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TESIS DOCTORAL

Application of new drying technologies to aromatic herbs and vegetables: effects on physico-chemical, sensory and functional properties.

Ángel Calín Sánchez

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Tesis doctoral realizada por Ángel Calín Sánchez, Ingeniero Agrónomo, en el Departamento de Tecnología Agroalimentaria de la Universidad Miguel Hernández de Elche, para la obtención del grado de Doctor.

Ángel Calín Sánchez

Orihuela,____de______________de 2014

ÁNGEL ANTONIO CARBONELL BARRACHINA, Catedrático de Universidad de la Universidad Miguel Hernández de Elche y,

ADAM FIGIEL, Profesor Titular de la *Wrocław University of Environmental and Life Sciences*:

HACEN CONSTAR

Que el presente trabajo ha sido realizado bajo nuestra dirección y recoge fielmente la labor realizada por el Ingeniero Agrónomo Ángel Calín Sánchez para optar al grado de Doctor.

Prof. Dr. Ángel A. Carbonell Barrachina Prof. Dr. Adam Figiel

Orihuela,____de______________de 2014

José Ramón Díaz Sánchez, Dr. Ingeniero Agrónomo, Catedrático de Escuela Universitaria y director del Departamento de Tecnología Agroalimentaria de la Universidad Miguel Hernández de Elche.

INFORMA:

Que da su conformidad a la lectura de la Tesis Doctoral presentada por Ángel Calín Sánchez, titulada "Application of new drying technologies to aromatic herbs and vegetables: effects on physico-chemical, sensory and functional properties" que se ha desarrollado dentro del programa de doctorado "Recursos y Tecnologías Agroalimentarias" de este departamento bajo la dirección del Prf. Dr. Ángel Antonio Carbonell Barrachina y del Prof. Dr. Adam Figiel, la cual consideran conforme en cuanto a forma y contenido para que sea presentada para su correspondiente exposición pública.

Y para que conste a los efectos oportunos firmo el presente documento en Orihuela,____de______________de 2014.

Fdo.: Prof. Dr. José Ramón Díaz Sánchez

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Estos son mis principios, si no le gustan tengo otros.

G. Marx

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ABSTRACT

Product quality of dehydrated fruits, vegetables and aromatic herbs is a key feature in innovation of future drying technology, which is closely related to development of novel drying techniques and process optimization. This was the general aim of the present Ph.D. Thesis.

The main objective of this Ph.D. dissertation was to evaluate the application of (i) convective drying, (ii) freeze drying, (iii) microwave drying, (iv) vacuum–microwave drying and a (v) combination of convective pre–drying followed by vacuum–microwave finishing drying in the processing of dehydrated (i) rosemary, (ii) basil, (iii) thyme, (iv) garlic and (v) pomegranate. The parameters under study were related to kinetics and energy consumption aspects together with quality parameters, such as chemical composition, functional properties and sensory quality.

The microwave drying kinetics of rosemary consisted of two periods: (i) linear until a critical point and (ii) exponential beyond that point. The time needed to dry rosemary was shorter for high values of microwave power and vacuum intensity. The drying kinetics of sweet basil using convective drying was described by a two term exponential model, while vacuum–microwave drying kinetics consisted of two periods: (i) linear until a critical point and (ii) exponential beyond that point. The convective drying kinetics of thyme was described by a two term exponential model, while vacuum–microwave drying kinetics consisted of two periods: (i) a constant rate period until a critical moisture ratio and (ii) falling rate period beyond that point. The drying kinetics of convective and vacuum–microwave drying of pomegranate arils and rind were described using seven basic drying models; however, vacuum–microwave finishing drying was modeled only by one term exponential equation. Drying kinetics of garlic slices dried by the convective method was described by a two–term exponential model, while drying kinetics of vacuum microwave finishing drying garlic was described by a one–term exponential function. Energy consumption of both pomegranate arils and rind was reduced when the air temperature and microwave wattage were increased. Regarding garlic slices, vacuum–microwave drying required less energy than convective drying. Convective drying energy consumption can be reduced by its combination with vacuum–microwave drying (convective pre–drying followed by vacuum–

microwave finishing drying) and this reduction was more important when the vacuum-microwave finishing drying was applied earlier.

The quality parameters under study included, volatile compounds, sugars and organic acids compositions, contents of punicalagins, ellagic acid, and total polyphenols, total antioxidant activity and sensory quality. In general, drying led to a reduction in all studied parameters; however, the behavior of each plant material was different. The total quantity of volatiles of fresh rosemary decreased during drying, independently of treatments. Soft conditions of vacuum-microwave drying (low vacuum level and microwave power) are recommended to get the highest concentrations of volatile compounds and the best sensory quality. The total quantity of volatiles of fresh sweet basil decreased considerably during both convective and vacuum-microwave drying. Combined methods were the best option for drying sweet basil; the time required was relatively short, and aroma quality was good according to instrumental data and sensory data. The total quantity of volatiles of fresh thyme was reduced by most of the drying treatments, except for the treatments with low wattage of vacuum-microwave drying. The combined method was the best option for drying thyme; the time required was relatively short, and aroma quality was good according to instrumental data and sensory evaluation results.

Phenolic content of garlic slices was not significantly improved by the used of the combined drying method compared with the convective one. However, a decrease in the moisture produced an increment in the antioxidant capacity of garlic slices. Dried garlic showed even higher antioxidant capacity than fresh samples. Results suggested that phenolic compounds and other chemical compounds, such as allicin, were responsible for the antioxidant capacity of dried garlic slices. Vacuum-microwave drying of pomegranate was the best drying treatment for arils, while rind required freeze drying or soft conditions of convective drying. Further research is needed to obtain proper results with combined drying techniques. With proper selection of the drying protocol, high-quality dried arils will be available for consumers; these arils will be characterized by high contents of fructose, punicalagins, total polyphenols, high antioxidant capacity and high intensities of garnet color, sweetness, sourness and fresh pomegranate aroma. Besides, dried rind with very high contents of active compounds and high antioxidant capacity will be also available as a functional ingredient.

On the whole, the optimal drying technology is different for each of the materials studied and specific conditions must be recommended after proper evaluation of the drying protocols.

RESUMEN

La calidad de las frutas, hortalizas y hierbas aromáticas deshidratadas es un punto clave en la innovación futura de la tecnología de la deshidratación, la cual está estrechamente ligada al desarrollo de nuevas técnicas de deshidratación y optimización del proceso. Este fue el objetivo general de la presente tesis doctoral.

El principal objetivo de la presente tesis doctoral fue el de evaluar la aplicación de (i) deshidratación convectiva, (ii) liofilización, (iii) deshidratación con microondas, (iv) deshidratación con microondas a vacío y una (v) combinación de pre-deshidratación convectiva seguida de una deshidratación final con microondas a vacío durante el procesado de (i) romero, (ii) albahaca, (iii) tomillo, (iv) ajo y (v) granada deshidratados. Los parámetros estudiados estuvieron relacionados con la cinética de deshidratación y el consumo energético así como con parámetros de calidad tales como, la composición química, propiedades funcionales y calidad organoléptica.

La cinética de deshidratación de romero con microondas consistió en dos periodos: (i) lineal hasta un punto crítico y (ii) exponencial más allá de ese punto. El tiempo necesario para deshidratar el romero fue menor cuanto mayores fueron las potencias de microondas y la intensidad de vacío. La cinética de deshidratación de albahaca durante la deshidratación convectiva, fue descrita por un modelo exponencial de dos términos, mientras que la deshidratación con microondas a vacío consistió en un modelo de dos periodos: (i) lineal hasta un punto crítico y (ii) exponencial más allá de ese punto. La cinética de deshidratación de tomillo durante la deshidratación convectiva se describió con un modelo exponencial de dos términos, mientras la cinética de deshidratación con microondas a vacío consistió en un modelo de dos periodos: (i) lineal hasta un punto crítico y (ii) un periodo de caída a partir de ese punto. La cinética de deshidratación de la deshidratación convectiva y con microondas a vacío de los arilos y corteza de granada fue descrita mediante siete modelos básicos de deshidratación; sin embargo, la deshidratación final con microondas a vacío, se modeló tan solo con una ecuación exponencial de un término. La cinética de deshidratación durante la deshidratación convectiva de ajo fue descrita mediante un modelo exponencial de dos términos, mientras que la cinética de la deshidratación final de ajo con microondas a vacío fue descrita con una función exponencial de un término.

El consumo energético tanto de los arilos de granada como de la corteza se redujo cuando se incrementaron la temperatura del aire y la potencia de microondas. En cuanto a las láminas de ajo, la deshidratación con microondas a vacío, requirió menos energía que la deshidratación convectiva. El consumo energético de la deshidratación convectiva se puede reducir con la combinación con la deshidratación con microondas a vacío (pre-deshidratación convectiva seguida de una deshidratación final con microondas a vacío) y esta reducción fue más importante cuando la deshidratación final se aplicó antes, es decir a mayor contenido de humedad.

Los parámetros de calidad bajo estudio, incluyeron, los compuestos volátiles, los azúcares y ácidos orgánicos, el contenido en punicalaginas y ácido elágico, los compuestos fenólicos totales, la capacidad antioxidante total y la calidad organoléptica. En general, la deshidratación produjo una reducción de todos los parámetros estudiados; sin embargo el comportamiento de cada material vegetal fue diferente. La cantidad total de compuestos volátiles del romero fresco se redujo durante la deshidratación, independientemente del tratamiento. Se recomiendan condiciones suaves de deshidratación con microondas a vacío (nivel bajo de vacío y de potencia de microondas) para alcanzar las mayores concentraciones de compuestos volátiles y la mayor calidad organoléptica. La cantidad total de compuestos volátiles de albahaca se redujo de manera considerable tanto en la deshidratación convectiva como en la deshidratación con microondas a vacío. Los métodos combinados de deshidratación fueron la mejor opción para la deshidratación del a albahaca; el tiempo necesario fue relativamente corto, y la calidad aromática fue buena de acuerdo con los parámetros instrumentales y sensoriales. La cantidad total de compuestos volátiles de tomillo, se redujo en la mayoría de los tratamientos de deshidratación, excepto en aquellos tratamientos con una baja potencia durante la deshidratación con microondas a vacío. El método combinado fue la mejor opción para la deshidratación de tomillo, el tiempo necesario fue relativamente corto, y la calidad aromática fue buena de acuerdo con los parámetros instrumentales y sensoriales.

El contenido en compuestos fenólicos de las láminas de ajo no se mejoró con el uso del método combinado de deshidratación en comparación con la deshidratación convectiva. Sin embargo, un descenso de la humedad produjo un incremento de la capacidad antioxidante de las láminas de ajo. El ajo deshidratado, mostró una mayor capacidad antioxidante que el producto fresco. Los resultados sugirieron que los compuestos fenólicos y otros compuestos químicos, tales como la alicina, fueron los responsables de la elevada capacidad antioxidante de las láminas de ajo deshidratado. La deshidratación con microondas a vacío fue el mejor tratamiento de deshidratación para los arilos de granada mientras que la liofilización o bien condiciones suaves de deshidratación convectiva fueron los mejores tratamientos para la corteza de granada. Se necesita una investigación más profunda para la obtención de resultados óptimos con las técnicas combinadas de deshidratación. Con una selección adecuada del protocolo de deshidratación, arilos deshidratados de gran calidad estarán disponibles para los consumidores; dichos arilos se caracterizarán por un elevado contenido en fructosa, punicalaginas y compuestos fenólicos, gran capacidad antioxidante y elevadas intensidades de color granate, dulzor, acidez y aroma a granada fresca. Además, también estará disponible corteza deshidratada, como un ingrediente funcional, con elevado contenido de compuestos bioactivos y gran capacidad antioxidante.

En general, la tecnología óptima de deshidratación es diferente para cada tipo de material vegetal estudiado y deben ser recomendadas condiciones específicas tras la evaluación de los protocolos de deshidratación.

ESTRUCTURA DE LA TESIS

Para la realización de la presente Tesis Doctoral se ha seguido una metodología basada en la publicación de artículos de investigación. Con esta Tesis Doctoral se pretende obtener el título de Doctor con mención Europea, para ello en la redacción de la misma, se ha seguido la normativa vigente de la Universidad Miguel Hernández, concretamente el artículo 1.2 donde se indica: "*Que parte de la Tesis Doctoral, al menos el resumen y las conclusiones, se haya redactado y presentado en una de las lenguas oficiales de la Unión Europea, distinta a alguna de las lenguas oficiales en España*". En este caso el idioma seleccionado es el inglés; y este idioma será empleado tanto para la redacción como para la exposición de parte de la Tesis.

La estructura de esta Tesis Doctoral consta de una breve Introducción en la que se incluye una revisión bibliográfica sobre la deshidratación como tratamiento de conservación de alimentos y su aplicación en productos vegetales, así como las principales técnicas que se emplean para este tipo de alimentos. También se incluye una breve revisión sobre la teoría y los modelos matemáticos que describen la deshidratación de frutas, hortalizas y hierbas aromáticas. Además, también se describen los aspectos relacionados con el consumo energético que tiene lugar durante el proceso de deshidratación. Para finalizar este capítulo introductorio, se describen los cambios que producen las diferentes técnicas de deshidratación sobre los atributos de calidad (color, composición y sensorial) de los productos vegetales.

En los dos capítulos posteriores se describen los Objetivos planteados y los Materiales y Métodos empleados para poder entender los distintos tipos de deshidratación y determinaciones físico-químicas realizadas.

A continuación, se recogen las Publicaciones Científicas que componen el núcleo de la presente Tesis Doctoral.

- La primera de las publicaciones recoge los resultados obtenidos en la aplicación de una técnica asistida de deshidratación, como es la deshidratación con microondas a vacío, y su aplicación en el romero. Este artículo se publicó en la revista *Journal of Food Engineering* y en él se estudian los efectos de las condiciones de presión y potencia de microondas a vacío sobre la cinética de secado, la temperatura, el contenido en aceites esenciales y la calidad sensorial.

- Las dos siguientes publicaciones recogen los resultados obtenidos tras la aplicación en albahaca y tomillo de una técnica combinada de deshidratación, consistente en un pre-secado convectivo (a distintas temperaturas) seguido de un secado final con microondas a vacío (a diferentes potencias de microondas). Así mismo, en estas publicaciones se aplicaron las mismas técnicas y condiciones de deshidratación de manera individual y se compararon con el método combinado citado anteriormente mostrando los resultados relacionados con la cinética de secado, la temperatura, el contenido en aceites esenciales y la calidad sensorial. Estos resultados se publicaron en las revistas *Food Research International* (albahaca) y *Drying Technology* (tomillo).
- La cuarta de las publicaciones hace referencia a la aplicación de técnicas combinadas de deshidratación (pre-secado convectivo seguido de un secado final con microondas a vacío) en ajo. Las muestras se compararon con unas muestras de referencia que fueron liofilizadas. Se recogieron los resultados relacionados con la cinética de secado, la temperatura, el consumo energético, el color, la capacidad antioxidante y el contenido en fenoles totales. Dichos resultados se publicaron en la revista *Food and Bioprocess Technology*.
- La quinta y sexta publicaciones tratan sobre la deshidratación de la granada en su parte comestible (arilos) y en la parte con mayor contenido en compuestos bioactivos (corteza). Se aplicaron técnicas combinadas de deshidratación y se compararon con el producto fresco y liofilizado. Los resultados generados muestran los efectos sobre ácidos orgánicos, azúcares y compuestos bioactivos. También se recogen resultados sobre la capacidad antioxidante, los fenoles totales, temperatura, densidad del bulbo, cinética de secado, consumo energético y la calidad sensorial. Ambas estudios se publicaron en la revista *Food and Bioprocess Technology.*

En el quinto capítulo se corresponde con Resultados y Discusión; en ella se presenta un resumen global de los resultados más relevantes obtenidos en los diferentes estudios realizados y se hace una discusión general de los mismos.

Finalmente, en el capítulo sexto se recogen las Conclusiones generales de todos los estudios que forman parte de la presente Tesis Doctoral, mientras que el séptimo y último capítulo corresponde a la Bibliografía consultada.

Chapter 1.- Introduction

1. INTRODUCTION

1.1. Drying as a preservation method

1.1.1. Definition of drying

Drying commonly describes the process of thermally removing the moisture from wet material to yield a solid-dried product. Moisture held in loose chemical combination, present as a liquid solution within the solid or even trapped in the microstructure of the solid, which exerts a vapor pressure less than that of pure liquid is called *bound moisture*. Moisture in excess of bound moisture is called *unbound moisture*.

When a wet solid is subjected to thermal drying, three processes occur simultaneously:

1) Transfer of energy (mostly as heat) from the surrounding environment to the wet solid.
2) Evaporation of the surface moisture.
3) Transfer of internal moisture to the surface of the solid and its subsequent evaporation due to process 2.

Energy transfer as heat from the surrounding environment to the wet solid is necessary to facilitate the both processes 2 and 3. The rate at which drying is accomplished is governed by the rate at which these two processes proceed. Energy transfer as heat from the surrounding environment to the wet solid can occur as a result of convection, conduction, or radiation and in some cases as a result of a combination of these effects. Industrial dryers differ in type and design, depending on the principal method of heat transfer employed. Process 1, the removal of water as vapor from the material surface, depends on the external conditions of temperature, air humidity and flow, area of exposed surface, and pressure. Process 2, the movement of moisture internally within the solid, is a function of the physical nature of the solid, the temperature, and its moisture content. In a drying operation any one of these processes may be the limiting factor governing the drying rate, although they both proceed simultaneously throughout the drying cycle (Mujumdar, 2006).

1.1.2. Dehydration of fruits, vegetables and aromatic herbs

The first known record of drying involved vegetables and appeared in the 18th century (Van Arsdel & Copley, 1963). Drying is a process in which water is removed to slow down the growth of spoilage microorganism, as well as the occurrence of unwanted chemical reactions. The terms *dried* and *dehydrated* are not synonymous (USDA, 2013). The US Department of Agriculture lists dehydrated foods as those with no more than 2.5% of water (dry basis), while dried foods apply to any food product with a low percentage of water but higher than 2.5% (dry basis).

Fruits and vegetables have gained commercial importance and their growth on a commercial scale has converted them into an important sector of the agricultural industry. Recent developments in agricultural technology have substantially increased the world production of fruits and vegetables. Consequently large proportions of several important commodities are handled, transported, and marketed all over the world; concomitant losses are calling for suitable post-harvest techniques to improve storage and processing and extend shelf life. Production and consumption of processed fruits and vegetables are also increasing in the modern and fast society (Mujumdar, 2006).

Most fruits and vegetables contain more than 80% water and are therefore highly perishable. Water loss and decay account for most of their losses, which are estimated to be above 30–40% in the developing countries of the tropics and subtropics (Salunkhe & Desai, 1984); the main reasons behind these losses are inadequate handling, transportation, and storage facilities. Apart from physical and economic losses, serious losses do occur in the availability of essential nutrients, notably vitamins and minerals. The need to reduce post-harvest losses of perishable horticultural commodities is of paramount importance for developing countries; it is primordial to increase their availability, especially in the present context when the constraints on food production (land, water, and energy) are continually increasing. It is widely accepted that the production of more and better food alone will not be enough and should go together with suitable postharvest conservation techniques (Mujumdar, 2006).

One of the main aims of food processing or preservation is to transform perishable foods, such as fruits, vegetables and aromatic herbs into stabilized products that can be stored for extended periods of time. Processing extends the availability of seasonal commodities, retaining their nutritive and esthetic values. Besides, it adds convenience to the products. Now the markets of fruit and vegetable products and ready-to-serve convenience foods all over the world have been widely expanded. Several processing technologies have been used on an industrial scale to preserve fruits and vegetables; the most popular ones are canning, freezing, and dehydration. Among these, dehydration is especially suited for developing countries with poorly established low temperature, refrigeration and thermal processing facilities. It offers a highly efficient and practical means of preservation to reduce post-harvest losses and offset the shortages in supplies. Dehydration operations have been used for decades in food processing industries for efficient long-term preservation of final commercial products.

This Ph.D. dissertation was intended to provide a comprehensive evaluation of the various drying techniques (traditional and modern) and their combinations as well as equipment developed and applied over the years especially for the dehydration of aromatic herbs, fruits and vegetables. Besides, the current document tried to cover the effects of different dehydration techniques on drying kinetics, energy consumption, chemical-, nutritional-, functional- and sensory-properties of specifically three aromatic herbs (rosemary, thyme and sweet basil), a traditional vegetable used worldwide: garlic, and a fruit which is currently becoming very popular due to its attractive aspect related to health benefits: pomegranate.

Since ancient times, aromatic herbs and spices have been added to different types of foods to improve their flavor and organoleptic properties. Dried leaves are used in fried chicken, salads, baked products, condiments, perfumes and soaps. Besides, essential oils of spices could also be used as functional ingredients (Viuda-Martos et al., 2011). Numerous studies have documented the antioxidant, antimicrobial, antiviral, anti-inflammatory, anti-ulcerous, anti-carcinogenic properties of plant essential oils (Viuda-Martos et al., 2010; Bozin et al., 2007). The two basic forms of culinary herbs are fresh and dried. Fresh herbs cannot be supplied in a profitable way to all world-wide locations. The volatile composition of the essential oils of aromatic herbs has been widely studied in recent years (Figiel et al., 2010; Szumny et al., 2010; Klimánková et al., 2008; Díaz-Maroto et al., 2004). It is well-known that the presence of essential oils and their composition determine the specific aroma of plants and the flavor of condiments.

Rosemary (*Rosmarinus officinalis* L.) is an aromatic, evergreen, shrubby herb indigenous to most European countries bordering the Mediterranean regions.

Sweet basil (*Ocimun basilicum* L.) is a popular culinary herb originated in India, Africa and southern Asia and nowadays cultivated world-wide (Makri & Kintzios, 2007; Putievsky & Galambosi, 1999). Sweet basil is used extensively to add a distinctive aroma and flavor to food, such as salads, pizzas, meats and soups.

The thyme (*Thymus vulgaris* L.) plant is a perennial herbaceous shrub belonging to the family *Lamiaceae*. It is commonly grown wild throughout the Mediterranean region (Spain, France and Italy) and in almost every Caribbean country (Hill, 1952).

Garlic (*Allium sativum* L.) is a semi-perishable spicy herb, which has been used worldwide as seasoning, spice and herbal remedy (Ahmad, 1996). Garlic is known to possess a vast variety of biological functions, such as antimicrobial (Kim, 2002), anticancer (Patel et al., 2004), anticardiovascular disorders (Gorinstein et al., 2007) and antioxidant properties (Bozin et al., 2008; Nuutila et al., 2003). These properties are related with the chemical composition of garlic, and more specifically with its content of phenolic and sulfur-containing compounds (Bozin et al., 2008; Chung, 2006; Benkeblia, 2005; Benkeblia, 2004).

