreement Number 245267) Which is also a collaborative project with DBT (India)[4].

11 Congreso Nacional de Medioambiente, CONAMA, 26-30 Noviembre 2012, Madrid

VALORIZACION DE SUBPRODUCTOS DE LA INDUSTRIA DE TRANSFORMADOS VEGETALES DEL SUDOE

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AZTI-TECNALIA*, AIDIA-CITA**, CENER***

PRESENTACION

Un problema para las PYMES europeas del sector alimentario, y en concreto del sector de transformados vegetales, es la gestión y valorización de sus subproductos (entre el 5 y el 50% del peso de la materia prima) que actualmente sigue sin estar resuelta para muchas de ellas, especialmente en algunos países del área del Sudoeste de Europa (España, Portugal y sur de Francia).

En los últimos años se ha avanzado mucho en el desarrollo de tecnologías de aprovechamiento de residuos. Sin embargo, dichas tecnologías no están suficientemente difundidas y/o validadas entre las PYMES del sector agroalimentario y en concreto en el de transformados vegetales.

El proyecto VALUE (2010-2013) es una iniciativa financiada por el Programa Operativo de Cooperación Territorial del Espacio Sudoeste Europeo (SUDOE 2007-2013) cofinanciado por fondos FEDER, que pretende a través de la transferencia de tecnologías y metodologías la valorización de residuos, bien mediante la obtención y aplicación de compuestos de interés para la mejora tecnológica de alimentos transformados o bien mediante la valorización energética de los residuos, teniendo siempre como objetivo último, incrementar la competitividad de las PYMES del sector.

El Consorcio participante en el proyecto VALUE se compone de 7 socios de 3 países y es coordinado por la Asociación para la Investigación, el Desarrollo y la Innovación Alimentaria de La Rioja (AIDIA). El resto de participantes son: en España, AZTI-Tecnalia del País Vasco, como centro especializado en investigación marina y alimentaria, la Federación Española de Industrias de Alimentación y Bebidas (FIAB), el CENER centro nacional especializado en energía renovables situado en Navarra, en Francia, APESA, asociación para el medio ambiente y la seguridad en Aquitania; CRT CATAR-CRITT centro de transferencia de recursos agrícolas en Toulouse y en Portugal el CVR RESIDUOS, centro técnico de valorización de residuos en Guimarães (Portugal).

TAREAS Y OBJETIVOS

Los principales objetivos del proyecto VALUE son:

- Llevar a cabo un diagnóstico de la situación actual en cuanto a cantidades y tipos de subproductos generados, gestión actual e infraestructiras disponibles en cada uno de los territorios del studio (España, Portugal y Sur de Francia).
- Dotar a las empresas (especialmente PYMES) del sector de transformados vegetales de información actualizada sobre las alternativas de valorización existentes, grado de desarrollo y mejores tecnologías disponibles (MTDs).
- LLevar a cabo experiencias piloto de valorización para la obtención de compuestos de valor añadido o su aprovechamiento energético con algunos de los subproductos de mayor interés, en estrecha colaboración con las empresas generadoras.
- Realizar una transferencia de los conocimientos y resultados obtenidos mediante la realización de talleres y jornadas de divulgación a las empresas y otros posibles sectores impliciados

RESULTADOS OBTENIDOS

Los resultados obtenidos hasta el momento pueden resumirse en:
.Elaboración de un estudio de diagnóstico de la generación de subproductos del sector de la transformación de vegetales en las tres zonas objeto de estudio.
.Elaboración de una base de datos que se encuentra disponible para su consulta en la página web del proyecto: *www.proyectovalue.eu*
.Realización de diversos talleres (Extremadura, Calahorra y Murcia) y de un Brokerage Event (Murcia) que ha permitido recoger las necesidades del sector y de otros agentes implicados
.Caracterización de diversos subproductos vegetales para la posterior realización de pruebas piloto a nivel experimental.