Finally, pomegranate (*Punica granatum* L.) is mainly cultivated in Iran, Afghanistan, India, Mediterranean countries and to some extent in USA, China, Japan and Russia (Raisi et al., 2008; Vardin & Fenercioglu, 2003). Spain is the greatest European producer (MARM, 2012) and its production is mainly located in the South-Eastern provinces, mainly Alicante (Andreu-Sevilla et al., 2008). The edible parts of pomegranates, arils, can be consumed fresh; however, the unattractive external appearance of a relatively high percentage (~20%) of fruits precludes their fresh consumption (Melgarejo & Salazar, 2003). Pomegranates are a well known source of many valuable substances, such as hydrolyzable tannins (punicalagins, punicalins) (Gil et al., 2000), condensed tannins (proanthocyanidins) (Poyrazoglu et al., 2002), anthocyanins (Hernández et al., 1999), phenolic acids (gallic acid, ellagic acid) (Mousavinejad et al., 2009), and organic acids (malic acid) (Poyrazoglu et al., 2002). All these compounds show high antioxidant activity (García-Alonso et al., 2004) and induce health benefits against cancer, cardiovascular and other diseases (Sun et al., 2002). Pomegranate peel (rind and carpelar membranes) is a richer source of antioxidants compared to edible arils (Li et al., 2006) and could be used as a nutraceutic supplement due to its elevated content of ellagitanins and ellagic acid (Espín et al., 2007), as well as functional ingredient for juices (Navarro et al., 2011). Thus, dried arils and peel are considered as proper by- and co-products, respectively.

1.2. Dehydration techniques in vegetal products.

Drying involves the application of high temperatures in order to vaporize and mobilize the moisture content within the vegetal product tissues. Thus, dehydration is a simultaneous combination of heat and mass transfer which needs energy to be applied.

Numerous dryers and dehydration techniques have been described as the most appropriate depending on the particular characteristics of each vegetal product. For this reason, in the following paragraphs, different dryers and dehydration methods are going to be described, mentioning in a special way those applied in the vegetal products described above and relevant in the current Ph.D. goal.

1.2.1. Convective hot air drying

Currently most of the dehydrated fruits and vegetables are produced by the technique of hot air drying, which is the simplest and less costly economical among the various methods. Different types of dryers have been designed, made, and commercially used based on this technique. In this method, heated air is brought into contact with the wet material to be dried to facilitate heat and mass transfer; convection is mainly involved. Two important aspects of mass transfer are: (i) the transfer of water to the surface of the material that is dried and (ii) the removal of water vapor from the surface.

To achieve high quality dehydrated products at a reasonable cost, dehydration must occur fairly rapidly. Four main factors affect the rate and total time of drying: (i) physical properties of the foodstuff, especially water diffusion coefficient, particle size and geometry; (ii) its geometrical arrangement in relation to air (cross-flow, through-flow, tray load, etc.); (iii) physical properties of air (temperature, humidity, velocity); and (iv) design characteristics of the drying equipment (cross-flow, through-flow, concurrent, countercurrent, agitated bed, pneumatic, etc.) (Holdsworth, 1971). The choice of the drying method for a food product is determined by targeted quality attributes, raw material and economy. The dryers generally used for the drying of fruits and vegetables are cabinet, kiln, tunnel, belt-trough, bin, pneumatic, and conveyor dryers. Among these, the cabinet, kiln, and bin dryers are batch operated, the belt-trough dryer is continuous and the tunnel dryer is semi-continuous.

This method, convective drying (CD), has several disadvantages and limitations. For instance, it has been clearly demonstrated that the high temperature used during the process involves the degradation of important flavor and nutritional compounds as well as the shrinkage takes place. These negative consequences are additionally intensified by the relatively long drying time.

This time can be drastically reduced substituting the hot air by the microwave energy, at least, in some steps of the dehydration process (Sharma and Prasad, 2004).

1.2.2. Microwave drying

Vega-Mercado et al. (2001) considered that the use of microwaves as the fourth generation drying technology. In general, drying with microwaves consists of 3 periods:

(i) Increasing of the heat in which microwave energy is transformed into thermal energy inside the wet material; thus increasing the temperature of the product with the time. Once the wet vapor pressure is over the atmospheric pressure, the material starts to loss the moisture content at a low rate.

(ii) Fast drying period, at which a stable temperature profile is established and the microwave energy is used for the moisture evaporation.

(iii)Reduced drying period, at which the local moisture is reduced until a level at which the required energy for the evaporation process is lower than the thermal energy supplied by the microwaves. This fact could cause an over-heating of the vegetal material (Zhang et al., 2006).

In general, microwave drying gathers the 4 most important requirements for food drying: operational speed, energetic efficiency, operational costs and quality of the dried product (Gunasekaran, 1999).

However, there are several limitations and disadvantages which take place during the microwave drying. Although the heating with microwave provides enough energy to generate the necessary heating in wet food products, one of its major inconvenients is the non-uniformity of the generated magnetic field. Taking into account that the success of the heating with microwaves in raw vegetables depends on the heating uniformity, this problem can be partially solved by the rotation of the device where the material is placed (Cohen and Yang, 1995).

According to Clark (1996) and Nijhuis et al. (1998), high temperatures of borders and corners of the food produce over-heating during the drying process which induces burning and consequently off flavors or non-desirable flavors.

1.2.3. Assisted and combined drying techniques.

As it was mentioned in the previous section, microwave drying has several disadvantages and limitations. In order to overcome these problems, different alternatives have been proposed: (i) the combination of microwave drying with a great variety of different drying methods and (ii) the application of microwave energy by beating instead of a continues heating which does not accelerate the water evaporation rate (Gunasekaran, 1999). In the following lines, several possible assisted and combination methods are described. Microwave drying assisted with hot air: hot air is an effective method for the production of dried fruits, vegetables and aromatic herbs (Min et al., 2005). The advantages and disadvantages of hot air drying were described previously. There are three possibilities about when these microwaves can be applied (Andrés et al., 2004).

- Application of the microwaves at the beginning of the drying process. In this option the internal part of the raw material is rapidly heated until the evaporation temperature is reached and the vapor is forced to go out of the external part of the surface, leading hot air to eliminate de vapor from the surface.
- Application of the microwaves when the drying rate starts to fall. In this moment, hot air drying is not able to remove the water from the internal parts of the material; therefore, the moisture content is concentrated in the middle of the product. The application of microwaves takes the moisture to the surface and it is eliminated into the surrounding environment.

  - Application of the microwaves when the drying rate is already falling or at very low moisture content. The application of microwaves in this point can be efficient in order to remove the bound water of the vegetal products. In general, a combination with the microwave energy reduces the shrinkage which takes place during the convective hot air drying.

- ✗ Microwave drying assisted with vacuum drying: drying with vacuum microwaves is a modern and efficient method for food preservation (Men'shutina et al., 2005). During the vacuum microwave drying, the energy of the microwaves is absorbed by the water molecules located in the whole volume of the material which is being dried. Low pressures induce faster water evaporation at low temperatures. This system is not yet very common in the food industries; however, there are a large number of scientific assays which have successfully used, such as methods in fruits, vegetables and aromatic herbs (Szumny et al., 2010; Figiel, 2009).
- ✗ Convective pre-drying with hot air followed by vacuum microwave finishing drying: a convective pre-drying with hot air and a final vacuum microwave drying could achieve a reduction in the total cost of the processing and improve the quality of the final product (Durance and Wang, 2002).

1.2.4. Freeze drying.

Freeze drying is currently a stable commercial process characterized by two steps: (i) the first step consists of freezing the water from the raw material, followed by (ii) a second step of heating to induce the sublimation of the water from the product. Sublimation of the ice can be achieved at the triple point of the water (**Figure 1**). Due to the fact that during this process the ice does not go through the liquid stage, the structure of the product is more stable. Besides, drying takes place without the exposure of the product to excessive temperatures and oxygen.

Freeze drying has numerous advantages:

I. Minimal shrinkage.
II. Minimal shift of soluble solids.

III. The porous structure leads to a better rehydration.

IV. High retention of volatile compounds.

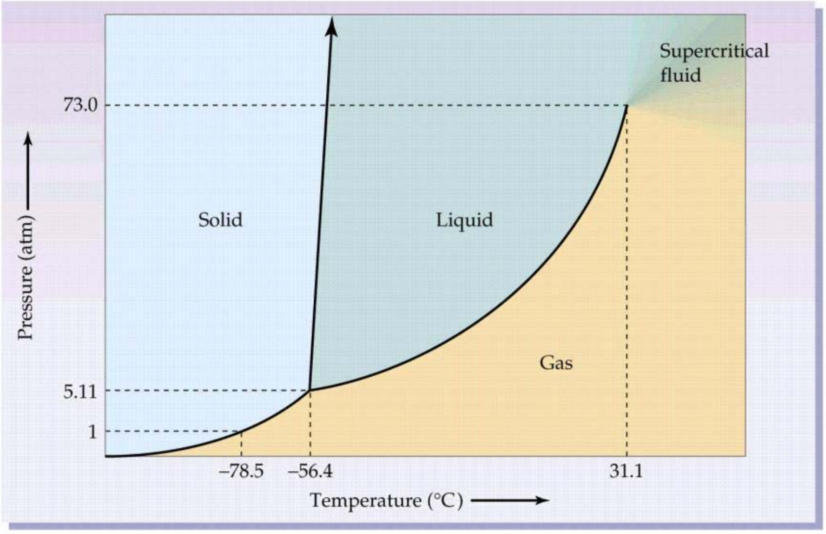

Figure 1: Diagram of the water phases.

Due to these advantages, it can be confirmed that freeze drying is the drying method leading to the best quality of the final product. However, its biggest limitation is the commercial application because of the total cost of both the facilities and processing. Industrial application of freeze drying includes a large number of foods with high price, such as exotic fruits, vegetables, soup ingredients, mushrooms and juices (Jayaraman & Das Gupta, 2006). Besides, there is a large number of scientific publications where freeze drying has been applied and used as control treatment (Wojdyło et al., 2009).

Finally, it is important to mention that there a large number of drying techniques; however, this section has been focused on those techniques currently employed in this Ph.D. dissertation. Apart from these techniques, solar, osmotic, ultrasounds and spray drying must be highlighted as some of the most studied in the last years.

1.3. The theory and mathematical modeling of food drying.

Drying is one of the most complex and least understood processes at the microscopic level, because of the difficulties and deficiencies in mathematical descriptions. It involves simultaneous, often coupled and multiphase, heat, mass, and momentum transfer phenomena (Yilbas et al., 2003). In addition, the drying of food materials is further complicated by the fact that both desirable and undesirable physical, chemical, and biochemical transformations may simultaneously occur during drying.

The underlying chemistry and physics of food drying are highly complicated; thus in practice, a dryer is considerably more complex than a device that merely removes moisture, and effective models are necessary for successful process design, optimization, energy integration, and full control.

Thin layer drying equations are important tools in mathematical modeling of drying. They are practical and provide give sufficiently good results. In order to use thin layer drying equations, the drying rate curves must be known. However, the considerable volume of work spent on elucidating a better understanding of moisture transport in solids is not covered in depth; in fact, drying rate curves have to be measured experimentally rather than calculated from fundamentals (Baker, 1997).

1.3.1. Mechanisms of drying.

The main mechanisms of drying are: (i) surface diffusion or liquid diffusion on the pore surfaces, (ii) liquid or vapor diffusion due to moisture concentration differences, and (iii) capillary action in granular and porous foods due to surface forces. In addition to these, thermal diffusion (defined as water flow caused by the vaporization–condensation sequence) and hydrodynamic flow (defined as water flow caused by the shrinkage and the pressure gradient), may also be seen in drying (Ozilgen & Ozdemir, 2001; Strumillo & Kudra, 1986). The dominant diffusion mechanism is a function of the moisture content and the structure of the food material and it determines the drying rate. The dominant mechanism can change during the process and, the determination of the dominant mechanism of drying is important in the modeling the process.

For hygroscopic products, generally the product dries at a constant rate and the subsequent falling rate period stops when equilibrium is established. In the constant rate period of drying, external conditions, such as temperature, drying air velocity, direction of air flow, relative humidity of the medium, physical form of product, the desirability of agitation, and the method of supporting the product during drying, are essential and the dominant diffusion mechanism is surface diffusion. Towards the end of the constant rate period, moisture has to be transported from the inside of the solid to the surface by capillary forces. The drying rate may still be constant until the moisture content has reached the critical moisture content and the surface film of the moisture has been reduced and some dry spots appear on the surface. Then, the first falling rate period or unsaturated surface drying begins. The drying rate falls even though the rate per unit wet solid surface area remains constant because the rate is calculated with respect to the overall solid surface area (Mujumdar & Menon, 1995). In this drying period, the dominant diffusion mechanism is liquid diffusion due to moisture concentration difference and internal conditions, such as moisture content, temperature, and structure of the product, are important.

1.3.2. Mathematical modeling of food drying.

Drying processes are modeled using two main models:

i. Distributed models, which consider simultaneous heat and mass transfer. They consider both the internal and external heat and mass transfers, and they are quite good in predicting the temperature and the moisture gradient in the product.
ii. Lumped parameter models, which do not consider the temperature gradient in the product and assume a uniform temperature distribution that equals the drying air temperature in the product.

The assumptions resembling the uniform temperature distribution and temperature equivalent of the ambient air and product are sources of error. This error occurs only at the beginning of the process and it may be reduced to acceptable levels by reducing the thickness of the product (Henderson and Pabis, 1961). With this need, thin layer drying gains importance and thin layer equations are derived.

1.3.3. Thin layer drying equations.

Thin layer drying generally implies drying as one layer of sample particles or slices (Akpinar, 2006). Because of its thin structure, the temperature distribution can be easily assumed as uniform and thin layer drying is very suitable for lumped parameter models.

Thin layer equations may be theoretical, semi-theoretical, and empirical models. Theoretical models explain the drying behavior of the product clearly and can be used at all process conditions, but they include many assumptions causing considerable errors. Semi-theoretical models are easier and need fewer assumptions due to the fact that they use some experimental data. On the other hand, they are valid only within the conditions applied in this particular process (Parry, 1985; Fortes & Okos, 1981). The empirical models have also similar characteristics to those of the semi-theoretical models. They strongly depend on the experimental conditions and give limited information about the drying behaviors of the product (Keey, 1972)

1.3.3.1. Theoretical background.

Isothermal conditions changing only with time may be assumed to prevail within the product, because the heat transfer rate within the product is two orders of magnitude greater than the rate of moisture transfer (Ozilgen & Ozdemir, 2001). The following statements must be assumed in theoretical models:

i. The particle is homogenous and isotropic.
ii. The material characteristics are constant, and shrinkage is neglected.
iii. Pressure variations are neglected.
iv. Evaporation occurs only at the surface.
v. Initially moisture distribution is uniform and symmetrical during process.
vi. When the surface diffusion is ended, the moisture equilibrium arises on the surface.
vii. Temperature distribution is uniform and equals to the ambient drying air temperature, namely the lumped system.
viii. The heat transfer is done by conduction within the product and by convection outside of the product.

ix. Effective moisture diffusivity versus moisture content is constant during drying.

MR (moisture ratio) can be determined according to the external conditions. If the relative humidity of the drying air is constant during the drying process, then the moisture equilibrium is constant too. In this respect, *MR* is determined using Eq. 1. If the relative humidity of the drying air continuously fluctuates, then the moisture equilibrium continuously varies and *MR* is determined using Eq.2 (Diamante & Munro, 1993);

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} \qquad (1)$$

$$MR = \frac{M_t}{M_i} \qquad (2)$$

where, M_i is the initial moisture content, M_t is the mean moisture content at time *t*, M_e is the equilibrium moisture content, and all these values are considered in dry basis.

1.3.3.2. Semi-theoretical models.

Semi–theoretical models can be classified according to their derivation as:

(i) Newton's law of cooling: These are semi–theoretical models derived by analogy with Newton's law of cooling. These models can be classified in sub groups as: (a) Lewis model and (b) Page model & modified forms.

(ii) Fick's second law of diffusion: The models in this group are semi–theoretical models derived from the Fick's second law of diffusion. These models can be classified in subgroups as: (a) single term exponential model and modified forms, (b) two term exponential model and modified forms and (c) three term exponential model.

MODELS DERIVED FROM NEWTON'S LAW OF COOLING

(a) *Lewis (Newton) Model*: This model is analogous to the Newton's law of cooling; thus, many investigators named this model as Newton's model. First, Lewis (1921) suggested that during the drying of porous hygroscopic materials, the change of moisture content of material in the falling rate period is proportional to the instantaneous difference between the moisture content and the expected moisture content when it comes into equilibrium with drying air. Accordingly it is assumed that the material is thin enough, or the air velocity is high, and the drying air conditions such as the temperature and the relative humidity are kept constant.

$$\frac{dM}{dt} = -K\,(M - M_e) \qquad (3)$$

where, *K* is the drying constant (s^{-1}). In the thin layer drying concept, the drying constant is the combination of drying transport properties, such as moisture diffusivity, thermal conductivity, interface heat, and mass coefficients (Marinos-Kouris & Maroulis, 1995). If *K* is independent from *M*, then Eq. 3 can be rewritten as:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = exp\,(-kt) \qquad (4)$$

(b) *Page Model:* Page (1949) modified the Lewis model to get a more accurate model by adding a dimensionless empirical constant *(n)* and applied to the mathematical modeling of shelled corn drying. Generally, *n* is named as the model constant (dimensionless).

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = exp\,(-kt^n) \qquad (5)$$

(c) *Modified Page Models*: Overhults et al. (1973) modified the Page model to describe the drying of soybeans. This modified form is generally known as the Modified Page-I Model:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = exp\,(-kt)^n \qquad (6)$$

In addition, White et al. (1978) used another modified form of the Page model to describe the drying of soybeans. This form is generally known as the Modified Page-II Model:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = exp\;-(kt)^n \qquad (7)$$

Diamente and Munro (1993) used another modified form of the Page model to describe the drying of sweet potato slices. This form is generally known as the Modified Page equation-II Model, where *l* is an empirical constant (dimensionless) which is related with the thickness of the potato slices.

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = exp\ -k(t/l^2)^n \qquad (8)$$

MODELS DERIVED FROM FICKS'S SECOND LAW OF DIFFUSION

(a) *Henderson and Pabis (Single term) Model*: Henderson and Pabis (1961) improved a model for drying by using Fick's second law of diffusion and applied the new model on drying of corns.

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = A_1 exp\,(-\frac{\pi^2 D_{eff}}{A_2}\ t) \qquad (9)$$

If D_{eff} (effective diffusivity coefficient) is constant during drying, then Eq. 9 can be rearranged by using the drying constant *k* as:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\ exp\ (-k\ t) \qquad (10)$$

where, *a* is defined as the indication of shape and generally named as model constant (dimensionless). These constants are obtained from experimental data. Equation 10 is generally known as the Henderson and Pabis Model.

(b) *Logarithmic (Asymptotic) Model:* Chandra and Singh (1995) proposed a new model including the logarithmic form of Henderson and Pabis model with an empirical term addition, and Yagcioglu et al. (1999) applied this model to the drying of laurel leaves, where *c* is an empirical constant (dimensionless).

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\ exp\ (-k\ t) + c \qquad (11)$$

(c) *Two terms Model*: Henderson (1974) proposed to use the first two term of the general series solution of Fick's second law of diffusion for correcting the shortcomings of the Henderson and Pabis Model. Then, Glenn (1978) used the resulting model in grain drying. With this argument, the new model was:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\ exp\ (-k\ t) + b\ \exp\ (-k_2 t) \qquad (12)$$

where, a, b are linked with the product shape and are generally named as model constants (dimensionless), and k_1, k_2 are the drying constants (s^{-1}). These constants are obtained from experimental data; Eq. 12 is generally known as the Two–Term Model.

(d) *Two term Exponential Model*: Sharaf–Eldeen et al. (1980) modified the Two–Term model by reducing the constant number and organizing the second exponential term's indication of shape constant.

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\,exp\,(-k\,t) + (1-a)\,exp\,(-kat) \qquad (13)$$

(e) *Modified Two-Term exponential Model*: Verma et al. (1985) modified the second exponential term of the Two–Term Exponential model by adding an empirical constant and applied it in the drying of rice.

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\,exp\,(-k\,t) + (1-a)\,exp\,(-gt) \qquad (14)$$

This modified model (Eq. 14) is known as the Verma Model. Kaseem (1998) rearranged the Verma model by separating the drying constant term k from g and proposed the transformed model as:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\,exp\,(-k\,t) + (1-a)\,exp\,(-kbt) \qquad (15)$$

This modified form (Eq. 15) is known as the Diffusion Approach model. These two modified models were applied in simultaneous drying of some products, and gave good results (Demir et al., 2007; Akpinar, 2006; Gunhan et al., 2005)

(f) *Modified Henderson and Pabis (Three Term Exponential) Model:* Karathanos (1999) improved the Henderson and Pabis and Two–Term models by adding the third term of the general series solution of Fick's second law of diffusion for correcting the shortcomings of the Henderson and Pabis and Two–Term models. Karathanos emphasized that the first term explains the latest part, the second term explains the intermediate part, and the third term explains the beginning part of the drying curve (*MR-t*) as:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)} = a\,exp\,(-k\,t) + b\,exp(-gt) + \;c\;\,exp(-ht) \quad (16)$$

where, *a*, *b*, and *c* are defined as the indication of shape and generally named as model constants (dimensionless), and *k*, *g*, and *h* are the drying constants (s^{-1}). These constants are obtained from experimental data; Eq. 16 is generally known as the Modified Henderson and Pabis model.

EMPIRICAL MODELS

(a) *Thompson Model*: Thompson et al. (1968) developed a model with the experimental results of drying shelled corn within the temperature range 60–150ºC.

$$t = a\,ln\,(MR) + \;\; b\,[\ln(MR)]^2 \qquad (17)$$

where, *a* and *b* were dimensionless constants obtained from experimental data. This model was also used to describe the drying characteristics of sorghum (Paulsen and Thompson, 1973).

(b) Wang and Singh (1978) created a model for intermittent drying of rice.

$$MR = 1 + b * t + a * t^2 \qquad (18)$$

where, *b** (s^{-1}) and a* (s^{-2}) were constants obtained from experimental data.

(c) Kaleemullah (2002) created an empirical model that included moisture ratio (*MR*), temperature (*T*), and time (*t*). They applied it to the drying of red chillies (Kaleemullah & Kailappan, 2006).

$$MR = \exp - c * T + b * t^{(pT+n)} \qquad (19)$$

where, constant *c*□ is in ○$C^{-1}s^{-1}$, constant *b*□ is in s^{-1}, *p* is in $°C^{-1}$ and *n* is dimensionless.