Las experiencias piloto seleccionadas para su realización en España han sido:
.La obtención de fibra y antioxidantes a partir de subproductos mediante el empleo de diversas técnicas de extracción y secado
.La realización de pruebas de obtención de bioetanol
.La realización de pruebas de obtención de biogás

Fig. 1. Extractos de polifenoles y fibra de cardo

Los principales resultados de las pruebas piloto son:

OBTENCION DE FIBRA Y ANTIOXIDANTES NATURALES

Se ha analizado el contenido en fibra dietética, polifenoles totales y capacidad antioxidante de los diferentes subproductos.
Se ha obtenido fibra de cardo combinando dos diferentes tecnologías de extracción (maceración y ultrasonidos) con dos métodos de secado diferentes (aire forzado y microondas).
Se ha medido la capacidad de retención de agua y el color de la fibra obtenida por cada método.

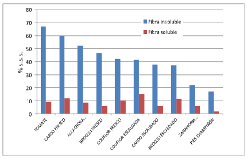

Fig.2 Contenido en fibra de los subproductos estudiados

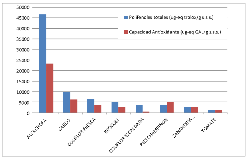

Fig.3. Contenido en polifenoles y capacidad antioxidante

OBTENCION DE BIOGAS

Se han realizado pruebas tanto en discontinuo (batch) con lodos de EDAR mezclados con vegetales y efluente de zumo de manzana, como pruebas en semicontinuo con alperujos, siempre en régimen mesófilo (37ºC). Los vegetales y el efluente de zumo mejoran ligeramente (5-20%) la producción de biogás de los lodos de EDAR, al ser incorporados en porcentajes que varían entre 5 y 15%. Los alperujos (5% Solidos volátiles) presentan rendimientos en torno a 0,250 NL biogás/gr tiempos de retención (HRT) de 37 días y cargas (OLR) de 1,16 gr Sólido Volátil (SV)/L·día, aunque actualmente se están llevando a cabo pruebas de co-digestión con purines de cerdo para mejorar los rendimientos y permitir una reducción del HRT y un aumento de la OLR.

Fig. 4. Planta piloto de biogás

OBTENCIÓN DE BIOETANOL

Se han llevado a cabo diferentes pruebas para la producción de bioetanol, a nivel de laboratorio y a escala piloto, con residuos procedentes de la industria de la mermelada y la elaboración de tortillas de patata precocinadas. Estos residuos han sido caracterizados y se han realizado unas pruebas iniciales que han ayudado a fijar las mejores condiciones en los ensayos a escala piloto. Tras fijar los parámetros de operación, los resultados obtenidos con el residuo procedente de la industria de procesado de mermelada han sido muy positivos obteniéndose concentraciones elevadas de etanol (hasta 96.2 g/l) en tiempo relativamente cortos y sin necesidad de la realización de pretratamientos previos.
Los resultados obtenidos con el residuo de tortilla de patata han sido también muy interesantes (rendimiento de producción de etanol de un 95%)

Fig 5. Planta piloto de etanol

CONCLUSIONES

.La fibra del cardo presenta las mejores propiedades tecnológicas si bien, la alcachofa destaca por su contenido en antioxidantes.
.La extracción asistida por ultrasonidos mejora la eficiencia en la extracción y parece facilitar el proceso de secado posterior.
.La producción de biogás a partir de subproductos vegetales debe ser estudiada en cada caso pero puede suponer una alternative adecuada tanto desde el punto de vista de la mejora de instalaciones ya existentes como para subproductos individualizados con una problemática ambiental elevada. Los resultados a obtener en el estudio de viabilidad serán determinantes para establecer las posibilidades reales de aplicación de esta tecnología al caso concreto de los alperujos.
.Los residuos ensayados para la producción de etanol se caracterizan por su alto contenido en agua y de azúcares solubles facilmente fermentables. Según el volumen generado podrían ser utilizados directamente en plantas de etanol o como co-productos en las plantas de bioetanol existentes de primera generación.

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www.proyectovalue.eu

Thermodynamic model of microwave drying of citrus peel with different treatments

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OUTLOOK: *Inside Orange Peel*

One of the critical steps for stabilization of citrus by-products is the drying operation.

The microwave drying operation includes mechanisms associated with the hot air drying and microwave heating. The coupling of both techniques produces unquantifiable cross-flow of heat and mass which is difficult to explain using traditional methodologies. The application of thermodynamics to the microstructure of the product allows the description and quantification of the real phenomena occurring during heating and tissue dehydration.

A correct quantification of microstructural transformations produced during the microwave drying process may allow the design of suitable structures for off-flavors extraction and fiber conformation processes with enhanced technological functionality.