1.3.4. Determination of appropriate model.

Mathematical modeling of the drying of food products often requires statistical methods of regression and correlation analysis. Linear and nonlinear regression analyses are important tools to find the relationship among different variables, especially, for those in which no established empirical relationships exist. As mentioned above, thin layer drying equations require *MR* variation *versus t.* Therefore, after *MR* data was plotted against *t*, regression analysis was performed with the selected models to determine the constant values that supply the best appropriateness of models. The validation of models can be checked with different statistical methods. The most widely used method in literature is performing correlation analysis; root mean square error (RMSE) analysis and the correlation coefficient (R^2) are the primary criterion for selecting the best equation to describe the drying curve equation and the highest R^2 value is required (Wang et al., 2007a; Akpinar et al., 2003a; Yaldiz et al., 2001; Kassem, 1998; Verma et al., 1985). In addition to R^2, RMSE is used to determine the best fit. The highest R^2 and the lowest RMSE values required to evaluate the goodness of fit (Wang et al., 2007b; Ertekin & Yaldiz, 2004; Akpinar et al., 2003b). R^2 and RMSE calculations can be done by equations below:

$$R^2 = \frac{\left[\sum_{i=1}^{N}(MR_{\exp_i} - \overline{MR_{\exp}}) \cdot (MR_{pre_i} - \overline{MR_{pre}})\right]^2}{\sum_{i=1}^{N}\left(MR_{\exp_i} - \overline{MR_{\exp}}\right)^2 \cdot \sum_{i=1}^{N}\left(MR_{pre_i} - \overline{MR_{pre}}\right)^2} \qquad (20)$$

$$RMSE = \sqrt{\frac{1}{N} \cdot \sum_{i=1}^{N}(MR_{\exp_i} - MR_{pre_i})^2} \qquad (21)$$

where, N is the number of observations, $MR_{pre,i}$ is the predicted moisture ratio values, $MR_{exp,i}$ is the experimental moisture ratio values.

1.4. Energy aspects in food dehydration

Thermal drying has long been recognized as one of the most energy-intensive operations in solids-liquid separation. Drying energy represents as much as 10–25% of the total energy consumption in the industry; although in some industrial sectors the percentage of drying energy is much higher, reaching 35% in paper production and even 50% in textile fabrics (Mujumdar, 2007; Kudra, 2004). It is difficult to estimate drying energy use in the agrifood sector because of the diversity of food products, multiplicity of food producers, and frequent use of process coproducts as supplementary fuel. Nevertheless, 12% was quoted for England and 27% for France in the 1990s and 2000s (Strumillo et al., 2007). At present, higher numbers can be anticipated because the percentage of drying energy is progressively increasing (Baker & McKenzie, 2005).

Because almost 99% of applications involve removal of water (Mujumdar, 2007), such high energy consumption is primarily linked to the latent heat of water vaporization, which is 2500 kJ kg^{-1} at 0°C. Convective hot air drying is still the most popular method applied to reduce the moisture content of fruits and vegetables; however, this method has several disadvantages and limitations. For instance, it has been demonstrated that the high temperature used during the process involves the degradation of important flavour compounds and nutritional ingredients, as well as negative colour alteration. Regarding energy consumption, much longer times are required when compared with more modern and efficient drying techniques. Besides, inefficient convective dryers, which account for about 85% of all industrial dryers (Mujumdar, 2007), are the second contributor to the high energy demands for convective hot air drying.

Several authors have reported their energy balances during drying of different materials, such as carrots (Nazghelichi et al., 2010) and mushrooms (Motevalli et al., 2011a). For instance, Kowalski & Mierzwa (2011) studied the drying of red bell pepper using convective, microwave and infrared heat sources applied separately and in different combinations; the objective of this study was to find the most convenient drying conditions (product of the best quality and minimum energy consumption). Motevalli et al. (2011b) evaluated the energy consumed during drying of pomegranate arils by different drying systems, including hot-air convection, use of microwave pretreatment with convection drying, microwave drying, vacuum drying and infrared drying.

An interesting option is the application of microwave energy to dried material; with this option the drying time and energy consumption can be greatly reduced (Sharma & Prasad, 2004) while the quality of the final products insured (Men'shutina et al., 2005). Besides, drying with the microwave method under vacuum is a modern and efficient method of food preservation (Durance & Wang, 2002). Lowered pressures induce faster evaporation of water from the material at relativity low temperature (Figiel et al., 2010); however, at the beginning of vacuum-microwave dehydration, the intensive water evaporation from the plant material may exceed the capacity of the vacuum pump. Therefore, a reduction in the amount of raw material being dried or the application of a large vacuum installation is needed. This problem can be overcome by pre-drying the material using convective hot air drying. As a result of pre-drying the mass loads of a vacuum-microwave equipment can be drastically decreased (Hu et al., 2006). Pre-drying of plant materials by convective method before vacuum-microwave finishing drying may reduce the total cost of dehydration and improve the quality of the commercial dehydrated product with a significant contribution to the fruit processing industry (Hu et al., 2006).

Another interesting option for drying certain fruits is osmotic dehydration prior to thermal drying because such a hybrid technology not only reduces energy consumption but also offers a product of enhanced quality (Grabowski et al., 2002).

These two extreme examples clearly indicate that energy consumption is an important issue in the drying of an increasing number of foods; this statement is even true for materials that contain significant amounts of easily removable water and that are dried in relatively efficient dryers. The attempts to improve energy efficiency start with an energy audit for a dryer in use, followed by a detailed analysis of the existing literature and technical information to identify different options to reduce energy consumption. However, the reported data should be considered with caution: inconsistent terminology and not fully appropriate calculation methods are found that, although starting with apparently identical indices, can lead to drastically different results (Kudra, 2004).

1.4.1. Energy consumption

Energy consumed (kJ) during drying must be calculated according to the power consumption (kW) of the heaters in convective dryers, the output power of magnetrons of microwave dryers, the power consumption of vacuum pumps or the power consumption of electric engines rotating the container in the case of vacuum–microwave or freeze dryers. The efficiency (ŋ) must be considered for each device as well as the drying time (*t*) in each specific drying method or technique.

1.4.2. Specific energy consumption

The specific energy consumptions can be determined as the ratio of energy consumption to the initial mass of the sample (*m*) or as the ratio of energy consumption to the mass of water (*W*) removed from the sample during drying. The following equations (22 & 23) can be used:

$$E = \frac{E}{m} \qquad \text{(kJ kg}^{-1}\text{ fresh weight)} \qquad (22)$$

$$E = \frac{E}{W} \qquad \text{(kJ kg}^{-1}\text{ water)} \qquad (23)$$

The presentation of specific energy consumption profile in kJ kg^{-1} fresh weight is more convenient from the practical point of view. However, presenting the final specific energy consumption in kJ kg^{-1} water gives the possibility to compare the obtained results with those reported by other authors dealing with drying of different materials. Usually, the increase in drying temperature decreases the energy consumption while drying plant materials (Motevalli et al., 2011b).

1.4.3. Energy efficiency

The energy efficiencies must be determined as the ratio of energy necessary for evaporation of water from the sample (E_{ev}) to the energy consumed while drying using the different drying methods (24).

$$\eta = \frac{E_{ev}}{E} \times 100 \qquad (24)$$

The value of E_{ev} was determined from the following equation (25) as a product of the mass of water evaporated from the sample (W) and the latent heat of vaporisation of water λ_w (kJ kg^{-1}).

$$E_{ev} = W \times \lambda_w \qquad (25)$$

The latent heat of vaporisation of water (λ_w) must be taken as the mean value of λ_w calculated for the temperature range occurring while drying. The energy efficiency is the most frequently quoted index in technical specifications (Kudra, 2004); therefore this index enables comparison of drying effectiveness for different methods and various raw materials.

1.5. Changes in the main quality attributes during food dehydration

Generally, all quality parameters of fruits and vegetables are affected by dehydration. However, the behavior of the different parameters is specific of the drying method and its conditions. The quality of dehydrated fruits is a key feature in developing innovative drying technologies (development of novel drying techniques and optimization of the process unit operations) (Mujumdar & Huang, 2007). It is also a key feature in determining the suitability of a dryer for a specific fruit, because the changes of the physical properties of fruits are specific drying technique. Currently, degradation of the dehydrated fruit due to the application of drying is a major concern. The selected drying technology must be able to minimize the changes of physical, chemical, functional and sensory properties of fruits in order to increase the dried product marketability.

The next sections of this Introduction section will deal with the description of the main quality attributes of fruits and vegetables and the effects of the different drying methods and conditions on them, especially those techniques used in the current Ph.D. dissertation.

1.5.1. Color changes during fruits and vegetables dehydration

Color is an important physical property of dehydrated fruits. It is important to visually assess the dehydrated fruit because the first judgment made by consumers on a food quality is by its physical appearance and color. Abnormal color will cause the product to be rejected by the consumers (Ávila & Silva, 1999; Lopez et al., 1997). Changes of color after dehydration are linked with the occurrence of high amounts of reducing sugars, such as glucose, sucrose, and fructose. These reducing sugars might undergo Maillard reaction through the interaction with amino-compounds during drying (Cornwell & Wrolstad, 1981). It has been reported that the Maillard reaction occurs after exposing the foods to air at high temperatures and during long drying times (Chou et al., 2000). In addition, the enzymatic reaction changes the characteristic color of the dehydrated fruits to brown or darker colors due to the oxidation of phenols to *o*-quinones (brown pigment or melanins) (Beveridge & Harrison, 1984). This color change forces food producers to add colorings to enhance their product’s appearance (Waliszewski et al., 1999). Color is also a sensory parameter widely used to guarantee high consumer acceptance of dehydrated fruit. Some of the dehydrated fruits are extremely hard, burnt, with off-flavor and tasteless due to improper drying. For instance, continuous drying with hot air and/or high temperature causes important quality degradation, such as unnatural color, wrinkled appearance, hard texture, and bitter and burnt flavors (Vadivambal & Jayas, 2007; Nijhuis et al., 1998). The appearance of mushrooms, garlic and beetroot changed to dark brown color after drying at high temperature due to browning reactions (Figiel, 2010; Figiel, 2009; Giri and Prasad, 2008).

Enzymatic browning, pigment degradation, oxidation of ascorbic acid and Maillard reactions are dependent on several factors, such as temperature, reactants concentration, pH, water activity and specific ion concentrations (Beveridge et al., 1986). According to Dills (1993), the drying time and drying duration are the major factors contributing to browning reactions and the change of the foods physical appearance. In this regard, different authors have described the effects of different drying techniques on the physical appearance of dehydrated fruits.

The scientific literature shows that vacuum-microwave drying, freeze drying or assisted techniques such as convective pre-drying followed by vacuum-microwave finish drying provide brighter samples than those dried by convective hot air drying (Figiel, 2010; Figiel, 2009; Giri & Prasad, 2008; Sharma & Prasad, 2004).

1.5.2. Changes in the bioactivity composition and antioxidant capacity as a result of dehydration of fruits and vegetables.

Nowadays consumers are health conscious and seek for healthy natural foodstuffs to have a nutritious diet; this current trend in food consumption leads to a significant increase in dietary intake of fruits.

Fresh fruit contains vitamins, phenolic compounds (anthocyanins, phenolic acids, flavonoids), carotenoids, organic acids, minerals and water, among other ingredients. Some of these compounds show high antioxidant activity (García-Alonso et al., 2004) and induce health benefits against cancer, cardiovascular and other diseases (Sun et al., 2002). A large number of studies have shown that the presence of phenolic compounds in food and especially in fruit, vegetables and aromatic herbs can be particularly important for consumers, because of their beneficial health effects. Besides antioxidant effects, phenolic compounds possess a wide spectrum of biochemical properties and can also have a beneficial effect in preventing the development of illnesses such as cancer and cardiovascular diseases (Lattanzio et al. 2003). The effects of the drying process on the phenolic substances of foods have been widely studied. Some authors have reported that phenolics decrease (Wojdylo et al., 2009; Zanoelo et al., 2006) after drying; for instance, Wojdylo et al. (2009) suggested that this decrease is mainly due to oxidation and thermal degradation reactions. On the other hand, other authors did not find any significant effect on the contents of these compounds (Dewanto et al., 2002). Thus, drying conditions play an important role in determining the quality of the final product, especially in terms of its antioxidant activity, color and pro-healthy properties. Therefore, it is very important to choose the optimal drying method for fruits and the best conditions for each of the steps involved in the drying protocol.

In general, the levels of the phenolic compounds found in dried fruits have been positively correlated to the antioxidant capacity; this relationship indicated that the decrease in the antioxidant activity resulted from the degradation of phenolic compounds at high temperatures, due to chemical, enzymatic and/or thermal decomposition (Nicoli et al., 1999). However, in some cases there is a lack of correlation between the phenolic content and antioxidant capacity. The antioxidant capacity in several intermediate stages of drying is significantly higher than at the beginning of the drying process, as previously reported by Manzocco et al. (2000). This behavior could be the result of two different factors:

(i) some phenolic compounds have greater antioxidant capacity in some intermediate oxidation stages (Manzocco et al., 2000), and

(ii) thermal processing may induce the formation of new compounds with high antioxidant capacity (Manzocco et al., 2000); these compounds could be those formed by the Maillard reaction (Wojdylo et al., 2009; Manzocco et al., 2000).

For instance, Li et al. (2007) reported an increase in allicin during the thermal processing of garlic powder. Allicin and its derived products have been described as potent natural antioxidants (Yong, 2006; Youji et al., 2006). Similar results were reported in white grapes (Kuskoski et al., 2005), where no correlation was found between phenolic compounds and antioxidant capacity; these results were attributed to the absence of anthocyanins in this kind of raisins.

1.5.3. Changes in the volatile compounds or essential oils during dehydration of aromatic herbs

The two basic forms of consuming culinary herbs are fresh and dried. Fresh herbs cannot be supplied in a profitable way to all world-wide locations. The essential oil flavor composition of aromatic herbs has been the subject of considerable research in recent years. It is well-known that the presence of essential oils and their composition determine the specific aroma of plants and the flavor of the resulting condiments. Thus, this section deals only with aromatic herbs as a richer source of volatile compounds than fruits and vegetables.

The main chemical families present in aromatic herbs are: *monoterpenes, monoterpenoids* and *phenylpropanoids*. In lower amount *alcohols, sesquiterpenes, sesquiterpenoids, aldehydes* and *esters* are also found. The composition and concentrations of essential oils from aromatic herbs depend on many factors, including climatic and soil conditions, stage of vegetative cycle, seasonal variation, etc. (Tomaino et al., 2005). Another fact that should be considered when studying the volatile composition of aromatic herbs is whether samples are a mixture of leaves, branches and stems or only leaves and flowers. For instance, Klimánková et al. (2008) reported that the total concentration of essential oils in leaves was more than 20 times higher than those of stems and branches of sweet basil.

In general, the drying process leads to significant losses of volatile compounds (Díaz-Maroto et al., 2004). Among the drying treatments, some authors have reported higher losses of volatiles in convective hot air drying and microwave drying as the air temperature (Díaz-Maroto et al., 2004) and the wattage (Rao et al., 1998) increased. However, these statements were not observed in Hungarian thyme; in this particular case as the air temperature increased, the losses decreased; this behavior was attributed to the longer processing at lower temperatures compared with the shorter times required for higher temperatures (Sárosi et al., 2013).

Some authors have considered an initial hypothesis regarding the improvement produced by the microwave drying compared with traditional convective hot air dying. This improvement was reported by many authors (Figiel et al., 2010; Díaz-Maroto et al., 2004; Rao et al., 1998) in oregano and basil dried; however, Szumny et al. (2010) reported that rosemary samples dried by convective drying showed higher yield of essential oils. All these authors agree in the fact that the essential oil yield varies considerably from one species to another. The important losses of volatile compounds might be diminished by using assisted and combined drying techniques. For instance, Figiel (2010) suggested that microwave drying assisted by vacuum increased the yield of essential oils in garlic. Besides, a convective pre-drying followed by microwave finishing drying increased the content of essential oils in samples of oregano (Figiel et al., 2010) and rosemary (Szumny et al., 2010). As a consequence, assisted techniques as vacuum-microwave drying and the combined techniques, such as convective pre-drying followed by vacuum-microwave finishing drying seem to be very promising options to dry aromatic herbs.

1.5.4. Sensory properties of dried fruits and vegetables

Descriptive sensory analysis (DSA) is used to quantitatively determine the intensities of the main sensory properties and attributes of food. Such analysis requires the use of a trained panel. The proper number of panelists ranges between 7 and 12 of highly trained panelists (Meilgaard et al., 1999; AENOR, 1997). DSA has been previously applied in the description of the main attributes of fruits, vegetables, but especially in aromatic herbs such as: sweet basil, parsley, bay leaf and spearmint (Díaz-Maroto et al., 2004), and rosemary (Díaz-Maroto et al., 2007). In general dried samples of aromatic herbs have been typified by significant increases in the intensities of attributes such as spicy, hay-like, sweet, earthy, woody, and infusion. At the same time, an increase in the temperature led to decreases of some attributes such as fresh, floral and herbaceous.

Regarding DSA of dried fruits, some of the most affected attributes were sweeteness, bitterness, adhesiveness and caramel flavor (Pallas et al., 2013). All these attributes are increased when the drying temperature also increased.

Product quality, consequently sensory properties, of dehydrated fruits is a key feature in innovation of future drying technology, which is closely related to: (i) development of novel drying techniques and (ii) process optimisation (Mujumdar & Huang, 2007). Sensory evaluation will be a perfect tool to determine whether the effects of a particular drying technique will lead to high quality products, with elevated guarantee of being accepted by consumers.

Chapter 2.- Objectives

2. OBJECTIVES

2.1. General aim

The main aim of this Ph.D. thesis is to determine the influence of traditional (convective drying and freeze drying), modern (microwave drying), assisted (vacuum-microwave drying) and combined (convective pre-drying followed by vacuum-microwave drying) drying technique on the main quality parameters of aromatic herbs, fruits and vegetables.

To reach this main aim, several specific objectives have been considered and will be described in the section 2.2.

2.2. Specific objectives

- ✗ Optimization of the microwave power and vacuum level during microwave and vacuum-microwave drying of rosemary. To reach this objective the following parameters were studied: drying kinetics, composition of volatile compounds and sensory assessment.
- ✗ Evaluation of the influence of drying parameters during convective and vacuum-microwave and their combination on drying kinetics, temperature, volatile compounds and sensory quality of basil and thyme.
- ✗ Determine the best conditions of convective pre-drying followed by vacuum-microwave finishing drying of garlic slices. The optimization was based on minimizing energy consumption and maximizing the antioxidant capacity of the product.
- ✗ Determine the influence of different drying methods (convective, vacuum-microwave, convective pre-drying followed by vacuum-microwave and freeze drying) on chemical composition, antioxidant capacity and sensory quality of dried pomegranate arils and rind.
- ✗ Evaluation of the influence of drying parameters during convective, vacuum-microwave and convective pre-drying followed by vacuum-microwave on drying kinetics and energy profile of pomegranate arils and rind.

Chapter 3.- Material and Methods

3. MATERIALS AND METHODS

In this section, a summary of the plant materials, drying techniques and conditions, analytical and mathematical determinations as well as the sensory evaluation is included.

3.1. Plant material

Fresh rosemary (*Rosmarinus officinalis* L.), basil (*Ocimum basilicum* L.) and thyme (*Thymus vulgaris* L.) plants were bought from a greenhouse “Swedeponic” in Kraśnicza Wola (Poland). Fresh garlic (*Allium sativum* L.) bulbs were purchased from a local market in Wrocław (Poland); however, they came from a different Polish city, Krakow. Finally, Fresh pomegranate fruits (*Punica granatum* L. cv. Mollar de Elche) were picked on the 30th of October 2010 in a commercial orchard in Elche (Alicante, Spain).

3.2. Drying procedure

a) Convective drying (CD) was conducted using drying equipment designed and built up in the Institute of Agricultural Engineering (Wrocław University of Environmental and Life Sciences). Convective method was operated at different temperatures with an air velocity of 0.8 m s^{-1}.

b) Vacuum microwave drying (VMD) was carried out in Plazmatronika SM 200 dryer (Wrocław, Poland) connected to a vacuum system consisting of a vacuum pump BL 30P (“Tepro”, Koszalin, Poland), a vacuum gauge MP 211 (“Elvac”, Bobolice, Poland), and a compensation reservoir of 0.15 m^3. The dryer was operated at different power and vacuum levels. Samples were placed in a cylindrical container of organic glass with a volume of 6.8 L. To avoid local over-heating, the container rotated at a speed of 6 rpm, and additionally an electric fan was installed at the bottom of the dryer producing an air stream of 22 °C at a velocity of 1 m s^{-1}.

c) Combined drying (CPD-VMFD) consisted of convective pre-drying (CPD) at different temperatures and times, followed by VM finish-drying (VMFD) with different microwave wattages.

d) Freeze drying (FD) was carried out in freeze drier OE–950 (Hungary) for 48 h at the pressure reduced of 65 Pa. The temperature in the drying chamber was –60 °C, while the heating plate reached 30 °C.

3.3. Drying kinetics

The drying kinetics was calculated using equations 1 and 2.

3.4. Determination of moisture content

The vacuum oven method was used to determine the moisture content (*M*) of the fresh and processed samples. Samples were dried in vacuum dryer (SPT–200, ZEAMiL Horyzont, Krakow, Poland) for 24 h. The operating temperature was 70 ºC. Moisture content was expressed in g of water per g of dry matter.

3.5. Energy consumption calculation

3.5.1. Energy consumption in convective method

Energy E_C consumed during CD (kJ) was calculated according to equation (26):

$$E_C = \left(\frac{N_f}{6} + N_h\right) \times t \qquad (26)$$

where N_f (kW) is power consumption by a fan blowing air to six pipes equipped with electric heaters of power consumption N_h (kW) and *t* is time of drying (s).

3.5.2. Energy consumption in vacuum-microwave method

Energy E_{VM} consumed during VMD (kJ) was calculated according to equation (27):

$$E_{VM} = \left(\frac{N_M}{\eta_M} + N_V + N_e\right) \times t \qquad (27)$$

where N_M and η_M are output power (kW) and efficiency of magnetrons respectively, (N_V) is power consumption (kW) by vacuum pump and (N_e) is power consumption (kW) by electric engine rotating the container.

3.5.3. Determination of specific energy consumption

The specific energy consumption (E') was calculated from the universal equation (28), which can be applied for both convective drying ($E'=E'_C$) as well as for combined drying consisted of CPD and VMFD ($E'=E'_{C\text{-}VM}$). This equation is the ratio of the sum of energy E_C and E_{VM} to the total mass of water removed from the fresh sample during drying by convective method (m_C) and VM method (m_{VM}):

$$E' = \frac{E_C + E_{VM}}{m_C + m_{VM}} \qquad (28)$$

For the entire convective drying, the values of E_{VM} and m_{VM} equal to zero, while for combined drying the values of E_C and m_C result from the time of convective pre-drying. The specific energy consumption was presented *versus* the water content, which was changing during drying. The energy savings using CPD–VMFD with respect to CD was calculated as the ratio of the difference in E'_C and $E'_{C\text{-}VM}$ to E'_C (29):

$$Es = \frac{E'_C - E'_{C-VM}}{E'_C} \times 100\% \qquad (29)$$

3.6. Temperature

Temperature readings were taken immediately after taking samples out of the VM dryer using an infrared camera Flir i50. The maximum temperature observed was recorded. It is expected that the local temperature within material during drying was higher. However, a direct measurement in the drying chamber under vacuum is not practically possible because the measuring elements are heated by the microwave emission.

3.7. Color

Color was evaluated by a Konica Minolta Chroma Meter CR-200 Reflectance System (CIE$L^*a^*b^*$) (Konica Minolta, Osaka, Japan). The device is a tristimulus colorimeter that measures four specific wavelengths in the visible range, specified by the *Commission Internationale de l'Eclairage* (CIE). Dried samples were crushed using an electric mill before measurement. The results were expressed as L^* (lightness), a^* (coordinate green-red), and b^* (coordinate yellow-blue). The measurements of color were conducted in triplicate.