CONTEXT & AIM

The citrus juice industry produces a great amount of waste (30T / year). There is a continuous demand to develop innovative approaches for the valorization of citrus by-products; transforming them into healthy food ingredients by applying environmentally and economically sustainable processes.

In previous work it was observed that microwave drying of citrus peels could potentially reduce evaporation costs, resulting in a stabilized product for further conversion into dietary fiber with optimal microbial, sensory and technological properties.

MATERIAL AND METHODS

Navel oranges were bought from a local supermarket and peeled at 0.5 cm thickness. Orange peels were cut in 2 cm cilinders with a core borer.

T_{air} was kept at 55ºC in all experiments.

For t = 5 min and t = 15 min, samples were prepared in triplicate and experiments were run individually (3 samples/ trial). Response variables were measured at the end of each drying experiment.

For t = 40 min, t = 60 min and t = 120 min samples were prepared in triplicate in one drying experiment (9 samples/ trial). Sam-

Table 1. Experimental set-up for modelization

	RESPONSE VARIABLES
DRYING METHODS	**0 min 5 min 15 min 40 min 60 min 120 min**
Hot Air (AC)	Moisture content wet basis (x_0) - Vacuum oven 60ºC until constant weight (AOAC) Mass (m_i, x_w, X_w) - Precision Scale Surface water activity (a_w) - Hygrometer Dielectric properties (ε', ε'') - Open Ended Coaxial Probe connected to a vector analyzer. Measurements were made in flavedo and albedo surfaces at 25ºC from 500 MHz to 20 GHz
AC + MW 2 W/g	
AC + MW 4 W/g	
AC + MW 6 W/g	

RESULTS

After 15 min drying with hot air at 55ºC moisture content (d.b.) was 1.71 kg w/ kg d.m. whereas when drying with hot air plus 6 Watt/g of microwave energy moisture content after 15 min was 1.27 kg w/ kg d.m. Also, after 120 min drying with hot air relative humidity was 0.38 kg w/ kg d.m., but when using 6 W/g of microwave energy during the same time, moisture content decreased to 0.12 kg w/ kg d.m.

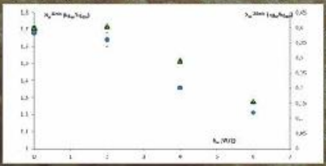

Figure 1. Effect of microwave dose on dry basis moisture content (X_w) at different timepoints: 15 min (Δ) and 120 min (●) during orange peel drying.

Figure 2 showed that the drying rate during the first 5 min of drying only with hot air was 0.124 ± 0.005 kg w/ min achieving a moisture content (d.b.) of 2.69 ± 0.01 kg w/ kg d.m. However, when using hot air combined with 6 W/ g the drying rate was 0.175 ± 0.005 kg w/ min and the moisture content after the first 5 min was 2.56 ± 0.01 kg w/ kg d.m. However, the desorption isotherms showed that the relationship between moisture content and water activity (Figure 3) was not affected by the drying treatments. Although microstructural differences showed a pore expansion on orange tissue pores.

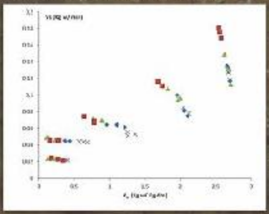

Figure 2. Drying curve of orange peel dried by hot air (AC ×), AC + 2 W/g (◆), AC + 4 W/g (▲), AC + 6 W/g (■).

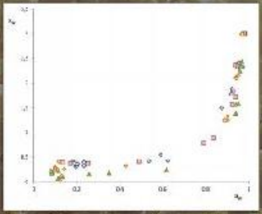

Figure 3. Desorption isotherms of orange peel dried by hot air (AC ■), AC + 2 W/g (◆), AC + 4 W/g (▲), AC + 6 W/g (✦).

Dielectric properties showed that at dipolar relaxation frequency (15 GHz), microwave signal decreases while there is water in liquid phase. Once the critical a_{wc} is reached (0.6 for albedo and 0.8 for flavedo), liquid phase disappears and the loss factor is nule.

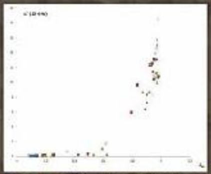

Figure 4: Relationship between loss factor ε'' (15 GHZ) and water activity of orange flavedo dried by hot air (AC ■), AC + 2 W/g (▲), AC + 4 W/g (×), AC + 5 W/g (◆).

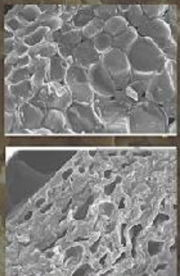

Figure 5: Images captured by Cryo-SEM microscopy (1000 x) showing the microstructure of fresh (a) and dried (b) orange flavedo using combination of hot air (55ºC) plus 2 W/g microwave energy

CONCLUSIONS

⇒ Higher microwave power levels increased the amount of water diffused through the orange peel tissue for the same drying time.

⇒ Drying rate was faster when combining hot air and microwave energy than only with hot air, showing that microwave energy helps heating the liquid phase and accelerates evaporation.

⇒ However, the amount of water desorbed it is not influenced by the drying treatment although changes on tissue microstructure are observed.

⇒ The measurement of dielectric properties allows determination of critical a_w, representing a practical control value to decide when microwave energy has no more effect in accelerating water evaporation.

REFERENCES

1. Castro-Giráldez, M., Fito, P.J., Fito, P. (2011). "Application of microwave dielectric spectroscopy for controlling long time osmotic dehydration of parenchymatic Apple tissue." Journal of Food Engineering 104: 227-233
2. Garau, M. C., S. Simal, et al. (2007). "Effect of air-drying temperature on physico-chemical properties of dietary fibre and antioxidant capacity of orange (Citrus aurantium v. Canoneta) by-products." Food Chemistry 104(3): 1014-1024.

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Effect of microwave drying on rheological and SENSORY PROPERTIES of CITRUS FIBER used for texturizing low fat potato purees.

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OUTLOOK:

Dietary fiber from citrus fruit is of higher quality than alternative sources such as cereals, due to its higher soluble dietary fiber ratio and associated bioactive compounds (flavonoids, polyphenols, carotenoids and vitamin C) with antioxidant properties, which may provide additional health-promoting effects.

In previous work it was observed that microwave drying of citrus peels could potentially reduce evaporation costs, resulting in a stabilized product for further conversion into dietary fiber with optimal microbial, sensory and technological properties.

CONTEXT & AIM

The citrus juice industry produces a great amount of waste (30T / year). There is a continuous demand to develop innovative approaches for the valorization of citrus by-products; transforming them into healthy food ingredients by applying environmentally and economically sustainable processes.

The main objective of this work was to study the impact that microwave treatment has on the physical and sensory properties of citrus fiber, and how it affects its capacity to increase viscosity when used for formulating low fat potato purees.

MATERIAL AND METHODS

2 different CITRUS FIBERS were used to reduce fat content of potato purees. The reference formula of potato puree was: 80% hydrated potato flakes and 20% cream. To study the effect of citrus fiber on reduced fat purees texture, cream content was replaced by water + 2 different citrus fiber (1% final content):

Fiber "COM" was from a commercial supplier and fiber "MW" was obtained by a novel process including microwave drying.

The process for fiber obtention is described as follows:

Raw material: orange by-products from Spanish juice processor.

STEPS: *Mincing* => *Blanching* (65ºC, 5 min) => *Drying* by combined hot air (55ºC, 2,5 m/s) + Microwave 2 W/g for 1h => *Milling* to 0.5 mm.

Sensory Evaluation

Sensory scores were assessed by a trained sensory panel using a quantitative descriptive (QDA) analysis protocol. The panel consisted of 7 assesors. Panelists were trained in the use of sensory texture attributes with samples similar to those later used for measurement. They were paid for their participation. Panel testing took place at the sensory facilities of Azti-Tecnalia. 4 different purees samples were assed by each panellist in five sessions (2 for training, 3 for replicates). The samples were: reference "REF", reference without cream "NOFIB", "COM" and "MW" . All products were presented once per session in a randomized order. Different texture attributes related with satiation were evaluated using an unstructured scale from 0 to 10: VISUAL (HETEREOGENEITY and VISCOSITY) and ORAL (GRANULOSITY, FATTY TEXTURE, CREMOSITY, VISCOSITY AND SATIATION.

Rheology Measurements

A controlled-stress AR 2000 rheometer was used with a geometry of 20 mm diameter with a cross-hatched surface and a gap of 2 mm. A stress sweep test from 0.01 to 1000 Pa was carried out at a constant frequency of 1 Hz and at 40ºC.