3.8. Bulk density

The bulk density of dried samples was determined by calculating the ratio of their mass to their bulk volume (30).

$$d_b = \frac{m}{V_b} \qquad (30)$$

The samples were weighted with an analytical scale with an accuracy of 0.001 g, while the bulk volume V_b was measured with a 250 mL graduated cylinder. The cylinder was filled with the samples and then it was gently shaken to obtain the smallest volume of the samples.

3.9. Extraction Procedure of Volatile Aroma Compounds

Hydrodistillation using a Deryng apparatus was used for the extraction of the volatile compounds of aromatic herbs (fresh and dried). A suspension of 2 g was placed in a 500 mL round flask together with 100 mL of double-distilled water, and 200 μg of 2-undecanone, as internal standard. Sample flask was heated after boiling for 1 h. The vapours were condensed by means of a cold refrigerant. One millilitre of cyclohexane was added to the Deryng apparatus at the beginning of the hydrodistillation process to retain the essential oil isolated from the samples. After 60 min of extraction, the solvent, containing the aroma compounds, was transferred into 2.5 mL vials and kept at -15°C until GC-MS analyses were performed. Analyses were run in triplicate.

3.10. Chromatographic Analyses

The isolation and identification of the volatile compounds were performed on a gas chromatograph (GC–MS), Saturn 2000 Varian Chrompack, with a column TRACE TR–5 (5% phenyl methylpolysiloxane) 30 m x 0.53 mm ID x 1.0 µm film. The mass spectrometer, equipped with an ion–trap analyzer, was set at 1508 for all analyses with an electron multiplier voltage of 1350 V. Scanning was performed from *m/z* 39 to 400 in electronic impact (EI) at 70 eV, mode at 1 scan s^{-1}. Analyses were carried out using helium as carrier gas at a flow rate of 1.0 mL min^{-1} in a split ratio of 1:20 and the following program: a) 80 °C for 0 min; b) rate of 5.0 °C min^{-1} from 80 to 200 °C; c) rate of 25°C min^{-1} from 200 to 280°C and hold for 5 min. Injector and detector were held at 200 and 300 °C, respectively. 1 μL of the extracts was always injected. Most of the compounds were identified by using 3 different analytical methods: 1) Kovats indices (KI), 2) GC–MS retention times (authentic chemicals), and 3) mass spectra, with similarity indexes >90% (authentic chemicals and NIST05 spectral library collection). Identification was considered tentative when it was based on only mass spectral data. The quantification of the volatile compounds was performed on a gas chromatograph, Shimadzu 2010, with a flame ionization detector (FID). The column and chromatographic conditions were those previously reported for the GC–MS analysis. The injector temperature was 200°C and nitrogen was used as carrier gas (1 mL min^{-1}). The quantification was obtained from electronic integration measurements using flame ionization detection (FID). 2–Undecanone was added as internal standard (200 μg) at the beginning of the distillation procedure to simulate the behaviour of volatile compounds; this chemical was used as internal standard after checking that it was absent in the samples, it separates well from other volatiles, it possesses similar FID and MS response factors to most of the volatiles in the aromatic herbs essential oil, it is stable at high temperatures and does not react with water. All the aroma standards used for identification and quantification purposes were food grade.

3.11. Extraction and determination of sugars and organic acids

Fresh samples were directly homogenized while dried samples were previously rehydrated with ultra pure water and phosphoric acid 0.1% (5 mL) and then homogenized. Both extracts were centrifuged at 15000 rpm for 20 min. One milliliter of the centrifuged liquid was filtered using a 0.45 µm Millipore filter and then injected into a Hewlett-Packard HPLC series 1100. The elution system consisted of 0.1% phosphoric acid with a flow rate of 0.5 mL min^{-1}. Organic acids were separated on a Supelcogel TM C-610H column (30 cm × 7.8 mm i.d., Supelco, Bellefonte, PA, USA) and Supelguard column (5 cm x 4.6 mm, Supelco) and detected using a diode-array detector set up at 210 nm. For sugar analyses, the same HPLC equipment, elution system, flow rate and columns were used. The detection of sugars was performed using a refractive index detector (HP 1100, G1362A). Standard curves for pure standards of organic acids (phytic, oxalic, citric, malic, quinic and ascorbic acids) and for sugars (glucose, fructose and sucrose) (Sigma, Poole, Dorset, UK), were used for quantification. Results for both organic acids and sugars were expressed as concentrations g 100^{-1} of dry weight (dw). Sugars and organic acids were determined in triplicate.

3.12. Antioxidant capacity and total phenolic compounds

The same extraction protocol was used for the quantification of both antioxidant capacity and total phenolic compounds. Briefly, 5 g of fresh or dried sample were weighed. 25 mL of ultrapure water were added with an extracting agent consisting of MeOH:H_2O (80:20) and HCl (1 %). The mixture was softly stirred and submitted to two consecutive sonication steps of 15 min each. After the sonication, the samples were left in tubes during 24 h at 4 ºC. Finally, samples were centrifuged for 10 min at 15 000 rpm (centrifuge, MPW 360, Warsaw, Poland). Supernatants were collected and both antioxidant capacity and total phenolic compounds were measured in the next 24 h.

For the free radical scavenging activities using the radical 2,2-diphenyl-1-picrylhydrazyl method (DPPH) supernatant were mixed with 40 µL of MeOH and added to 950 µL of a 0.094 mM DPPH solution. The absorbance at 515 nm was measured after 50 min of reaction; during this time samples were sealed with parafilm to avoid evaporation losses. The decrease in absorbance was measured in a Uvikon XS spectrophotometer (Bio-Tek Instrument, Winooski, VT). Results were expressed as mg of Trolox equivalent 100 g^{-1} dw (dried weight). Tests were run in triplicate. Antioxidant capacity was measured by the ABTS spectrophotometric assay. Briefly, ABTS was dissolved in ultrapure water at 7 mM concentration. ABTS radical cation ($ABTS^{\bullet+}$) was produced by reacting

ABTS stock solution with 2.45 mM potassium persulfate. Then, the mixture was left to stand in the dark at room temperature for 16 h before use. After the addition of 30 µL of supernatant to 3.0 mL of diluted $ABTS^{\bullet+}$ solution [A_{734nm}= 0.700 (±0.02)], the absorbance was read exactly 6 min after initial mixing. All determinations were performed in triplicate. The results of the assay were expressed relative to µM Trolox per 100 g of dw.

Total polyphenols (TP) were quantified using Folin–Ciocalteu reagent. Briefly, each sample was diluted in 5 mL of MeOH/water (80:20 v/v) + 2 mM NaF and then centrifuged at 15000 rpm for 20 min. Absorption was measured at 760 nm using a spectrophotometer (ThermoSpectronic Heγios, UK). Results were expressed as mg gallic acid equivalent g^{-1} dw.

3.13. Sensory evaluation with trained panel

Descriptive sensory analysis (DSA) with a trained panel was used to describe fresh and dried samples. A panel of 7 panelists, ages 20 to 55 years (3 female and 4 male) was trained in descriptive evaluation of fruits and fruit based products. All panelists work at Miguel Hernández University and have a wide experience in sensory evaluation of fruits and herbs. The study was carried out at UMH facilities (individual booths with controlled illumination and temperature) during three different sessions. In each session, panelists tested all samples; the samples order for each panelist was randomized. Fresh or dried samples were served, at 21 °C together with the appropriate questionnaire; samples were served one at a time and waiting 5 minutes between samples. Water was provided to consumers for palate cleansing between samples. In each questionnaire, panelists were asked, to evaluate the intensity of the different attributes depending on each sample. The individual products were scored for the intensity of different attributes on a scale of 0 to 10, where 0=no perceptible intensity and 10=extremely high intensity. Panelists relied on their training experience to score products, which were presented coded with 3-digit numbers in the test design. Sensory tests were run in triplicate.

3.14. Statistical Analysis

The results obtained in the study were subjected to statistical analysis. Table Curve 2D Windows v2.03 (Jandel Scientific Software, USA) enabled mathematical modelling with the highest values of determination coefficient (R^2) and the lowest values of root mean square error (RMSE). One-way analysis of variance (ANOVA) was performed using Statistica v. 8.0 (StatSoft, Inc., Tulsa, USA) in order to find out whether the differences in the mean values were significant. Homogeneous groups were determined with the Tukey's test at a significance level of $\alpha = 0.05$.

Chapter 4.- Publications

PUBLICATION 1

Effects of vacuum level and microwave power on rosemary volatile composition during vacuum-microwave drying

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Effects of vacuum level and microwave power on rosemary volatile composition during vacuum–microwave drying

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ABSTRACT

The influence of the vacuum level and the microwave power on aroma compounds and sensory quality of *Rosmarinus officinalis* dehydrated by vacuum–microwave (VM) method was evaluated. VM drying kinetics consisted of two periods: linear until a critical point and exponential beyond that point. The time needed to dry rosemary was shorter for high values of microwave power and vacuum intensity. Volatile compounds of rosemary samples were extracted by steam–hydrodistillation and analyzed by GC–MS. Thirty-one compounds were identified, with α-pinene, verbenone and 1,8-cineole being the major components; monoterpenoids were the predominant chemical family. The total quantity of volatiles of fresh rosemary (27.2 g kg^{-1}) decreased during drying, independently of treatments, to a mean of 14.8 g kg^{-1}. Soft conditions of VM drying (low vacuum level and microwave power) are recommended to get the highest concentrations of volatiles and the best sensory quality (e.g. 72–74 kPa and 360 W).

1. Introduction

Rosemary (*Rosmarinus officinalis* L.) is an aromatic, evergreen, shrubby herb typical of Mediterranean countries. Since ancient times, aromatic herbs and spices have been added to different types of foods to improve the flavor and organoleptic properties. Dried rosemary leaves are used in fried chicken, salads, baked products, condiments, perfumes and soaps. Besides, essential oils of spices and/or herbs could also be used as functional ingredients (Viuda-Martos et al., in press). Numerous studies have documented the antioxidant, antimicrobial, antiviral, anti-inflammatory, anti-ulcerous, anti-carcinogenic properties of plant essential oils (Viuda-Martos et al., 2010; Bozin et al., 2007).

The two basic forms of culinary herbs are fresh and dried. Fresh herbs cannot be supplied in a profitable way to all world-wide locations. The essential oil flavor composition of rosemary has been the subject of considerable research in recent years. Rosemary essential oil contains mainly monoterpenes and monoterpene derivatives (95–98%), the remainder (2–5%) being sesquiterpenes (Angioni et al., 2004; Díaz-Maroto et al., 2007). The principal volatile compounds in rosemary are camphor and 1,8-cineole, followed by borneol, verbenone, α-pinene and camphene (Pino et al., 1998; Rao et al., 1998; Díaz-Maroto et al., 2007).

Drying is the most popular preservation method which makes ensuring of the microbiological safety of biological products. The main purpose of drying food products is to allow longer periods of storage to preserve and make them available to consumers during the whole year (Maroulis and Saravacos, 2003). Dehydration of herbs can be performed using different methods and they will affect the different activities of rosemary (Jałoszyński et al., 2008) and also the aroma composition of its essential oil.

Convective drying has been commonly selected technique to dry fruits and vegetables, including herbs. However this method has several disadvantages and limitations; for instance, it has been seen that the temperature used during the process involves a loss of cell functionality and consequently changes in nutritional and sensory quality (Spiess and Beshnilian, 1998).

Microwave drying is a new addition in the existing drying techniques, versus convective air-drying (cabinet, flat bed, tunnel), spray, vacuum, foam mat and freeze-drying (Prabhanjan et al., 1995). The conversion of microwave energy into heat in the food is because of the presence of water. The drying time can be greatly reduced (Sharma and Prasad, 2001) and the quality of the finished product ensured (Yongsawatdigul and Gunasekaran, 1996) by applying microwave energy to dried material.

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Nomenclature

a, t'	function parameters	LSD	least significant difference
ANOVA	analysis of variance	M	moisture content (kg kg^{-1} db)
db	dry basis	M_0	initial moisture content (kg kg^{-1} db)
DSA	descriptive sensory analysis	M_e	equilibrium moisture content (kg kg^{-1} db)
dw	dry weight	MR	moisture ratio
GC–MS	gas chromatography–mass spectrometry	R^2	coefficient of determination
HD	hydrodistillation	t	time (min)
K	critical point of drying process	VM	vacuum microwave
k_1, k_2	drying constants (min^{-1})		

Vacuum–microwave (VM) has been investigated as a potential method for obtaining high quality dehydrated food products including fruits, vegetables and grains. VM combines the advantages of both microwave heating and vacuum drying. During VM drying the energy of microwaves is absorbed by water located in the whole volume of the material being dried. This creates a large vapour pressure in the centre of the material, allowing rapid transfer of moisture to the surrounding vacuum and preventing structural collapse. This process, well-known as the puffing phenomenon, creates a porous texture of the food and in this way it reduces its density (Sham et al., 2001). VM technique has been already applied to reduce the moisture content of many plant materials, such as carrots (Lin et al., 1998), cranberries (Sunjka et al., 2004), strawberries (Krulis et al., 2005; Wojdyło et al., 2009), tomatoes (Durance and Wang, 2002), peanuts (Delwiche et al., 1986), bananas (Mousa and Farid, 2002), apples (Sham et al., 2001), mushrooms (Rodríguez et al., 2005), garlic (Figiel, 2009), oregano (Figiel et al., 2010), beetroots (Figiel, 2010) and rosemary (Szumny et al., 2010).

In the previous study by Szumny et al. (2010), general conditions for VM drying were used and no good results were obtained, even compared with convective drying. However, in the present study different conditions for the microwave power intensity and the vacuum level were assayed to optimize the drying of rosemary using VM; optimization of drying conditions was based on the composition of volatile compounds. Drying kinetics was also studied to determine the time needed to obtain dried rosemary.

2. Materials and methods

2.1. Plant material and processing of samples

Fresh rosemary plants (*Rosmarinus officinalis* L.) were bought from a greenhouse "Swedeponic" in Kraśnicza Wola (Poland). Plants were chopped into 2–3 cm long pieces and their initial moisture M_0 was 4.52 kg fresh matter per kg dry matter.

Immediately after cutting, samples of approximately 60 g (only one mass of product was assayed in this study) were subjected to the following drying protocol: Microwave drying was carried out in Plazmatronika SM 200 dryer (Wrocław, Poland) connected to a vacuum system consisted of vacuum pump BL 30P ("Tepro", Koszalin, Poland), vacuum gauge MP 211 ("Elvac", Bobolice, Poland), and compensation reservoir of 0.15 m^3 (Fig. 1). Rosemary samples were placed in cylindrical container made of organic glass with volume of 6.8 L. Five different levels of vacuum were assayed: 72–74, 78–80, 94–96 and 96–98 kPa, at the microwave power of 360 W. Additional drying was performed at 240 and 480 W under vacuum 72–74 kPa or 0 kPa (atmospheric pressure). Microwave powers 240, 360 and 480 W, generated by the two amplitude controlled magnetrons located at the top of the dryer, provided microwave power concentrations of 4, 6 and 8 W/g, respectively, for an initial sample mass of 60 g. Preliminary tests showed that for the vacuum system used in this study, the optimal mass of fresh plant material should not exceed 60 g; otherwise the excessive vapour condensing over the reservoir surface made the drying process very difficult, particularly for the highest microwave power concentration. To avoid a local over-heating of herb samples the container rotated at a speed of 6 rpm. During this rotation the sample position underwent periodical changes by the friction force acting on the internal surface of the container. Additionally, the microwave field was homogenised by the four-blade aluminium distributor rotating below the magnetrons. Moreover, the container was air-cooled using an air stream of 22 °C and velocity 1 m s^{-1} produced by the electric fan installed at the bottom of the dryer.

The drying kinetics was determined on the basis of mass losses of rosemary samples. The moisture ratio MR was determined from the equation:

$$MR = \frac{M - M_e}{M_0 - M_e} \tag{1}$$

Measuring of the sample mass was possible thanks to the intermittent microwave heating consisted of power-on and power-off cycles. The duration of power-on cycle was 4, 3 and 2 min for microwave powers 240, 360 and 480 W, respectively. In this way the sample was exposed to the similar energy values despite of the microwave power applied. The power-off cycle took 60 s. During this time the following operations were made: stopping of the drum rotation, vacuum releasing, oven opening, measuring of the sample mass, oven closing, vacuum creating, starting of the drum rotation.

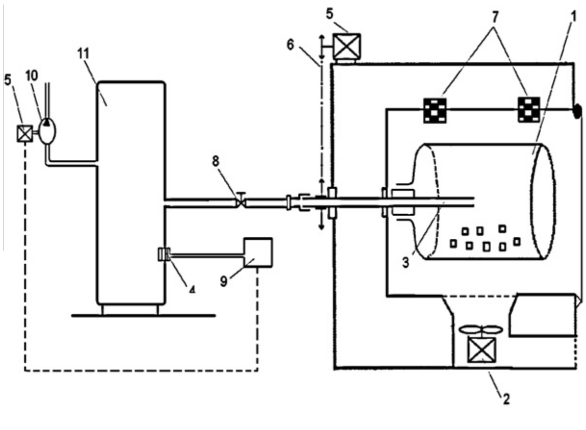

Fig. 1. Schematic diagram of vacuum–microwave dryer SM 200 (1. vacuum-drum, 2. fan, 3. air pipe, 4. vacuum sensor, 5. electric motor, 6. transmission chain, 7. magnetrons, 8. valve, 9. vacuum gauge, 10. vacuum pump and 11. compensation reservoir).

2.2. Extraction procedure of volatile aroma compounds

Hydrodistillation (HD) using a Dering apparatus was used for aroma extraction of rosemary (fresh and dried). A suspension of 3 g of rosemary was placed in a 500 mL round flask together with 100 mL of deionised water and 100 μg of benzephenone, as internal standard. Sample flask was heated after boiling for 1 h. The vapours were condensed by means of a cold refrigerant. After 60 min of extraction, the solvent, 1 mL of cyclohexane, containing the aroma compounds, was collected in 2.5 mL vials and kept at −15 °C until GC–MS analyses were performed. Analyses were run in triplicate.

2.3. Chromatographic analyses

The isolation and identification of the volatile compounds were performed on a gas chromatograph (GC–MS), Saturn 2000 Varian Chrompack, with a column TRACE TR-5 (5% phenyl methylpolysiloxane) 30 m × 0.53 mm ID × 1.0 μm film. The mass spectrometer, equipped with an ion-trap analyzer, was set at 1508 for all analyses with an electron multiplier voltage of 1350 V. Scanning was performed from m/z 39 to 400 in electronic impact (EI) at 70 eV, mode at 1 scan s^{-1}. Analyses were carried out using helium as carrier gas at a flow rate of 1.0 mL min^{-1} in a split ratio of 1:20 and the following program: (a) 80 °C for 0 min; (b) rate of 5.0 °C min^{-1} from 80 to 200 °C; (c) rate of 25 °C min^{-1} from 200 to 280 °C and hold for 5 min. Injector and detector were held at 200 and 300 °C, respectively. 2 μL of the extracts were always injected.

Most of the compounds were identified by using three different analytical methods: (1) Kovats indices (KI), (2) GC–MS retention times (authentic chemicals) and (3) mass spectra (authentic chemicals and NIST05 spectral library collection; NIST, 2010). Identification was considered tentative when it was based on only mass spectral data.

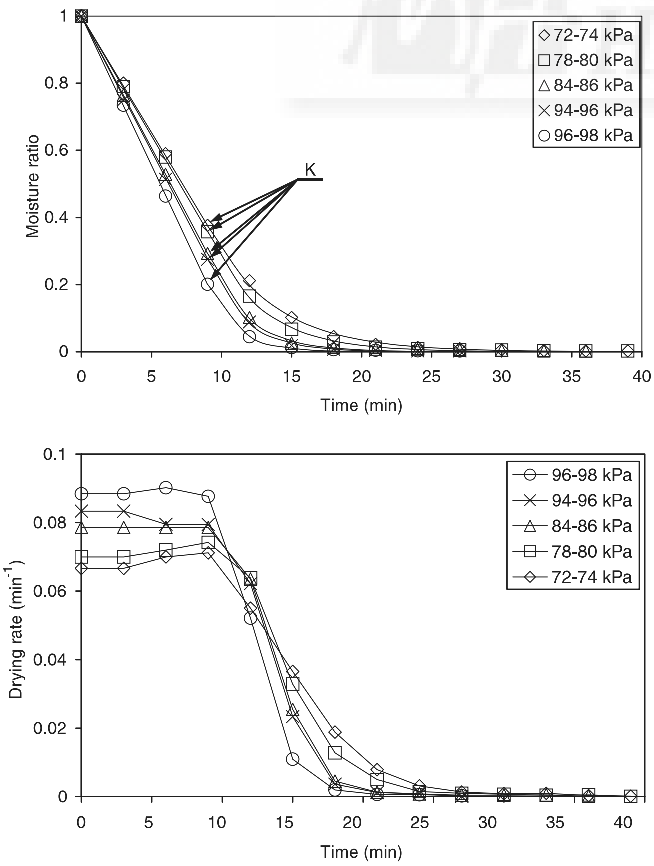

Fig. 2. Effects of vacuum level on rosemary vacuum–microwave drying kinetics.

The quantification of the volatile compounds was performed on a gas chromatograph, Shimadzu 2010, with a flame ionization detector (FID). The column and chromatographic conditions were those previously reported for the GC–MS analysis. The injector temperature was 250 °C and nitrogen was used as carrier gas (1 mL min^{-1}). The quantification was obtained from electronic integration measurements using flame ionization detection (FID). Benzophenone was added as internal standard (100 μg) at the beginning of the extraction procedure. All the aroma standards used for identification and quantification purposes were food grade (Sigma–Aldrich, Flavors and Fragrances).

2.4. Sensory evaluation with trained panel

Sensory evaluation with trained panel was used to discriminate the intensities of the main aromatic characteristics of rosemary samples. Rosemary was tested by a panel of seven panellists, ages 24–48 years (three female and four male, all members of the University Miguel Hernandez), with sensory evaluation experience and trained in descriptive evaluation of fruits and vegetables (AENOR, 1997; Meilgaard et al., 1999).

Descriptive sensory analysis (DSA) has been successfully used for comparing odour and taste attributes in foods and their products (Alasalvar et al., 2003; Vázquez-Araújo et al., 2008). Rosemary samples were assessed using an aroma profile method (Meilgaard et al., 1999). Prior to DSA, panellists discussed the aroma attributes properties of rosemary during two preliminary orientation sessions, each lasting 90 min, until they had agreed on their use of aroma attributes. During these orientation experiments, panellists evaluated 10 different coded samples of fresh and dried rosemary from different geographical areas of Spain. Panellists agreed in 11 odour attributes (as previously reported by Díaz-Maroto et al., 2007): fresh rosemary, vegetable, pine, herbaceous, balsamic, spice, hay-like, sweet, earthy, woody and infusion. Samples with the highest and lowest intensities of these attributes were used as standards.

Measurements were performed in individual booths with controlled illumination and temperature (AENOR, 1997; Meilgaard et al., 1999).

The individual products were scored for the intensity of different aroma attributes on a scale of 0–10, where:

- 0 = no perceptible intensity.
- 10 = extremely high intensity.