Statistical Analysis

Statistical analysis was carried out with R 2.14.0 programme (R Development Core Team), using the packages Commander and Agricolae.

REFERENCES

Perrigue, M. M., P. Monsivais, and A. Drewnowski. 2009. Added Soluble Fiber Enhances the Satiating Power of Low-Energy-Density Liquid Yogurts. J. Am. Diet. Assoc. 109(11):1862-1868.
Tarrega, A. and E. Costell. 2006. Effect of composition on the rheological behaviour and sensory properties of semisolid dairy dessert. Food Hydrocolloids 20(6):914-922.
Zia-ur-Rehman, Z., M. Islam, and W. H. Shah. 2003. Effect of microwave and conventional cooking on insoluble dietary fibre components of vegetables. Food Chem. 80(2):237-240.

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RESULTS

Table 1. Results of the one-way ANOVA (samples) of the sensory attributes and Kruskal Wallis (samples) of the rheological parameters

Samples	visual Homog.	visual Visc.	Gran.	Crem.	Fatty	Visc.	Satiation	G' (Pa)	G'' (Pa)
COM	4,164	7,273	4,995	4,382	2,227	6,355	5,968	7024,33	899,33
MW	4,341	7,359	4,545	4,409	1,968	6,291	5,823	3517,00	506,20
NOFIB	3,827	4,932	3,200	4,005	2,109	4,227	4,195	1173,87	155,07
REF	1,243	7,157	2,600	5,371	2,071	4,857	4,971	1227,80	160,27
p-value	ns	***	**	ns	ns	***	**	*	*

ns= no significative; (*) $p \leq 0.05$; (**) $p \leq 0.01$; (***)

There was a strong correlation (88.4%) among the sensory and rheological profile of texturized purees. **VISCOSITY**, **GRANULOSITY** and **SATIATION** were the sensory attributes that explain the differences among samples (Table 1). Fiber enriched purees with no cream had similar viscosity than the reference with cream, but were perceived as more granulose. COM puree had the highest viscosity modulus (G"), whereas MW puree had a similar viscoelasticity than the full fat reference with a higher visual and oral viscosity than COM puree. Cremosity and fatty texture were associated with the reference and were attributes poorly perceived in fiber enriched purees. The multifactor diagram showed that MW puree also generated higher satiation effect.

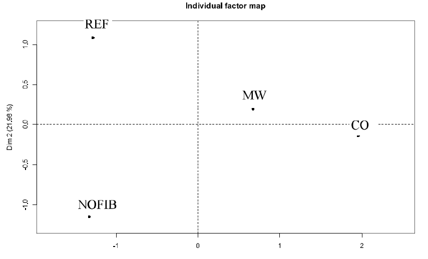

Figure 2 . Representation of the samples with multifactor analysis.

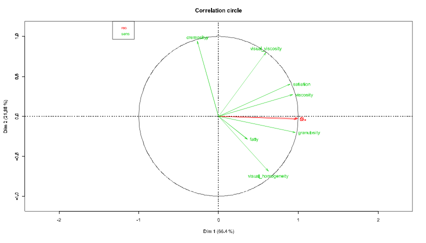

Figure 3 . Representation of the variables with multifactor analysis.

CONCLUSIONS

FAT CONTENT OF POTATO PUREES WAS REDUCED BY USING CITRUS FIBERS TO GENERATE SIMILAR TEXTURES AND SATIATION EFFECTS THAN CREAM. CITRUS FIBERS OBTAINED BY MICROWAVE DRYING PROVIDED A MORE VISCOUS TEXTURE AND GENERATED A HIGHER SATIATION EFFECT THAN COMMERCIAL CITRUS FIBERS PROBABLY DUE TO FIBER EXPANSION DUTING MICROWAVE DRYING. SENSORY PERCEPTION CHANGED DUE TO THE INFLUENCE OF THE DRYING PROCESS, SHOWING A STRONG CORRELATION BETWEEN PROCESS - STRUCTURE - PROPERTIES.