Panellists relied on their training experience to score products and rosemary samples were presented in 100 mL plastic beakers with lids, which stood at room temperature for 30 min prior to analyses.

2.5. Statistical analysis

One-way analysis of variance (ANOVA) and multiple-range test were used for comparison of the results. Homogenous groups and the least significant difference (LSD) were determined according to Tukey's test (at significance level of $p \leqslant 0.05$). The statistical analyses were done using Statgraphics Plus 5.0 software (Manugistics, Inc., Rockville, MD, USA).

3. Results and discussion

3.1. Drying kinetics

The effects of vacuum level and microwave power on vacuum–microwave kinetics of rosemary are shown in Figs. 2 and 3,

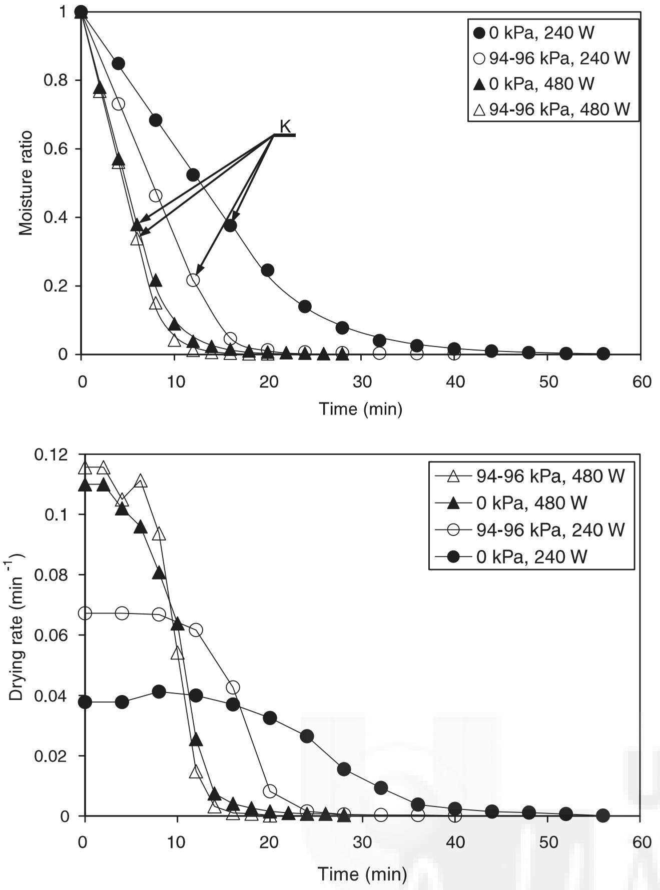

Fig. 3. Effects of microwave power (240 and 480 W) at different vacuum levels (0 and 94–96 kPa) on rosemary vacuum–microwave drying kinetics.

respectively. The two typical periods, divided by a critical point *K*, were observed. The critical point *K* is the end of the first drying period characterized by constant drying rate and the beginning of the second drying period characterized by falling drying rate (Pabis and Jaros, 2002). The *K* point was calculated after testing which drying time provided the longest possible initial linear period but with high values of R^2. The decrease in moisture content during the first drying period (until the critical point *K* was reached) was described by a linear function:

$$MR = 1 - k_1 \cdot t \tag{2}$$

while in the second drying period (falling drying rate stage: from point *K* until the end of the drying process) water loss was described by the modified Henderson–Pabis model:

$$MR = a \cdot e^{-k_2 \cdot (t - t')} \tag{3}$$

A similar drying kinetics was found for oregano herb dehydrated by VM method (Jałoszyński et al., 2008).

The experimental values of the parameters a, t' and drying constants k_1 and k_2 from functions (2) and (3) as well as the drying times are summarized in Table 1. The drying constant k_1 is a tangent value of the strait line representing the drying kinetics in the first drying period. This constant also indicates the theoretical value of drying rate in that period. Modification of Henderson–Pabis model by introducing the negative value of t' provides valuable information. Namely, parameters a and t' in Eq. (3) are moisture and time coordinates of the critical point *K*, respectively. This equation is somewhat complex due to existing of three parameters: a, k_2 and t'. However, when resigning from parameter t', the value of parameter a in the conventional Henderson–Pabis model would equals the hypothetic value of *MR* obtained for $t = 0$. This information seems to be less important than the one concerning the real value of *MR* obtained at the critical point *K*, where the second drying period starts after time t'. Achieving of this information is possible because applying of the parameter t' shifts the vertical axis of *X*–*Y* coordinate system until the critical point *K*.

An increase in the vacuum level from 72 to 74 kPa until 96–98 kPa at a microwave power 360 W increased the values of the drying constants k_1 and k_2 from 0.0693 to 0.0889 and from 0.2166 to 0.4902, respectively and decreased the value of parameter a from 0.3750 to 0.2009. The value of parameter t' remained constant, 9 min. An increase in microwave power from 240 to 480 W increased the values of the drying constants k_1 and k_2 despite of the vacuum level. However, the increase was more noticeable for the atmospheric pressure (no vacuum) than for the vacuum level 94–96 kPa.

The drying time was shorter when values of the drying constants k_1 and k_2 were higher. The increase in vacuum level from 72 to 74 kPa until 96–98 kPa at microwave power 360 W decreased the time of drying from 39 until 27 min. On the other hand, the increase in microwave power from 240 up to 480 W decreased the time of drying from 40 to 20 min and from 56 to 28 min at 94–96 kPa and 0 kPa, respectively. In a recent study (Szumny et al., 2010), it was reported that convective drying of rosemary at 60 °C using an air velocity of 1.2 m s^{-1} lasted as much as 180 min.

3.2. Volatile compounds of rosemary

In this particular experiment, the total concentration of volatile compounds in fresh rosemary (mixtures of leaves, branches and stems) was 27.2 g kg^{-1} dw, which is significantly lower that the concentration previously reported by Szumny et al. (2010) also in fresh Polish rosemary (135 g kg^{-1}). The differences could be related to differences in cultivars, cultivation cycle and plant age.

Table 1
Parameters of drying kinetics (a, t', k_1 and k_2), as well as drying time for different vacuum–microwave drying conditions.

Drying conditions		Drying kinetics						Drying time (min)
Vacuum (kPa)	Power (W)	$MR = 1 - k_1 \cdot t$		$MR = a \cdot e^{-k_2 \cdot (t-t')}$				
		k_1	R^2	a	k_2	t'	R^2	
96–98	360	0.0889	0.9999	0.2009	0.4902	9	0.9987	27
94–96	360	0.0803	0.9999	0.2761	0.3932	9	0.9987	27
84–86	360	0.0786	0.9999	0.2932	0.3630	9	0.9980	36
78–80	360	0.0713	0.9998	0.3585	0.2675	9	0.9990	39
72–74	360	0.0693	0.9998	0.3750	0.2166	9	0.9978	39
94–96	240	0.0654	0.9996	0.2165	0.3746	12	0.9978	40
94–96	480	0.1096	0.9996	0.3414	0.4596	6	0.9954	20
0	240	0.0391	0.9997	0.3837	0.1274	16	0.9970	56
0	480	0.1035	0.9991	0.3851	0.3348	6	0.9945	28

The volatile compounds from this Polish fresh rosemary samples could be grouped in chemical families as follows: monoterpenoids (55.6%), monoterpenes (34.3%), sesquiterpenes (6.7%), sesquiterpenoids (2.3%), ketones (0.9%), aldehydes (0.1%) and alcohols (<0.1%). Therefore, the predominant group was monoterpenoids, with monoterpenes and monoterpenoids representing 89.9% of total volatiles. In Szumny et al. (2010), monoterpenes (50%) predominated over monoterpenoids (38%). Bozin et al. (2007) reported a similar distribution of monoterpenes (48%) and monoterpenoids (48%) in Serbian rosemary samples.

In the current experiment, a total of 41 compounds were identified. These compounds included mainly monoterpenes, monoterpenoids and sesquiterpenes. α-Pinene (5.38 g kg^{-1}) was the major compound in Polish fresh rosemary and represented 19.8% of total volatiles, followed by verbenone (3.91 g kg^{-1}), 1,8-cineole (2.75 g kg^{-1}), camphor (2.65 g kg^{-1}) and borneol (2.20 g kg^{-1}).

The subspecies and geographical source greatly influence herbs biological activities and volatile compositions. Flamini et al. (2002) studied the chemical composition of essential oils from two Italian rosemary ecotypes; these authors concluded that the Cevoli ecotype could be classified as an α-pinene chemotype (α-pinene and 1,8-cineole represented 20.6% and 6.6%, respectively, of total volatile compounds), whereas Lunigiana was a 1,8-cineole chemotype (α-pinene and 1,8-cineole represented 13.2% and 40.2%, respectively). The Polish rosemary under study here could be classified as an α-pinene chemotype (α-pinene and 1,8-cineole represented 19.8% and 10.1%, respectively); but it is necessary to mention that this plant material was characterized by high levels of verbenone (14.4%). On the other hand, this classification is not always valid and some clarifications must be made when describing their volatile composition. For instance, Bozin et al. (2007) studied the volatile composition and antimicrobial and antioxidant activities of

Table 2
Concentrations of the volatile compounds of rosemary during vacuum–microwave drying as affected by vacuum level at 360 W.

Peak name	Time (min)	Kovats indexes		ANOVA	Fresh RsM	Vacuum level (kPa) at 360 W				
		Exp.	Lit.[e]			72–74	78–80	84–86	94–96	96–98
					Concentration (g kg^{-1} dw)					
α-Thujene	7.08	928	932	NS[a]	0.01[b]	0.02	0.02	0.02	0.02	0.02
Trcyclene	7.18	939	944	NS	0.03	0.06	0.06	0.05	0.05	0.05
α-Pinene	7.41	948	946	**	5.38a[c]	4.64ab	4.18bc	3.68c	3.60c	3.78c
Camphene	7.91	969	960	NS	1.35	1.05	0.81	1.01	1.05	1.01
1-Octen-3-ol	8.18	979	982	NS	0.01	0.02	0.02	0.02	0.01	0.01
3-Octanone	8.36	986	988	*	0.25a	0.17b	0.18b	0.13b	0.11b	0.12b
β-Pinene	8.48	998	981	*	0.62a	0.39b	0.34b	0.32b	0.28b	0.30b
trans-Isolimonene[d]	8.62	1002	985	*	0.69a	0.33b	0.29b	0.31b	0.32b	0.28b
2,3-Dihydro-1,8-cineole	8.80	1005	993	NS	0.00	0.01	0.01	0.01	0.01	0.01
α-Phellandrene	9.23	1009	1021	NS	0.02	0.03	0.03	0.02	0.02	0.02
α-Terpinene	9.50	1015	1013	NS	0.05	0.07	0.07	0.06	0.06	0.06
p-Cymene	9.71	1021	1015	NS	0.07	0.06	0.06	0.05	0.05	0.04
Limonene	9.86	1037	1027	*	0.68a	0.44b	0.32b	0.42b	0.35b	0.38b
1,8-Cineole	10.06	1049	1048	**	2.75a	1.42b	1.28b	1.17b	1.15b	1.13b
Benzeneacetaldehyde	10.31	1060	1053	NS	0.03	0.06	0.06	0.03	0.05	0.05
γ-Terpinene	10.61	1069	1066	*	0.16a	0.10b	0.09b	0.09b	0.08b	0.09b
cis-Sabinene hydrate	11.03	1084	1089	*	0.01b	0.05a	0.05a	0.04a	0.05a	0.05a
Terpinolene	11.44	1099	1098	**	0.27a	0.12b	0.12b	0.11b	0.10b	0.11b
Linalool	11.57	1103	1101	***	0.63a	0.25b	0.21b	0.21b	0.18b	0.21b
trans-Sabinene hydrate	11.95	1116	1107	*	0.01b	0.06a	0.05a	0.05a	0.05a	0.04a
α-Pinene epoxide isomer 1[d]	12.35	1122	1096	NS	0.01	0.00	0.01	0.01	0.00	0.00
α-Pinene epoxide isomer 2[d]	12.84	1135	1116	NS	0.01	0.00	0.01	0.01	0.00	0.00
cis-Verbenol	13.31	1164	1151	***	0.30a	0.10b	0.09b	0.08b	0.07b	0.07b
Camphor	13.56	1172	1156	***	2.65a	1.49b	1.32b	1.22b	1.30b	1.15b
Pinocamphone	13.86	1185	1169	*	0.00b	0.08a	0.07a	0.06a	0.10a	0.05a
Isoborneol	13.97	1190	1164	NS	0.03	0.08	0.09	0.06	0.10	0.06
Borneol	14.20	1195	1179	***	2.20a	0.45b	0.56b	0.47b	0.45b	0.33b
Isopinocamphone[d]	14.36	1203	1181	***	1.97a	0.52b	0.46b	0.35b	0.43b	0.36b
α-Terpineol	14.68	1211	1192	*	0.56a	0.39ab	0.22b	0.18b	0.18b	0.17b
α-Campholenol[d]	14.83	1221	1195	***	0.00c	0.39a	0.16b	0.14b	0.13b	0.12b
Verbenone	15.24	1230	1223	***	3.91a	1.92b	1.59b	1.38b	1.35b	1.39b
cis-Verbenyl acetate	16.93	1255	1266	*	0.00b	0.06a	0.05a	0.04a	0.05a	0.02ab
Bornyl acetate	17.18	1301	1305	***	0.04a	1.50a	1.65a	1.66a	1.87a	1.38
Carvacrol	17.36	1308	1309	NS	0.02	0.02	0.02	0.01	0.02	0.01
Myrtenyl acetate	18.16	1332	1326	NS	0.00	0.00	0.01	0.00	0.00	0.01
α-Terpinyl acetate	18.28	1343	1335	NS	0.00	0.03	0.03	0.02	0.03	0.02
Dihydrocarveol acetate isomer 1[d]	19.33	1360	1342	NS	0.00	0.04	0.04	0.03	0.04	0.03
Dihydrocarveol acetate isomer 2[d]	19.54	1372	1355	*	0.01b	0.08a	0.08a	0.06a	0.07a	0.07a
trans-Caryophyllene	21.20	1453	1428	***	1.57a	0.37b	0.38b	0.31b	0.39b	0.34b
Humulene	22.12	1489	1451	**	0.26a	0.05b	0.05b	0.04b	0.05b	0.04b
β-Caryophyllene oxide	25.44	1616	1615	***	0.63a	0.10b	0.09b	0.06b	0.06b	0.06b
Total				***	27.2a	17.0b	15.2bc	14.0c	14.3c	13.4c

[*] Significant at $p < 0.05$.

[**] Significant at $p < 0.01$.

[***] Significant at $p < 0.001$.

[a] NS = not significant F ratio ($p < 0.05$).

[b] Treatment means of the ANOVA test (values are the mean value of three replications).

[c] Values followed by the same letter, within the same raw, are not significant different ($p < 0.05$), Tukey's multiple-range test.

[d] Compound tentatively identified.

[e] Kovats indexes: experimental and literature (NIST, 2010).

Table 3
Concentrations of the volatile compounds of rosemary during vacuum–microwave drying as affected by microwave power and vacuum level.

Peak name	ANOVA	Fresh RsM	240 W		480 W	
			0 kPa	94–96 kPa	0 kPa	94–96 kPa
		Concentration ($g\ kg^{-1}$ dw)				
α-Thujene	NS[a]	0.01[b]	0.02	0.01	0.02	0.01
Trcyclene	NS	0.03	0.05	0.04	0.06	0.03
α-Pinene	***	5.38a[c]	4.39b	3.16c	3.72bc	2.56c
Camphene	**	1.35a	1.24a	0.75b	1.18a	0.73b
1-Octen-3-ol	NS	0.01	0.02	0.01	0.02	0.01
3-Octanone	*	0.25a	0.17ab	0.11b	0.07b	0.11b
β-Pinene	*	0.62a	0.34b	0.25b	0.26b	0.23b
trans-Isolimonene[d]	**	0.69a	0.40b	0.25c	0.33bc	0.23c
2,3-Dihydro-1,8-cineole	NS	0.00	0.01	0.01	0.01	0.01
α-Phellandrene	NS	0.02	0.03	0.02	0.02	0.02
α-Terpinene	NS	0.05	0.06	0.05	0.06	0.05
p-Cymene	NS	0.07	0.05	0.04	0.06	0.04
Limonene	*	0.68a	0.45ab	0.31b	0.24b	0.27b
1,8-Cineole	**	2.75a	1.45b	1.00c	1.31b	1.01c
Benzeneacetaldehyde	NS	0.03	0.06	0.04	0.06	0.03
γ-Terpinene	*	0.16a	0.10b	0.07b	0.08b	0.07b
cis-Sabinene hydrate	NS	0.01	0.06	0.04	0.06	0.04
Terpinolene	*	0.27a	0.14b	0.10b	0.08b	0.08b
Linalool	**	0.63a	0.27b	0.18c	0.11c	0.17c
trans-Sabinene hydrate	NS	0.01	0.07	0.04	0.06	0.04
α-Pinene epoxide isomer 1[d]	NS	0.01	0.01	0.00	0.00	0.00
α-Pinene epoxide isomer 2[d]	NS	0.01	0.01	0.00	0.00	0.00
cis-Verbenol	*	0.30a	0.13b	0.07b	0.10b	0.07b
Camphor	**	2.65a	1.70b	1.55b	1.16c	1.23c
Pinocamphone	NS	0.00	0.05	0.03	0.05	0.05
Isoborneol	NS	0.03	0.11	0.07	0.06	0.05
Borneol	**	2.20a	0.95b	0.45c	0.57c	0.45c
Isopinocamphone[d]	**	1.97a	0.57b	0.38b	0.55b	0.38b
α-Terpineol	**	0.56a	0.26b	0.17b	0.19b	0.16b
α-Campholenol[d]	**	0.00b	0.19a	0.13a	0.02b	0.12a
Verbenone	***	3.91a	2.05b	1.22c	1.37c	1.21c
cis-Verbenyl acetate	NS	0.00	0.07	0.02	0.06	0.04
Bornyl acetate	***	0.04c	2.28a	1.25b	1.80ab	1.50b
Carvacrol	NS	0.02	0.02	0.01	0.01	0.01
Myrtenyl acetate	NS	0.00	0.01	0.00	0.00	0.00
α-Terpinyl acetate	NS	0.00	0.04	0.02	0.03	0.02
Dihydrocarveol acetate isomer 1[d]	NS	0.00	0.04	0.03	0.04	0.03
Dihydrocarveol acetate isomer 2[d]	*	0.01b	0.09a	0.06c	0.08c	0.06a
trans-Caryophyllene	***	1.57a	0.49b	0.36b	0.48b	0.33b
Humulene	**	0.26a	0.06b	0.05b	0.06b	0.04b
β-Caryophyllene oxide	**	0.63a	0.09b	0.05b	0.10b	0.05b
Total	***	27.2a	18.6b	12.4c	14.6bc	11.6c

* Significant at $p < 0.05$.
** Significant at $p < 0.01$.
*** Significant at $p < 0.001$.
[a] NS = not significant *F* ratio ($p < 0.05$).
[b] Treatment means of the ANOVA test (values are the mean value of three replications).
[c] Values followed by the same letter, within the same raw, are not significant different ($p < 0.05$), Tukey's multiple-range test.
[d] Compound tentatively identified.

rosemary from the Republic of Serbia and found that this essential oil could not be categorized in one of the two previously described chemotypes because the concentrations of both, α-pinene and 1,8-cineole, were lower than reported earlier; the main compounds found were limonene (22%) and camphor (22%).

Other authors have classified rosemary samples according to their contents of 1,8-cineole, linalool and verbenone and the essential oil yield. Varela et al. (2009) studied 87 spontaneous populations of *R. officinalis* collected in Spain and classified them according their volatiles composition. Among all samples, 38 had high 1,8-cineole content (>24%) and high yield of essential oil (>2%), six showed high 1,8-cineole/linalool ratio, three samples had high linalool content, and only two samples present high verbenone content (≈5%). This particular Polish fresh rosemary could be considered as having a high yield of essential oil (2.7% in dried weight), but with a low contents of 1,8-cineole (10.1%) and linalool (2.3%), with a ratio 1,8-cineole/linalool of 4.4 but with high contents of verbenone (14.4%).

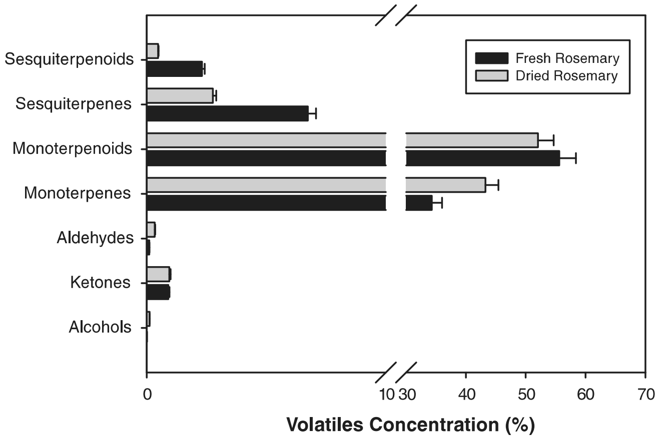

Fig. 4. Effects of vacuum–microwave drying on the main chemical families of volatile compounds from rosemary essential oils.

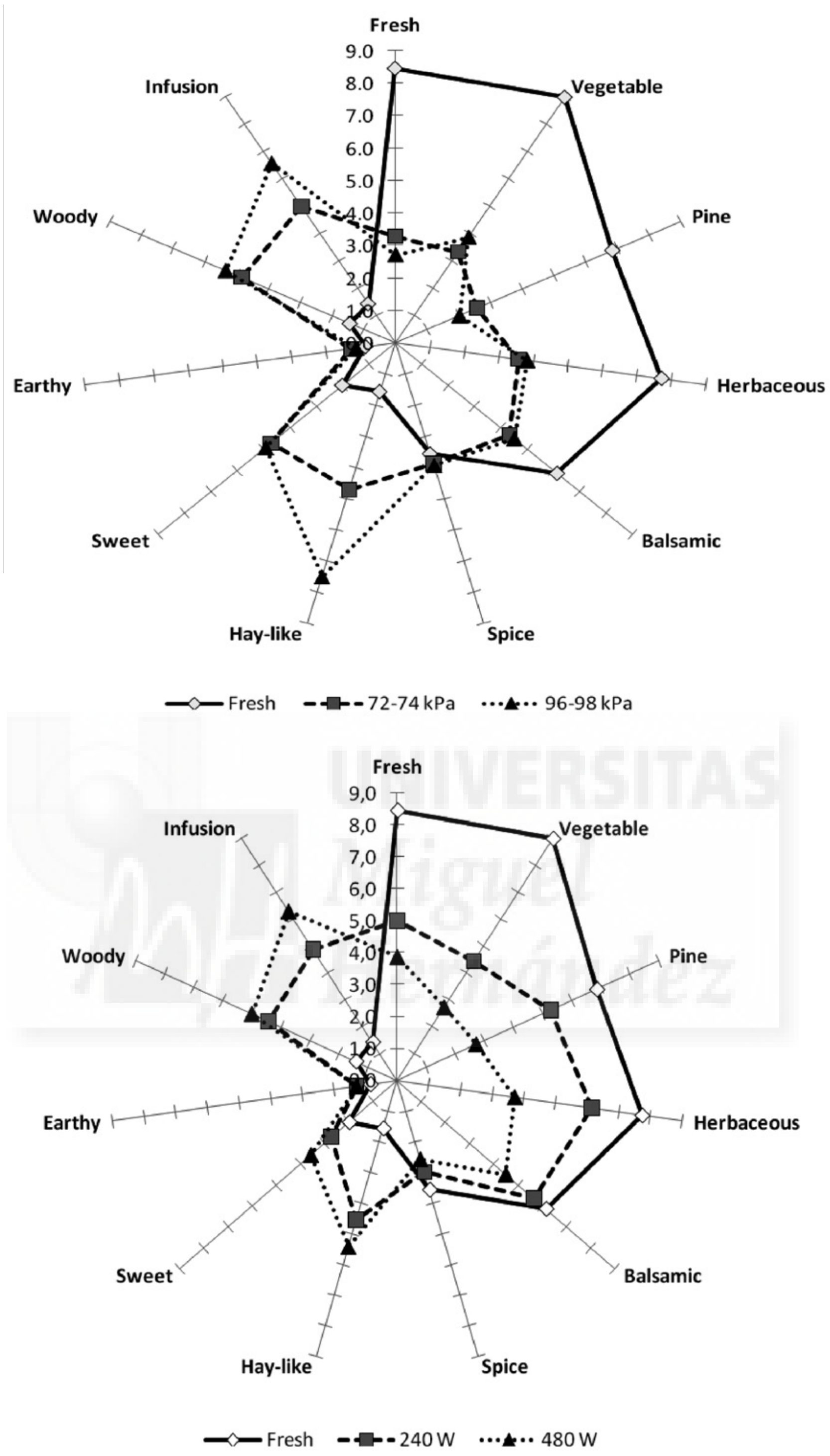

Fig. 5. Descriptive sensory analysis of aroma attributes in rosemary samples as affected by vacuum level (at 360 W) and microwave power (at 0 kPa).

3.3. Effect of the vacuum level and microwave power on volatile composition

The losses of volatile compounds caused during microwave and/or vacuum–microwave dryings vary considerably from one species to another. Whereas this method produces greater volatile losses than oven drying of rosemary, in basil it gives a high-quality product, although strong changes are induced in the essential oil profile (Díaz-Maroto et al., 2004; Rao et al., 1998; Antonelli et al., 1998; Yousif et al., 1999). However, the optimization of the working conditions of VM drying developed during the current experiment led to concentrations of total volatiles close or even higher than those previously reported for rosemary convective drying (Szumny et al., 2010). The conditions leading to the highest concentrations of total volatiles were: 72–74 kPa at 360 W (62.5% of total volatile compounds present in fresh rosemary samples) (Table 2) and 0 kPa at 240 W (68.3%) (Table 3), while that reported for convective dried samples were 64.6% (Szumny et al., 2010).

In general, after drying of rosemary samples the relative percentage of monoterpenes significantly increased while sesquiterpenes decreased; the percentage of monoterpenoids remained almost constant during the drying process (Fig. 4).

Table 2 shows the volatile compounds identified in fresh and VM dried rosemary samples at a constant microwave power (360 W) and increasing levels of vacuum. Fresh rosemary had a total concentration of volatile compounds of 27.2 g kg^{-1} while the highest concentration in VM dried samples was found for 72–74 kPa and 360 W (17.0 g kg^{-1}), with slight but not statistically significant decreases for higher values of vacuum level (mean value of 14.2 ± 0.4 g kg^{-1}). In this way, VM dried samples contained 54.4% of the fresh rosemary volatiles; this data agreed well with previously data published with our group, 54.1% (Szumny et al., 2010).

Most of the compounds initially found in the volatile profile of fresh rosemary significantly decreased during the VM drying process. For instance, the concentration of 1,8-cineole was 2.75 g kg^{-1} dw in fresh rosemary samples and its concentration decreased to 1.23 g kg^{-1} in VM dried samples (mean of samples dried at 360 W using different vacuum levels) (Table 2). On the other hand, bornyl acetate was the only compound, which concentration increased after this thermal process; its concentration increased from 0.04 g kg^{-1} up to a mean value of 1.61 g kg^{-1}. Due to the chemical family and structure of bornyl acetate it can be considered that it was generated from compounds, such as borneol, which concentration decreased from 2.20 g kg^{-1} in fresh samples to 0.45 g kg^{-1} in dried rosemary.

In summary, data on Table 2 showed that the higher the vacuum intensity in the drying system for a specific microwave power (360 W) and the higher the power intensity (Table 3), the lower the concentration of total volatiles. However, the higher the vacuum intensity and the microwave power, the shorter the time needed to dry the samples (Table 1). Consequently, equilibrium must be reached between the time and the energy put into the VM drying system (power and vacuum level). The best conditions were 72–74 kPa at 360 W (39 min were needed to dry samples) and especially 240 W and 0 kPa (56 min are required). These results proved that VM could be used in drying of very sensitive materials, such as rosemary, but high vacuum levels and low microwave powers should be used; this situation will require relatively long drying times but always shorter than those required for convective drying, which takes 3 h (Szumny et al., 2010). The significant difference in drying time causes that VM drying is less energy consuming than convective drying. For instance, Durance and Wang (2002) proved that the least energy consumption occurred in the 100% VM process when drying tomatoes using different combinations of VM and convective methods.

3.4. Sensory analyses

Fig. 5 shows the descriptive sensory analysis (DSA) profiles of different rosemary samples as affected by vacuum level and microwave power. A detailed study of the DSA data revealed that the assessors were able of distinguishing four groups of samples: (1) fresh rosemary, (2) rosemary dried at 0 kPa and 240 W, (3) samples dried at 72–74 kPa and 360 W and (4) samples dried at 0 kPa and 480 W and at 58 kPa and 360 W. Fresh rosemary was characterized by intense fresh, vegetable, pine, herbaceous and balsamic odour notes. Samples belonging to the last group were typified by their characteristic and intense sweet and infusion-like odours and by a series of attributes that are typical of dryness, especially hay-like. These last descriptors were previously described in other dry herbs such as parsley, bay leaf, spearmint, basil (Díaz-Maroto et al., 2004) and rosemary (Díaz-Maroto et al., 2007; Szumny et al., 2010).

No significant spice notes were found in neither the fresh nor dried samples of Polish rosemary; this statement could be related with the fact that eugenol and thymol were not found in the aroma extracts (Rao et al., 1998; Díaz-Maroto et al., 2004).

In general, VM drying of fresh rosemary implied decreases of some attributes: fresh, vegetable, pine, herbaceous and balsamic, and increases of some others: hay-like, earthy, woody and infusion. Samples dried using soft vacuum and microwave (e.g. 240 W and 0 kPa) showed much better sensory profiles (closer to those of fresh rosemary) than samples dried using intense VM drying conditions (high power and intense vacuum).

4. Conclusions

The drying kinetics of rosemary dehydrated by VM method could be described by two drying periods: first – linear and second – exponential characterized by falling drying rate. Thirty-one compounds were identified, with α-pinene, verbenone and 1,8-cineole being the major components; monoterpenoids were the predominant chemical family. The total quantity of volatiles of fresh rosemary (27.2 g kg^{-1}) decreased during drying, independently of treatments, to a mean of 14.8 g kg^{-1}. The higher the vacuum intensity in the drying system for a specific microwave power and the higher the power intensity, the lower the concentration of total volatiles. However, the higher the vacuum intensity and the microwave power, the shorter the time needed to dry the samples. Experimental results proved that VM could be used in drying of very sensitive materials, such as rosemary, but very high vacuum levels and low microwave powers should be used; this situation will require relatively long drying times but always shorter than those required for convective drying. The best conditions were 72–74 kPa and 360 W (39 min were needed to dry samples) and 240 W and 0 kPa (56 min were required); almost 180 min are required for drying of rosemary using pure convective methods. Consequently, samples dried using soft vacuum and microwave showed much better sensory profiles than samples dried using intense VM drying conditions (high power and intense vacuum).

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PUBLICATION 2

Volatile composition of sweet basil essential oil (*Ocimum basilicum* L.) as affected by drying method

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The influence of drying method on aroma compounds of sweet basil (Ocimum basilicum L.) was evaluated. The drying methods tested were convective (CD) and vacuum-microwave (VMD), as well as a combination of convective pre-drying and VM finish-drying (CPD–VMFD). Sweet basil's drying kinetics for CD was described by a two term exponential model, while VMD kinetics consisted of two periods: linear until a critical point and exponential beyond that point. Volatile compounds of basil samples were extracted by hydrodistillation and analyzed by GC/FID and GC/MS. Forty compounds were tentatively identified, with methyleugenol, eugenol, eucalyptol, and linalool being the major components. The total quantity of volatiles of fresh sweet basil, 32.1 g kg^{-1}, decreased considerably during both CD and VMD, 14.4 g kg^{-1}. The CPD-VMFD (40 °C and 360 W) was the best option for drying sweet basil, the time required was relatively short (≈250 min), and aroma quality was good according to instrumental data (total concentration of volatiles 16.7 g kg^{-1}) and sensory data (high intensities of fresh and floral notes).

1. Introduction

Sweet basil (*Ocimun basilicum* L.) is a popular culinary herb originated in India, Africa and southern Asia and nowadays cultivated world-wide (Makri & Kintzios, 2007; Putievsky & Galambosi, 1999). Sweet basil is used extensively to add a distinctive aroma and flavour to food, such as salads, pizzas, meats and soups. It is well-known that the presence of essential oils and their composition determine the specific aroma of plants and the flavour of condiments. Essential oils of spices and/or herbs could also be used as functional ingredients (Viuda-Martos, Rúiz-Navajas, Fernández-López, & Pérez-Álvarez, 2011). Numerous studies have documented that sweet basil contains high concentrations of phenolic compounds (especially rosmarinic acid and caffeic acid), which are characterised by high antioxidant capacity (Lee & Scagel, 2009; Surveswaran, Cai, Corke, & Sun, 2007).

Many studies about the volatile composition of sweet basil have been carried out. Sweet basil essential oil contains mainly monoterpenes, sesquiterpenes, alcohols, aldehydes, ketones, esters and miscellaneous compounds (Lee, Umano, Shibamoto, & Lee, 2005). The most important compounds are affected by the geographical source, for instance linalool and estragole were dominant in Egyptian sweet basil (Karawya, Hashin, & Hifnaway, 1974), linalool, estragole and eugenol in Israeli sweet basil (Fleisher, 1981), eugenol, methyleugenol, eucalyptol and linalool in Italian sweet basil (Di Cesare, Forni, Viscardi, & Nani, 2003) and linalool and eugenol in Spanish sweet basil (Díaz-Maroto, Sánchez Palomo, Castro, González Viñas, & Pérez-Coello, 2004).

Herbs can be marketed as fresh or dried products. Fresh herbs cannot be supplied in a profitable way to all world-wide locations. One of the preservation methods ensuring microbial safety and extending shelf-life of foods is drying. Convective drying (CD) is still the most popular method applied to reduce the moisture content of fruits and vegetables, including herbs. However, this method has several disadvantages and limitations. For instance, it has been clearly demonstrated that the high temperature used during the process involves the degradation of important flavour and nutritional compounds; these negative consequences are additionally intensified by the relatively long drying time. This time can be drastically reduced (Sharma & Prasad, 2004) and the quality of finished product ensured (Yongsawatdigul & Gunasekaran, 1996) by replacing hot air by microwave energy, at least in some steps of the drying process. Besides, the use of low pressure can additionally shorten the drying time.

Drying using vacuum-microwave (VM) technology is a modern and efficient method of food preservation (Men´shutina, Gordienko, Voinovskii, & Kudra, 2005). During VM drying (VMD) the energy of microwaves is absorbed by the water molecules located in the whole volume of the material being dried. Lowered pressures induce faster evaporation of water from the material at relativity low temperature. The VMD system is not yet common in the agro-food industry, although investigations are being conducted on drying products

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Nomenclature

a	function parameter
K	critical point of drying process
k	drying constant (min^{-1})
db	dry basis
M	moisture content (kg kg^{-1} db)
M_e	equilibrium moisture content (kg kg^{-1} db)
M_0	initial moisture content (kg kg^{-1} db)
MR	moisture ratio
R^2	coefficient of determination
T	temperature (°C)
t	time (min)
t'	time coordinate of the critical point K
t''	time of convective pre-drying
ANOVA	analysis of variance
CD	convective drying
CPD	convective pre-drying
DSA	descriptive sensory analysis
GC/MS	gas chromatography–mass spectrometry detector
GC/FID	gas chromatography–flame ionization detector
HD	hydrodistillation
LSD	least significant difference
SDE	simultaneous distillation–extraction
wb	wet basis
VM	vacuum microwave
VMD	vacuum microwave drying
VMFD	vacuum microwave finish-drying

such as carrots (Lin, Durance, & Scaman, 1998), tomatoes (Durance & Wang, 2002) and garlic cloves and slices (Figiel, 2009).

Pre-drying of plant materials by convective method before VM finishing drying (CPD–VMFD) may reduce the total cost of dehydration and improve the quality of the commercial dehydrated product (Durance & Wang, 2002). Different studies have reported the effects of the vacuum-microwave method on the quality of some herbs such as sweet basil (Yousif, Scaman, Durance, & Girard, 1999), mint leaves (Therdthai & Zhou, 2009), rosemary (Szumny, Figiel, Gutiérrez-Ortíz, & Carbonell-Barrachina, 2010) and oregano (Figiel, Szumny, Gutiérrez-Ortíz, & Carbonell-Barrachina, 2010). However no research study has been conducted on the effects of the combined method, CPD–VMFD, on the quality of sweet basil. The sequential application of convective and VM drying could make a significant contribution to the herbs, fruits and vegetables processing industry. Therefore, the main objective of this study was to evaluate the effects of two drying methods (CD and VMD) and their combination (CPD–VMFD) on the quality and volatile composition of sweet basil.

2. Materials and methods

2.1. Plant material and processing of samples

Sweet basil plants (*O. basilicum* L.) were bought from a greenhouse "Swedeponic" in Kraśnicza Wola (Poland). Later the aerial parts of the plants (shoots) were chopped into pieces of 2–3 cm and were manually mixed for homogenisation. The moisture content was determined by drying samples in a vacuum oven (SPT-200 vacuum drier, ZEAMiL Horyzont, Kraków, Poland) for 12 h at 60 °C; these conditions led to final constant weights. The initial moisture content of the plants (M_0) was 14.48 kg water per kg dry matter, which corresponds to 93.5% (wb). The moisture content of the samples at the end of the drying protocols ranged from 0.044 to 0.055 kg water per kg dry matter.

Sweet basil samples of approximately 60 g were subjected to three different drying protocols:

1. Convective drying was carried out using a drying equipment designed and built up in the Institute of Agricultural Engineering (Wrocław University of Environmental and Life Sciences). Sweet basil samples (≈60 g) were placed in a tray of 100 mm diameter without kneading. Convective drying was conducted at three different temperatures: 40, 50 or 60 °C with an air velocity of 0.8 m s^{-1}.
2. Microwave drying was carried out in Plazmatronika SM 200 dryer (Wrocław, Poland) connected to a vacuum system consisting of a vacuum pump BL 30P ("Tepro", Koszalin, Poland), a vacuum gauge MP 211 ("Elvac", Bobolice, Poland), and a compensation reservoir of 0.15 m^3. The dryer was operated at three different power levels: 240, 360 or 480 W. Sweet basil samples were placed in a cylindrical container of organic glass with a volume of 6.8 L. The pressure in the container ranged from 4 to 6 kPa. To avoid local over-heating of herbs, the container rotated at a speed of 6 rpm, and additionally an electric fan was installed at the bottom of the dryer producing an air stream of 22 °C at a velocity of 1 m s^{-1}.
3. Combined drying consisted of convective pre-drying (CPD) at temperatures 40, 50 or 60 °C until a pre-established moisture content of 4 kg kg^{-1} db was reached, followed by VM finish-drying (VMFD) at 360 W. Additional runs of VMFD were performed with microwave wattages of 240 and 480 W after CPD at temperature 50 °C. The times of CPD necessary to obtain the pre-established moisture content (4 kg kg^{-1} db), were estimated on the basis of the CD kinetics previously determined for temperatures 40, 50 and 60 °C.

2.2. Drying kinetics

The drying kinetics was determined on the basis of mass losses of the sweet basil samples. The moisture ratio *MR* was determined using the Eq. (1):

$$MR = \frac{M(t) - M_e}{M_0 - M_e} \tag{1}$$

Different functions/models, as simple as possible, were fit to the experimental points representing the decrease of MR with time using Table Curve 2D Windows v2.03 (Jandel Scientific Software, USA) and with the objective of maximizing the coefficient of determination (R^2); only the model providing the best R^2 is described in the manuscript.

2.3. Temperature

Sweet basil samples were placed on a tray just after taking them out of the VM dryer and temperature was immediately measured using an infrared thermometer. It is expected that the local temperature of material inside the VM dryer is higher; however, a direct measurement in the drying chamber is not possible because the measuring elements will be heated by the microwave emission.

2.4. Extraction procedure of volatile aroma compounds

Hydrodistillation (HD) using a Deryng apparatus was used for the extraction of the volatile compounds of sweet basil (fresh and dried). Two grams of sweet basil were placed in a 500 mL round flask together with 100 mL of double-distilled water, and 200 μg of 2-undecanone, as internal standard. Sample flask was heated after boiling for 1 h. The vapours were condensed by means of a cold refrigerant. After 60 min of extraction, the solvent, 1 mL of cyclohexane, containing the aroma compounds, was collected in 2.5 mL vials and kept at −15 °C until the GC/FID and GC/MS analyses were performed. Analyses were run in triplicate.

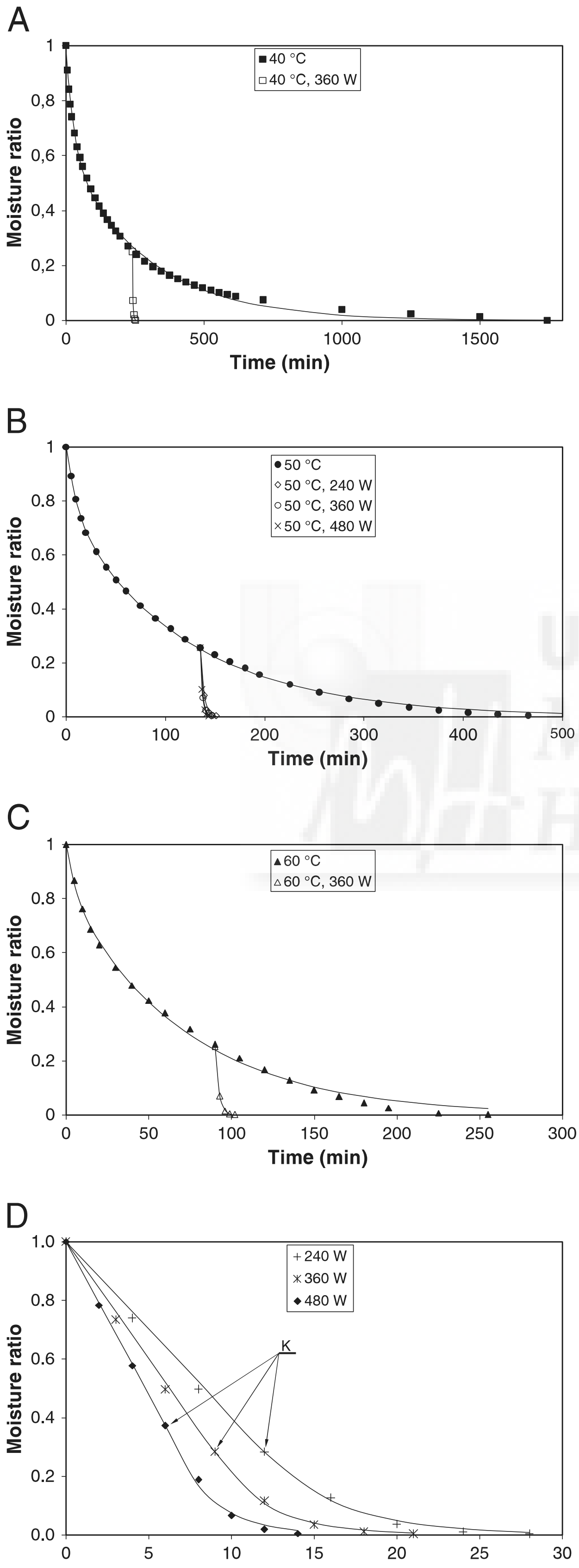

Fig. 1. Drying kinetics of basil herb dehydrated by: (A) convective method at 40 °C and finished-dried at 360 W of microwave power; (B) convective method at 50 °C and finished-dried at 240, 360 and 480 W of microwave power; (C) convective method at 60 °C and finished-dried at 360 W of microwave power; and, (D) vacuum-microwave method at 240, 360 and 480 W of microwave power.

2.5. Chromatographic analyses

The isolation and identification of the volatile compounds were performed on a gas chromatograph coupled with a mass spectrometry detector (GC/MS), Saturn 2000 Varian Chrompack, with a column TRACE TR-5 (5% phenyl methylpolysiloxane) 30 m × 0.53 mm ID × 1.0 μm film. Scanning was performed from 39 to 400 m/z in electronic impact (EI) at 70 eV, mode at 1 scan s^{-1}. Analyses were carried out using helium as carrier gas at a flow rate of 1.0 mL min^{-1} in a split ratio of 1:20 and the following program: a) 80 °C for 0 min; b) rate of 5.0 °C min^{-1} from 80 to 200 °C; c) rate of 25 °C min^{-1} from 200 to 280 °C and hold for 5 min. Injector and detector were held at 200 and 300 °C, respectively. One microlitre of the extracts was always injected.

Most of the compounds were identified by using 3 different analytical methods: 1) retention indices (KI), 2) GC/MS retention times (authentic chemicals), and 3) mass spectra, with similarity indexes >90% (authentic chemicals and NIST05 spectral library collection; NIST, 2012). Identification was considered tentative when it was based on only mass spectral data.

The quantification of the volatile compounds was performed on a gas chromatograph, Shimadzu 2010, with a flame ionization detector (FID). The column and chromatographic conditions were those previously reported for the GC/MS analysis. The injector temperature was 200 °C and nitrogen was used as carrier gas (1 mL min^{-1}). The quantification was obtained from electronic integration measurements. 2-Undecanone was added as internal standard (200 μg) at the beginning of the distillation procedure to simulate the behaviour of sweet basil volatile compounds; this chemical was used as internal standard after checking that it was absent in sweet basil, it separates well from other volatiles, it possesses similar FID and MS response factors to most of the volatiles in the sweet basil essential oil, it is stable at high temperatures and does not react with water. All the aroma standards used for identification and quantification purposes were food grade (SAFC, 2011).

2.6. Sensory evaluation with trained panel

Sensory evaluation with trained panel was used to discriminate the intensities of the main aromatic characteristics of the sweet basil samples. Sweet basil was evaluated by a panel of 8 panellists, ages 23 to 44 years (4 females and 4 males, all members of the University Miguel Hernandez), with wide sensory evaluation experience (over 500 h) and trained in descriptive evaluation of herbs, fruits and vegetables (AENOR, 1997; Meilgaard, Civille, & Carr, 1999).