Acknowledgements

This work is part of LASAIFOOD project and is financed by Departamento de Desarrollo Económico y Competitividad of the Basque Government in collaboration with Instituto Universitario de Ingeniería de Alimentos para el Desarrollo (IAAD) at Universidad Politécnica de Valencia.

casi todas las infraestructuras fueron sobredimensionadas en los años de incubación de la crisis y recuerda que «muchos responsables políticos que hoy critican el programa AGUA fueron los mayores defensores del desarrollismo a ul-

añade Baltanás.

En 2005, con una de las sequías «más graves registradas, ningún suministro atendido con desalación en las cuencas mediterráneas tuvo ningún tipo de problema, fuera demanda urbana o agrícola, frente a las dificultades y restricciones sufridas por otros sistemas de recursos, incluidos los riegos del trasvase Tajo/Segura, que si en ese momento hubieran podido dispo-

bles para los tipos de usuarios previstos», incluida la agricultura, y su recuperación debe facilitarse con la obligada reforma legislativa que introduzca «mayor racionalidad» en la gestión económica del agua, «porque no se trata de que —con-

como la falta de lealtad institucional de algunas Administraciones favorables al trasvase del Ebro, que pusieron todos los obstáculos imaginables al desarrollo del Programa durante su ejecución por el anterior Ministerio de Medio Ambiente».

Natural. Investigadores de la Universidad Politècnica de València y de AZTI-Tecnalia han desarrollado un proceso para obtener fibras dietéticas a partir de cítricos

Las naranjas también adelgazan

▶ Los subproductos de la elaboración de zumos aportan fibras de más calidad que la de algunos cereales

J. S. VALENCIA

■ La calidad de la fibra dietética de naranja es mayor que algunas fuentes de fibras alternativas, como los cereales, muy utilizadas como complementos dietéticos, según concluye una investigación realizada en la Universidad Politècnica de Valencia (UPV).

Los investigadores han logrado desarrollar a nivel de laboratorio un proceso que permite obtener fibras dietéticas a partir de subproductos cítricos —especialmente de la pulpa y la corteza que se desecha en la elaboración de zumos— e incorporarlas posteriormente a nuevos alimentos que ven mejoradas sus cualidades gracias a las fibras.

La fibra procedente de la naranja es de mayor calidad y contiene compuestos bioactivos con propiedades antioxidantes (flavonoides, polifenoles, carotenoides y vitamina C) que pueden tener efectos beneficiosos sobre la salud y que están ausentes en estas otras fuentes de fibra, según informan los investigadores. «Creemos que se trata un ingrediente con potencial valor para la obtención de nuevos productos más saludables», asegura Clara Talens, investigadora de la Unidad de Investigación Alimentaria de AZTI-Tecnalia.


Pedro J. Fito, M. Castro y Clara Talens, de la UPV. LEVANTE-EMV

El nuevo proceso permite mejorar algunos «prototipos» de alimentos enriquecidos con fibras de naranja como las populares barritas de cereales o los «snaks» recubiertos de chocolate.

Aire caliente y microondas

En la elaboración de la fibra se ha utilizado como técnica de secado aire caliente en combinación con microondas para que el proceso sea «más eficiente», menos costoso y para que la fibra retenga más agua. «Esto abre la puerta a formular alimentos que tengan mayor poder saciante y con un bajo contenido en grasa» apunta Clara Talens.

Pedro J. Fito, investigador del Instituto de Ingeniería de Alimentos para el Desarrollo de la UPV, añade a estas ventajas la de dar una salida a los subproductos de la industria del zumo—casi un 50% de la fruta— cuyo aprovechamiento actual se reduce a la alimentación animal.

La contaminación decae un 50% en las aves tras prohibirse el cartucho de plomo

LEVANTE-EMV. VALENCIA

■ La contaminación de la carne de las aves acuáticas y su intoxicación por perdigones de plomo ha disminuido un 50% tras la prohibición en 2001 del uso de este tipo de munición en los humedales, según un estudio del centro de Investigación en Recursos Cinegéticos, que señala también que el cumplimiento de este mandato por parte de los cazadores ha sido muy alto.

El perdigón de plomo fue prohibido en 2001 la Albufera de Valencia, el Delta del Ebro y el resto de los humedales españoles de importancia internacional incluidos en la lista Ramsar.

Diez años más tarde, esta prohibición —que en otros países rige para todo tipo de caza— y la consecuente adopción del uso del perdigón de acero por parte de los cazadores ha empezado a dar sus frutos, según el estudio que publica la revista Environment International.