Samples of sweet basil were assessed using an odour profile method (Meilgaard et al., 1999). Initially, panellists discussed the odour attributes properties of sweet basil during two preliminary orientation sessions, each lasting 90 min, until they had agreed on their use of odour attributes. During these orientation sessions, panellists evaluated different coded samples of fresh and dried sweet basil from different geographical areas of Spain and commercial brands. Panellists agreed that the odour of sweet basil samples could be described using ten attributes: fresh sweet basil, vegetable, herbaceous, balsamic, spice, hay-like, sweet, earthy, woody and infusion. Samples with the highest and lowest intensities of these attributes were used as standards.

Measurements were performed in individual booths with controlled illumination and temperature (AENOR, 1997; Meilgaard et al., 1999). The individual products were scored for the intensity of different odour attributes on a scale of 0 to 10, where:

- 0 = Non perceptible intensity.
- 10 = extremely high intensity.

Samples were coded with 3-digit numbers and presented in 100 mL plastic beakers with lids, which stood at room temperature for 30 min prior to analyses.

2.7. Statistical analysis

One-way analysis of variance (ANOVA) and multiple range test were used for comparison of the experimental results. Homogenous groups and the least significant difference (LSD) were determined according to Tukey's test (at significance level of $p \leq 0.05$). The statistical analyses were done using Statgraphics Plus 5.0 software (Manugistics, Inc., Rockville, MD, U.S.A.).

3. Results and discussion

3.1. Drying kinetics

According to experimental data obtained during convective drying (CD), it was stated that the loss of water content in sweet basil (Fig. 1A–C) can be described by means of a two-term exponential model function (2):

$$MR = b_1 \cdot e^{-k_1 \cdot t} + b_2 \cdot e^{-k_2 \cdot t} \tag{2}$$

The mathematical structure of this model indicates that the decrease in the moisture ratio occurs in two phases, which are characterised by the way the drying rate changes with the moisture ratio (Fig. 2). The first phase lasts until *MR* reaches an approximate value of 0.7 and it is characterised by a fast change of the drying rate with the *MR*. The faster decrease in the drying rate in the first phase was associated with values of the drying constant k_1 being more than 10 times higher than those of k_2 (Table 2).

During vacuum-microwave drying (VMD) (Fig. 1D), two drying periods, divided by a critical point (*K*), were observed (Pabis & Jaros, 2002). The critical point *K* was achieved for experimental points at moisture ratios of 0.280, 0.283 and 0.372 kg kg^{-1} after 12, 9 and 6 min of drying at 240, 360 and 480 W, respectively. The decrease in moisture content during the first drying phase (until *K* was reached) was described by a linear function (3):

$$MR = 1 - a \cdot t \tag{3}$$

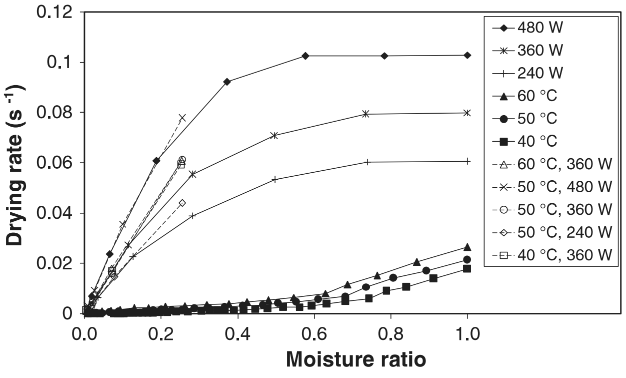

Fig. 2. Drying rate versus moisture ratio for sweet basil herb dehydrated by VM method at 240, 360, and 480 W, convective method at air temperatures 40, 50 and 60 °C as well as VM finish drying at 240, 360 and 480 W preceded by convective pre-drying at air temperatures 40, 50 and 60 °C.

while during the second drying phase (falling drying rate stage: from point *K* until the end of the drying process), the water loss was described by an exponential function (4):

$$MR = b \cdot e^{-k \cdot (t - t')} \tag{4}$$

A similar drying kinetics was previously found in oregano dehydrated by the VM system (Jałoszyński, Figiel, & Wojdyło, 2008).

Parameter *a* is the slope of the strait line representing the drying kinetics in the first drying phase; this parameter represents the value of drying rate in that phase. Parameters *b* and *t′* are moisture and time coordinates of the critical point K, respectively. An increase in the microwave power from 240 until 480 W was related with increases in the values of parameter *a*, drying constant *k*, and *b* from 0.0698 to 0.1045, from 0.2306 to 0.4067, and from 0.2860 to 0.3776, respectively (Table 2). The values of parameter *t′* were 12, 9 and 6 min for microwave powers of 240, 360 and 480 W, respectively.

The highest the values of *a* and *k*, the shortest the drying time. Convective drying at 40 and 60 °C lasted as much as 1744 and 255 min, respectively (Table 1). An increase in the microwave power from 240 until 480 W reduced the drying time from 28 down to 14 min (Table 2).

In the combined method (CPD-VMFD), the drying kinetics of sweet basil had also an exponential character. An increase in the microwave power from 240 until 480 W (at 50 °C) resulted in a significant increase in the value of drying constant *k* from 0.3023 to 0.5081 (Table 3). On the other hand, the effect of the CPD temperature on the values of *k* was negligible. Fig. 2 shows that the slope of the drying rate lines for samples VM finish-dried at the same microwave power, 360 W, was almost the same despite of the air temperature during the convective pre-drying step. In general, the slopes of the VMD drying rate lines were much higher than those of the CD lines due to the big difference in the drying rate values. Therefore, the drying rate lines for combined method are not continuous in pre-established moisture content at which convective pre-drying was replaced by VM finish drying.

However, the total drying time for sweet basil samples dehydrated by the combined method (CPD-VMFD) decreased as the temperature of the CPD stage increased. Increasing CPD temperature from 40 to 60 °C (at 360 W) decreased the total drying time from 252 to 102 min (Table 3). The positive effect of microwave power on shortening of total drying time was not significant due to the long CPD duration indicated by parameter *t″*. In this case, an increase in the microwave power from 240 to 480 W (at 50 °C) resulted in a decrease of the total drying time from 151 to 143 min (Table 3).

3.2. Temperature

It was found that increasing the microwave power from 240 to 480 W during VMD of sweet basil samples slightly increased the maximum temperature of the samples from 40.4 to 42.9 °C (Table 2); however, differences were not statistically significant. On the other hand, an increase in the microwave power from 240 to 480 W during VMFD significantly increased the maximum temperature of the

Table 1
Parameters of convective drying kinetics: b_1, b_2, k_1 *and* k_2 as well as time of drying for different drying temperatures.

Drying temp. (°C)	Drying kinetics					Drying time (min)
	$MR = b_1 \cdot e^{-k_1 \cdot t} + b_2 \cdot e^{-k_2 \cdot t}$					
	b_1	k_1	b_2	k_2	R^2	
40	0.3661	34.57×10^{-3}	0.6144	3.42×10^{-3}	0.9983	1744
50	0.2386	90.33×10^{-3}	0.7656	8.29×10^{-3}	0.9995	465
60	0.1636	162.8×10^{-3}	0.8399	13.86×10^{-3}	0.9972	255

Table 2
Parameters of VM drying kinetics: *a*, *b*, *t′* and *k* as well as time of drying and sample temperature for different microwave powers.

Power (W)	Drying kinetics						VM drying time (min)	Sample temperature (°C)
	$MR=1-a\cdot t$		$MR=b\cdot e^{-k\cdot(t-t')}$					
	a	R^2	b	k	t'	R^2		
240	0.0698	0.9980	0.2860	0.2306	12	0.9936	28	40.4 ± 2.8 a
360	0.0798	0.9975	0.2838	0.3246	9	0.9970	21	41.5 ± 2.9 a
480	0.1045	0.9998	0.3776	0.4067	6	0.9911	14	42.9 ± 5.2 a

Values followed by the same letter, within the same row, are not significantly different ($p<0.05$), Tukey's multiple-range test.

samples from 37.8 to 42.8 °C (Table 3). It can also be stated that the temperature of hot air used during CPD had no significant effect on the temperature of the dried samples. This was due to the fact that CPD samples were left to cool down to room temperature before starting VMFD. Nevertheless, the temperatures obtained during VMD were higher than those recorded while VMFD due to the longer microwave radiation (Tables 2 and 3). In a previous study conducted using rosemary (Szumny et al., 2010), it was concluded that the temperature of samples was affected by both the time and wattage of the microwave radiation, with longer time and higher wattages leading to increased temperatures. These conclusions supported previous findings of other researchers, such as Drouzas and Schubert (1996).

3.3. Volatile compounds in fresh sweet basil

Table 4 shows the volatile profile of fresh Polish sweet basil shoots, extracted by hydrodistillation. A typical chromatogram of volatile compounds of fresh sweet basil shoots is shown in Fig. 3. The volatile compounds from this Polish fresh sweet basil could be group in the following main chemical groups: phenylpropanoids (representing 74.1% of total concentration of volatiles), followed by monoterpenoids (13.7%) and sesquiterpenes (9.7%). Monoterpenes (1.2%), sesquiterpenoids (1.1%), aldehydes (<0.1%), alcohols (<0.1%) were also identified but in much lower concentrations.

Within the *O. basilicum* L. species, there are many different subspecies characterised by specific odour, physical properties and chemical composition (Baritaux, Richard, Touche, & Derbesy, 1992; Díaz-Maroto et al., 2004). The volatile profile of fresh Polish sweet basil shoots was similar to those previously reported for Mediterranean sweet basil cultivars, especially for Italian and Spanish sweet basils, dominated by methyleugenol, eugenol, eucalyptol and linalool. Di Cesare et al. (2003) found that eucalyptol, linalool, eugenol, and methyleugenol predominated in basil from Liguria (Italy), while methylchavicol (estragole), which is a common aroma compound in many other basil essential oils, was not present.

Díaz-Maroto et al. (2004) studied basil cultivated under ecological conditions in Ciudad Real (Spain) and stated that their sample was characterised by its high content of linalool, the absence of methylchavicol and a relative large content of eugenol. Marotti, Piccaglia, and Giovanelli (1996) evaluated a similar chemotype from Italy and classified it as linalool and eugenol type.

Table 3
Parameters of VM finish-drying (VMFD) kinetics: *b*, *t″* and *k* as well as times of drying and sample temperature for different drying conditions.

Drying conditions		Drying kinetics				Total drying time (min)	VMFD time (min)	Sample temperature (°C)
Temp. (°C)	Power (W)	$MR=b\cdot e^{-k\cdot(t-t'')}$						
		b	k	t''	R^2			
40	360	0.2512	0.4130	240	0.9999	252	12	40.5 ± 3.3 ab
50	240	0.2550	0.3023	135	0.9996	151	16	37.8 ± 3.3 a
50	360	0.2544	0.4212	135	0.9997	147	12	40.8 ± 1.5 ab
50	480	0.2559	0.5081	135	0.9979	143	8	42.8 ± 2.9 b
60	360	0.2542	0.4284	90	0.9998	102	12	40.3 ± 2.6 ab

Values followed by the same letter, within the same row, are not significantly different ($p<0.05$), Tukey's multiple-range test.

The total concentration of volatile compounds in the mixture of leaves, branches and stems used in this experiment was 32.1 g kg^{-1} db (dry basis). A total of 40 compounds were tentatively identified, while 2 more were isolated but could not be identified. Methyleugenol, eugenol, eucalyptol and linalool were the most abundant compounds in the fresh sweet basil sample under study, with concentrations being 20.1, 3.6, 2.1, and 1.3 g kg^{-1} db, and representing 62.8, 11.4, 6.6, and 4.1% of total volatiles concentration, respectively. The percentages and relative concentrations of these four compounds could be important in determining the quality of the different dried samples of sweet basil.

Díaz-Maroto et al. (2004) found a total concentration of volatiles of approximately 8.7 g kg^{-1} db in leaves of ecological sweet basil. Lee et al. (2005) reported a total concentration of volatiles of 9.5 g kg^{-1} db in dried sweet basil leaves from California.

Differences among the composition of sweet basil samples reported here and in others studies from the literature could be due to the fact that in this experiment leaves, branches and stems (shoots) were mixed and analyzed all together, while in many other studies only leaves were used. Usually, the plant parts used for essential oil production are the flowering aerial tops (leaves, twigs, and flowers); however for obtaining dried-products the whole above ground material is used. Klimánková et al. (2008) reported that the overall emissions of volatiles from leaves and blossom of sweet basil were very similar, while the volatiles content in stems and branches was more than 20 times lower.

3.4. Volatile compounds in dried sweet basil

Table 4 shows the volatile compounds identified in fresh and dried sweet basil samples. In general, CD and VMD led to significant volatile losses (Díaz-Maroto et al., 2004), which increased with higher air temperatures and higher microwave power. Consequently, the best results from a volatile composition point of view were obtained for samples convectively dried at 40 °C and VM-dried at 240 W. The total concentrations of volatile compounds in fresh as well as pure convective (40 °C) and VM-dried (240 W) sweet basil samples were 32.1, 14.4, and 14.4 g kg^{-1} db, respectively (Table 4); thus, convection and VM-dried samples contained approximately 45% of the fresh sweet basil volatiles content.

This study also revealed that an increase in the intensity of the treatments (higher temperatures or higher microwave power) led to higher losses of volatiles in CD compared to VMD. For instance, total concentrations of volatile compounds were reduced from 14.4 to 9.6 g kg^{-1} db (33.3% decrease) when the air temperature was increased from 40 to 60 °C, while this concentration was reduced from 14.4 to 13.5 g kg^{-1} db (6.3% decrease) when the microwave wattage increased from 240 to 480 W. These data proved that VMD is well suited for sweet basil plants. Besides, the data on the sensory tests proved the slightly higher quality of samples dried with VM compared to the ones dried using hot air. This slightly higher quality could be related to fact that VM-dried sweet basil presented higher concentrations of eugenol and eucalyptol than convective dried samples, similar concentration of linalool, and only lower concentration of methyleugenol.

The initial working hypothesis was that VMD should provide a final product of better quality than CD. The losses originated during VMD vary considerably from one species to another; whereas this method produces greater volatile losses than CD in rosemary, in sweet basil it leads to a high-quality product, although strong changes are induced in the essential oil profile (Antonelli, Fabbri, & Boselli, 1998; Díaz-Maroto et al., 2004; Rao, Singh, Raghavan, & Abraham, 1998; Yousif et al., 1999).

Table 4
Concentrations of the volatile compounds of sweet basil as affected by the convective and vacuum microwave drying method.

Compound	Peak	Chemical family	Retention indexes		ANOVA	Fresh sweet basil	Convective			VM	
							40 °C	50 °C	60 °C	240 W	480 W
			Exp.[γ]	Lit.[γ]		Concentration (g kg^{-1} db)					
cis-3-Hexen-1-ol	1	Alcohol	859	850	ns[†]	0.01[‡]	0.01	0.01	0.01	0.01	0.01
α-Pinene	2	Monoterpene	946	939	ns	0.06	0.02	0.01	0.03	0.02	0.04
Camphene	3	Monoterpene	965	954	ns	0.01	0.01	0.01	0.01	0.01	0.01
1-Octen-3-ol	4	Alcohol	977	982	ns	0.01	0.01	0.01	0.01	0.01	0.01
Sabinene	5	Monoterpene	980	975	ns	0.02	0.02	0.01	0.02	0.02	0.02
β-Myrcene	6	Monoterpene	985	991	ns	0.03	0.02	0.02	0.02	0.03	0.04
β-Pinene	7	Monoterpene	991	979	ns	0.08	0.05	0.02	0.04	0.05	0.05
Octanal	8	Aldehyde	996	993	ns	0.01	0.01	0.01	0.01	0.01	0.01
α-Phellandrene	9	Monoterpene	1014	1003	ns	0.01	0.01	0.01	0.01	0.01	0.01
α-Terpinene	10	Monoterpene	1026	1017	ns	0.01	0.01	0.01	0.01	0.01	0.01
Limonene	11	Monoterpene	1031	1029	ns	0.04	0.02	0.01	0.01	0.03	0.03
Eucalyptol	12	Monoterpenoid	1038	1031	**	2.12 a	0.83 bc	0.58 c	0.72 bc	1.15 b	1.00 b
γ-Terpinene	13	Monoterpene	1070	1060	ns	0.04	0.01	0.01	0.01	0.01	0.01
cis-Sabinene hydrate	14	Monoterpenoid	1077	1070	ns	0.01	0.01	0.01	0.01	0.01	0.02
Terpinolene	15	Monoterpene	1081	1089	ns	0.09	0.03	0.02	0.02	0.07	0.05
Linalool	16	Monoterpenoid	1087	1097	***	1.31 a	0.35 b	0.28 b	0.32 b	0.34 b	0.30 b
trans-Sabinene hydrate	17	Monoterpenoid	1093	1098	ns	0.01	0.01	0.01	0.01	0.01	0.01
1-Octen-3-yl-acetate	18	Esther	1126	1113	ns	0.01	0.01	0.01	0.01	0.01	0.01
Camphor	19	Monoterpenoid	1157	1146	**	0.21 a	0.11 b	0.08 b	0.08 b	0.09 b	0.10 b
1-Terpineol	20	Monoterpenoid	1170	1159	ns	0.01	0.01	0.01	0.08	0.01	0.10
Borneol	21	Monoterpenoid	1178	1169	ns	0.03	0.01	0.01	0.01	0.01	0.10
4-Terpineol	22	Monoterpenoid	1180	1177	ns	0.01	0.01	0.01	0.01	0.01	0.01
α-Terpineol	23	Monoterpenoid	1194	1189	*	0.22 a	0.25 b	0.02 b	0.06 b	0.07 b	0.06 b
Carvone	24	Monoterpenoid	1262	1243	***	0.22 a	0.01 b	0.01 b	0.01 b	0.01 b	0.01 b
Bornyl acetate	25	Monoterpenoid	1274	1289	**	0.20 a	0.10 b	0.04 b	0.10 b	0.10 b	0.10 b
Thymol	26	Monoterpenoid	1278	1277	ns	0.04	0.01	0.01	0.01	0.07	0.05
Unidentified	27		1301		ns	0.01	0.01	0.01	0.01	0.01	0.01
Unidentified	28		1319		ns	0.01	0.01	0.01	0.01	0.01	0.01
α-Cubebene[¥]	29	Sesquiterpene	1328	1351	ns	0.01	0.01	0.01	0.01	0.01	0.01
Eugenol	30	Phenylpropanoid	1343	1359	***	3.64 a	1.09 bc	0.96 bc	0.79 c	1.47 b	0.84 c
Copaene[¥]	31	Sesquiterpene	1370	1377	ns	0.01	0.01	0.01	0.01	0.01	0.02
β-Cubebene[¥]	32	Sesquiterpene	1381	1388	ns	0.04	0.03	0.02	0.02	0.02	0.03
Methyleugenol	33	Phenylpropanoid	1390	1404	***	20.1 a	9.46 b	9.10 b	5.79 c	8.85 b	8.48 b
Caryophyllene	34	Sesquiterpene	1424	1419	**	1.13 a	0.50 b	0.46 b	0.50 b	0.57 b	0.41 b
α-Farnesene	35	Sesquiterpene	1432	1428	*	0.68 a	0.33 b	0.27 b	0.19 c	0.34 b	0.42 b
α-Humulene[¥]	36	Sesquiterpene	1463	1455	**	0.25 a	0.11 b	0.11 b	0.07 b	0.09 b	0.15 b
β-Farnesene	37	Sesquiterpene	1480	1460	ns	0.06	0.03	0.02	0.03	0.03	0.03
Germacrene D[¥]	38	Sesquiterpene	1487	1485	**	0.63 a	0.39 b	0.23 c	0.20 c	0.34 b	0.36 b
α-Selinene[¥]	39	Sesquiterpene	1502	1498	*	0.18 a	0.11 b	0.08 b	0.08 b	0.11 b	0.13 b
γ-Cadinene[¥]	40	Sesquiterpene	1520	1514	ns	0.13	0.12	0.11	0.10	0.13	0.14
γ-Eudesmol[¥]	41	Sesquiterpenoid	1625	1632	ns	0.04	0.01	0.01	0.01	0.01	0.02
trans-Cadinol[¥]	42	Sesquiterpenoid	1653	1640	*	0.33 a	0.21 b	0.20 b	0.17 b	0.18 b	0.22 b
TOTAL					**	32.1 a	14.4 b	12.9 b	9.6 c	14.4 b	13.5 b

[†] n.s. = not significant F ratio ($p<0.05$); *, **, and ***, significant at $p<0.05$, 0.01, and 0.001, respectively. [‡] Treatment means of the ANOVA test (values are the mean value of 3 replications). Values followed by the same letter, within the same row, are not significantly different ($p<0.05$), Tukey's multiple-range test. [¥] Tentatively identified. [γ] Exp. = experimental, Lit. = literature; NIST (2012).

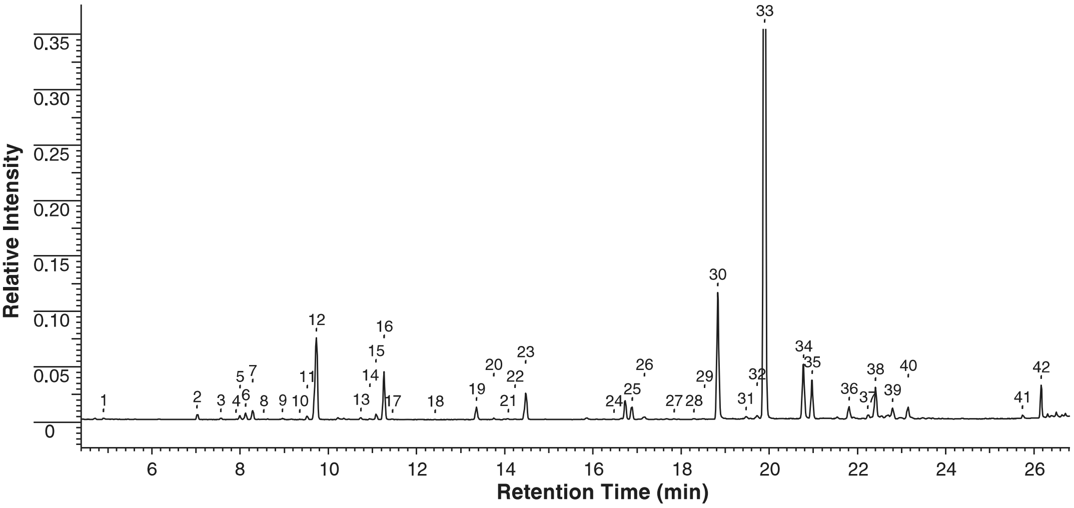

Fig. 3. Example of the chromatograms found in dried sweet basil samples (for peak identification see Table 4).

Table 5
Concentrations of the volatile compounds of sweet basil as affected by the convective pre-drying and vacuum microwave finishing drying method.

Compound	ANOVA	CPD-VMFD					
		360 W			50 °C		
		40 °C	50 °C	60 °C	240 W	360 W	480 W
cis-3-Hexen-1-ol	ns[†]	0.01[‡]	0.01	0.01	0.01	0.01	0.01
α-Pinene	ns	0.05	0.04	0.03	0.04	0.05	0.03
Camphene	ns	0.01	0.01	0.01	0.01	0.01	0.01
1-Octen-3-ol	ns	0.01	0.01	0.01	0.01	0.01	0.01
Sabinene	ns	0.02	0.02	0.02	0.02	0.02	0.03
β-Myrcene	ns	0.03	0.03	0.03	0.03	0.03	0.03
β-Pinene	ns	0.06	0.04	0.02	0.05	0.06	0.06
Octanal	ns	0.01	0.01	0.01	0.01	0.01	0.06
α-Phellandrene	ns	0.01	0.01	0.01	0.01	0.01	0.06
α-Terpinene	ns	0.01	0.01	0.01	0.01	0.01	0.01
Limonene	ns	0.03	0.02	0.01	0.02	0.02	0.02
Eucalyptol	*	1.36 a[¥]	1.18 b	0.89 c	1.12 b	1.18 b	0.97 c
γ-Terpinene	ns	0.01	0.01	0.01	0.01	0.01	0.02
cis-Sabinene hydrate	ns	0.01	0.01	0.01	0.01	0.01	0.01
Terpinolene	ns	0.05	0.04	0.03	0.05	0.05	0.03
Linalool	**	1.09 a	0.87 b	0.56 c	0.34 d	0.34 d	0.70 bc
trans-Sabinene hydrate	ns	0.01	0.01	0.01	0.01	0.01	0.01
1-Octen-3-yl-acetate	ns	0.01	0.01	0.01	0.01	0.01	0.01
Camphor	*	0.15 a	0.11 ab	0.07 b	0.11 ab	0.11 ab	0.07 b
1-Terpineol	**	0.01 b	0.01 b	0.01 b	0.11 a	0.01 b	0.01 b
Borneol	**	0.01 b	0.01 b	0.01 b	0.11 a	0.01 b	0.02 b
4-Terpineol	ns	0.01	0.01	0.01	0.01	0.01	0.01
α-Terpineol	ns	0.10	0.08	0.06	0.09	0.08	0.07
Carvone	ns	0.01	0.01	0.01	0.01	0.01	0.01
Bornyl acetate	*	0.14 a	0.10 a	0.04 b	0.10 a	0.10 a	0.06 b
Thymol	*	0.07 a	0.06 a	0.04 ab	0.01 b	0.01 b	0.01 b
Unidentified	ns	0.01	0.03	0.04	0.01	0.01	0.01
Unidentified	ns	0.01	0.02	0.04	0.01	0.01	0.01
α-Cubebene	ns	0.01	0.01	0.01	0.01	0.01	0.01
Eugenol	***	2.88 a	2.37 a	1.63 b	1.13 c	1.11 c	2.04 ab
Copaene	ns	0.01	0.01	0.01	0.01	0.01	0.01
β-Cubebene	ns	0.03	0.03	0.02	0.02	0.03	0.02
Methyleugenol	***	8.11 ab	7.08 b	5.38 c	9.61 a	8.64 a	5.11 c
Caryophyllene	*	0.74 a	0.60 a	0.40 b	0.64 a	0.54 ab	0.58 ab
α-Farnesene	*	0.43 a	0.35 b	0.25 c	0.35 b	0.46 a	0.34 b
α-Humulene	ns	0.11	0.10	0.07	0.12	0.11	0.08
β-Farnesene	ns	0.04	0.03	0.02	0.04	0.03	0.03
Germacrene D	*	0.36 a	0.28 a	0.17 b	0.32 a	0.32 a	0.26 a
α-Selinene	ns	0.17	0.14	0.10	0.10	0.13	0.12
γ-Cadinene	ns	0.19	0.14	0.08	0.11	0.14	0.08
γ-Eudesmol	ns	0.02	0.01	0.01	0.01	0.01	0.02
trans-Cadinol	ns	0.26	0.22	0.16	0.19	0.24	0.21
TOTAL	**	16.7 a	14.2 b	10.3 c	15.0 ab	14.0 b	11.3 c

[†] n.s. = not significant F ratio ($p<0.05$); *, **, and ***, significant at $p<0.05$, 0.01, and 0.001, respectively. [‡] Treatment means of the ANOVA test (values are the mean value of 3 replications). [¥] Values followed by the same letter, within the same row, are not significantly different ($p<0.05$), Tukey's multiple-range test.

The changes with treatments conditions for individual chemicals were quite similar to those previously described for the total concentration of volatile compounds. For instance, the concentrations of eugenol were 3.64 in fresh sweet basil and decreased to 1.09, 0.96 and 0.79 g kg^{-1} db for convective dried samples at 40, 50 and 60 °C,

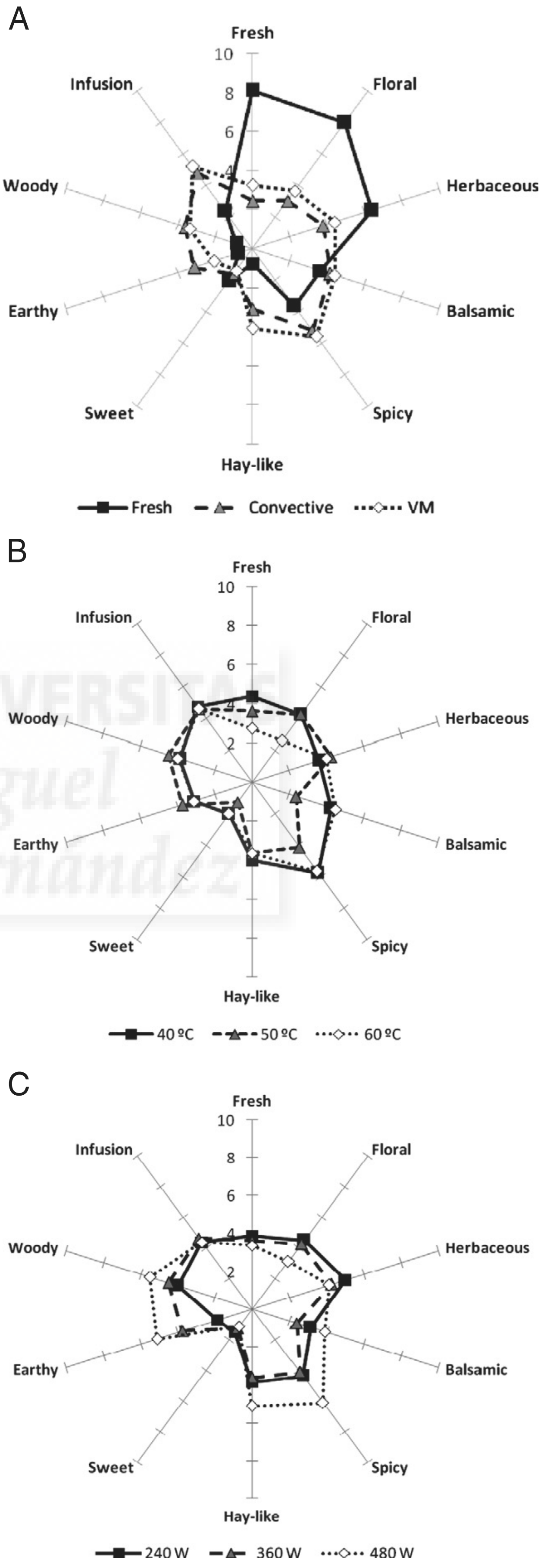

Fig. 4. Descriptive sensory analysis of aroma attributes in sweet basil samples as affected by the drying method. (A): convective (40 °C) and VM (240 W); (B): CPD-VMFD at 360 W; (C): CPD-VMFD at 50 °C.

respectively and to 1.47 and 0.84 g kg^{-1} db for VM-dried samples at 240 and 480 W, respectively.

According to Rao et al. (1998), the loss of volatile oil in herbs is related to energy input in the microwave oven. Our experimental results agreed quite well with this statement. Sweet basil samples dried using CPD-VMFD presented significant volatile losses as the treatment intensity (temperature or microwave power) increased. Samples pre-dried at 40, 50 or 60 °C and finish-dried at 360 W presented total volatile concentrations of 16.7, 14.2 and 10.3 g kg^{-1} db, respectively (Table 5). In a similar trend, samples pre-dried at 50 °C and finish-dried at 240, 360 and 480 W presented total volatile concentrations of 15.0, 14.0 and 11.3 g kg^{-1} db, respectively (Table 5).

3.5. Sensory evaluation with trained panel

Fig. 4 shows the DSA (descriptive sensory analysis) profiles of different sweet basil samples. The descriptors selected for the DSA of sweet basil were previously used in sweet basil and other dry herbs, such as parsley, bay leaf and spearmint (Díaz-Maroto et al., 2004), and rosemary (Díaz-Maroto, Pérez-Coello, Sánchez-Palomo, & González-Viñas, 2007). The fresh sweet basil was characterised by intense fresh (8.1), floral (8.0) and herbaceous (6.4) odour notes. The convective (40 °C) and VM (240 W) dried samples were typified by significant ($p<0.01$) increases in the intensities of the following attributes as compared to the fresh sample: spicy (mean of 5.3 for convective and VM dried samples compared to 3.6 in fresh sweet basil), hay-like (mean of 3.6 compared to 0.8), sweet (1.5 compared to 0.8), earthy (mean of 2.6 compared to 0.8), woody (mean of 3.5 compared to 0.9) and infusion (mean of 5.0 compared to 2.4).

An increase in the temperature of the hot air during CPD in the combined method (CPD-VMFD) from 40 to 60 °C at 360 W only resulted in significant ($p<0.01$) decreases of the intensities of the fresh and floral notes; no other significant or clear trend was observed.

An increase in the microwave power from 240 W to 480 W during CPD-VMFD at 50 °C resulted in significant ($p<0.01$) decreases of fresh, floral and herbaceous notes and significant ($p<0.001$) increases of spicy, hay-like, earthy and woody notes; the intensities of the attributes: balsamic, sweet and infusion were not significantly affected by the microwave power.

In general, drying of fresh sweet basil implied decreases of some attributes: fresh, floral and herbaceous, and increases of some others: spicy, hay-like, sweet, earthy, woody and infusion. The effects of the microwave power during VMFD on the sensory quality of dried sweet basil were more important than those of the temperature of the hot air during the CPD, with higher temperatures and microwave powers resulting in dried products of lower sensory quality (lower intensities of fresh notes and higher intensities of dried notes). The decrease in the attributes typical of fresh sweet basil, such as fresh, floral and herbaceous during the drying process could intensify the spicy odour observed in the dried samples.

Our final recommendation, based on the results from chemical as well as sensory analyses, is to use CPD (40 °C)–VMFD (360 W). An additional advantage of drying at these conditions was the relatively short time, 252 min, required to dry the samples (Table 3).

4. Conclusions

The drying kinetics of sweet basil dehydrated with convective method (CD) and with CPD–VMFD (convective-pre-drying and vacuum microwave finish-drying) were described with a exponential models, while for samples entirely dehydrated by VM (vacuum microwave) method two drying periods were found: linear and exponential characterised by falling drying rate. The sample temperature was higher during VMD than in CPD–VMFD. In general, significant differences were found in the aroma quality of sweet basil dried by different methods. The dried samples with a higher quantity of volatile compounds were those which were dried using CPD at 40 °C and VMFD at 360 W. Drying using exclusively VM might be recommended in sweet basil due to good quality of dried samples; in this way, an increase in the intensity of the treatment (higher microwave power) did result in small decreases of total volatiles concentration, while for instance an increase in the temperature of the hot air used for convective drying resulted in high reductions of total volatiles. In general, drying of fresh sweet basil decreased the intensities of fresh sweet basil, floral and herbaceous notes while increase those of spicy, hay-like, sweet, earthy, woody and infusion notes. According to the sensory data, the effects of microwave power (VMFD) were more important than those of the hot air temperature (CPD). The best option to dry sweet basil according to the results obtained in this study is: CPD–VMFD (40 °C and 360 W); this conclusion was based on the following facts: (i) a relatively short time was required to dry the samples (≈250 min), (ii) high concentration of total volatiles was found, and (iii) samples presented a sensory profile typical of high-quality dried products.

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PUBLICATION 3

Effects of drying methods on the composition of thyme (*Thymus vulgaris* L.) essential oil

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Effects of Drying Methods on the Composition of Thyme (*Thymus vulgaris* L.) Essential Oil

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The influence of drying method on aroma compounds of thyme (*Thymus vulgaris* L.) was evaluated. The drying methods tested were convective drying, vacuum–microwave drying, and freeze drying, as well as a combination of convective predrying and VM finish drying. Thyme's convective drying kinetics are described by a two-term exponential model, and VM drying kinetics consisted of two periods: a constant rate period until a critical moisture ratio (values of 0.311, 0.242, and 0.162 kg kg^{-1} for 240, 360, and 480 W, respectively) was obtained and a falling rate period beyond that point. Volatile compounds of thyme samples were extracted by hydrodistillation and analyzed by gas chromatography. Thirty-three compounds were tentatively identified; thymol, γ-terpinene, p-cymene, caryophyllene, and α-terpinene were the major components. The total quantity of volatiles of fresh thyme (1,167 mg 100 g^{-1} db) was reduced by most of the drying treatments, with the exception of VM at 240 and 360 W. The combined method with 40°C and 240 W was the best option for drying thyme; the time required was relatively short ($\approx$ 301 min) and aroma quality was good according to instrumental data (total concentration of volatiles 1,127 mg 100 g^{-1} db) and sensory evaluation results (high scores for fresh thyme and vegetable odors).

Keywords Aromatic herbs; Essential oils; Food drying; Hot air drying; Thymol; Vacuum–microwave drying

INTRODUCTION

The production of aromatic crops, such as oregano, rosemary, thyme, lavender, and mint, is increasing in Mediterranean countries due to the different applications of these crops, such as ornamental cropping or food production, and also due to the antimicrobial, antifungal, insecticidal, and antioxidant effects of their essential oils.[1–3]

The thyme (*Thymus vulgaris* L.) plant is a perennial herbaceous shrub belonging to the family Lamiaceae. It is commonly grown wild throughout the Mediterranean region (Spain, France, and Italy) and in almost every Caribbean country.[4]

Thyme is an aromatic medicinal plant of increasing economic importance for Europe, North Africa, and North America.[5] The leaves can be used fresh or dried as a spice. Moreover, they can be used as herbal teas and condiments. Essential oil extracted from fresh leaves and flowers can be used as an aroma additive in food, pharmaceuticals, and cosmetics[6,7] and has been described as a storage alternative to chemical compounds due to its fungicidal ability in fruits.[8,9] Thyme also has different beneficial effects; for example, antiseptic, carminative, antimicrobial, and antioxidative properties.[10] Thyme is highly perishable, and drying is a useful means to increase the shelf life of thyme for further use.

Drying is a preservation method used to ensure the microbial safety of biological products. Convective drying (CD) is still the most popular method applied to reduce the moisture content of fruits and vegetables. However, this method has several disadvantages and limitations; for instance, it the temperature used during the process results in degradation of important flavor compounds and nutritional functions, as well as color alteration. Freeze drying (FD) is also a popular drying method that has been successfully applied in strawberries[11] but has resulted in some loss of flavor.[12]

The drying time can be greatly reduced[13] and the quality of finished product insured[14] by applying microwave energy to the dried material. Drying using a microwave method under a vacuum is a modern, efficient method of food preservation.[15] Lower pressures induce faster evaporation of water from the material at relativity low

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temperature,[16] which can reduce the chemical alterations within the dried product.[17] The vacuum–microwave (VM) method is not yet common in the industry, though drying of tomatoes,[15,18] basil,[19] rosemary,[20,21] oregano,[16] beetroot,[22] and garlic cloves and slices,[23] among others, has been investigated. However, at the beginning of VM dehydration the intensive water evaporation from the plant material may exceed the vacuum pump capacity. This requires a reduction in the raw material subjected to drying or application of a large vacuum installation. This problem can be overcome by predrying of the material using a convective method. As a result of predrying, the mass loads of VM equipment can be radically decreased.[24]

Predrying of the plant materials by convective method before convective predrying combined with vacuum–microwave finish drying (CPD-VMFD) may reduce the total cost of dehydration and improve the quality of commercially dehydrated products, posing a significant contribution to the fruit processing industry.[24] However, no research has been conducted on the effects of the combined method, CPD-VMFD, on the quality of thyme.

Volatile aroma compounds are the most sensitive components in food drying.[25] The effect of drying on the composition of volatile flavor constituents of various aromatic plants and vegetables has been the subject of numerous studies,[16,19–21] which have shown that the changes in the concentrations of the volatile compounds during drying depend on several factors, such as the drying method and characteristics of the product being dried.

Therefore, the main objective of this study was to explore the possibility of using different conditions (time, temperature, and wattage) of CD, VM drying (VMD), and CPD-VMFD for processing thyme based on the odor quality and volatile composition of dried products.

MATERIALS AND METHODS

Plant Material and Processing of Samples

Fresh thyme plants (*Thymus vulgaris* L.) were bought from a Swedeponic greenhouse in Kraśnicza Wola, Poland, chopped into 2- to 3-cm pieces, and mixed for homogenization. The initial moisture content, M_0, of the plants was 11.2 kg water/kg dry matter, which corresponds to 91.8% (wb). The moisture content was determined by drying samples in a vacuum oven (model SPT-200, ZEAMiL Horyzont, Kraków, Poland) for 12 h at 60°C to a final constant weight. The final moisture contents of all maximally dried samples were similar and averaged 0.06 kg water/kg dry matter.

Thyme samples of approximately 60 g were subjected to four different drying protocols:

1. Convective drying was done using drying equipment designed and built at the Institute of Agricultural Engineering, Wroclaw University of Environmental and Life Sciences. Thyme samples (≈ 60 g) were placed in a 100-mm-diameter tray without compaction. Convective drying was conducted at three different temperatures, 40, 50, and 60°C, with an air velocity of $0.8\,\mathrm{m\,s^{-1}}$. The hot air stream flowed perpendicular to the layer of material been dried, which was not fluidized even during the final stages of the drying process.
2. Microwave drying was carried out in a model SM 200 dryer (Plazmatronika, Wroclaw, Poland) connected to a vacuum system consisting of a vacuum pump (model BL 30P, Tepro, Koszalin, Poland), a vacuum gauge (model MP 211, Elvac, Bobolice, Poland), and a $0.15\,\mathrm{m^3}$ compensation reservoir. The dryer was operated at three different power levels: 240, 360, and 480 W. Thyme samples were placed in a cylindrical container of organic glass with a volume of 6.8 L. The pressure in the container varied from 4 to 6 kPa. To avoid local overheating of herbs, the container rotated at a speed of 6 rpm, and an electric fan was installed at the bottom of the dryer, producing an air stream of 22°C at a velocity of $1\,\mathrm{m\,s^{-1}}$.
3. Combined drying consisted of CPD at temperatures 40, 50, and 60°C until a preestablished moisture content of $3\,\mathrm{kg\ kg^{-1}}$ db, followed by VMFD at 240, 360, and 480 W for each convective drying condition. The times of CPD necessary to obtain the preestablished moisture content ($3\,\mathrm{kg\ kg^{-1}}$ db) at 40, 50, and 60°C were 285, 105, and 65 min, respectively; these times were estimated on the basis of the CD kinetics previously determined.
4. Freeze drying was performed during 24 h at a pressure of 65 Pa and temperature of −40°C in the drying chamber. The temperature of the heating plate causing the process of sublimation was 30°C.

Drying Kinetics

The drying kinetics were determined on the basis of mass losses of thyme samples. The moisture ratio, MR, was determined from the equation:

$$MR = \frac{M(t) - M_e}{M_0 - M_e} \tag{1}$$

The equilibrium moisture content M_e was determined during the final stage of drying as an asymptotic value of the function fitted to the experimental points using Table Curve 2D Windows v2.03 (Jandel Scientific Software, San José, CA, USA).[26] The M_e values were a bit lower than final moisture content of maximally dried samples. Such low values of M_e had a negligible effect on MR, which depended mainly on the values of $M(t)$ and M_0. Therefore, some authors[27,28] determined MR as the ratio of $M(t)$ to M_0.

Different functions/models, as simple as possible, were fit to the experimental points representing the decrease in

MR with time using Table Curve 2D Windows v2.03 with the objective of maximizing the coefficient of determination (R^2); only the model providing the best R^2 is described in this article.

Temperature

Thyme samples were removed from the VM dryer and placed on a tray and immediately subjected to temperature measurement with an infrared thermometer. The maximum temperature observed was recorded. It is expected that the local temperature within the material during drying was higher; however, a direct measurement in the drying chamber under vacuum is not possible because the measuring elements are heated by the microwave emission.

Extraction Procedure of Volatile Aroma Compounds

Hydrodistillation (HD) using a Deryng apparatus was used for the extraction of the volatile compounds of thyme (fresh and dried). A suspension of 2 g of thyme was placed in a 500-mL round flask together with 100 mL of double-distilled water and 200 µg of 2-undecanone as the internal standard. The sample flask was heated for 1 h after reaching the boiling point. The vapors were condensed by means of a cold refrigerant. One milliliter of cyclohexane was added to the Deryng apparatus at the beginning of the hydrodistillation process to retain the essential oil isolated from the thyme samples. After 60 min of extraction, the solvent, containing the aroma compounds, was transferred into 2.5-mL vials and kept at −15°C until gas chromatography–mass spectrometry (GC-MS) analyses were performed. Analyses were run in triplicate.

Chromatographic Analyses

Isolation and identification of the volatile compounds were performed on a gas chromatograph (Saturn 2000 Varian Chrompack, Altmann Analytik GmbH & Co. KG, Munich, Germany) with a TRACE TR-5 column (5% phenyl methylpolysiloxane) with a 30 m × 0.53 mm ID × 1.0 µm film. The mass spectrometer, equipped with an ion trap analyzer, was set at 1508 m/z for all analyses with an electron multiplier voltage of 1,350 V. Scanning was performed from m/z 39 to 400 in electronic impact (EI) at 70 eV mode at 1 scan s^{-1}. Analyses were carried out using helium as the carrier gas at a flow rate of 1.0 mL min^{-1} in a split ratio of 1:20 and the following program: (a) 80°C for 0 min; (b) rate of 5.0°C min^{-1} from 80 to 200°C; (c) rate of 25°C min^{-1} from 200 to 280°C and hold for 5 min. The injector and detector were held at 200 and 300°C, respectively. One microliter of the extracts was injected.

Most of the compounds were identified by using three different analytical methods: (1) Kovats index (KI), (2) GC-MS retention times (authentic chemicals), and (3) mass spectra, with similarity indexes >90% (authentic chemicals and NIST05 spectral library collection). Identification was considered tentative when it was based only on mass spectral data.

Quantification of the volatile compounds was performed on a GC (model 2010, Shimadzu, Tokyo, Japan) with a flame ionization detector (FID). The column and chromatographic conditions were those previously reported for the GC-MS analysis. The injector temperature was 200°C and nitrogen was used as the carrier gas (1 mL min^{-1}). Quantification was obtained from electronic integration measurements using FID. 2-Undecanone was added as the internal standard (200 µg) at the beginning of the distillation procedure to simulate the behavior of volatile compounds in thyme. This chemical was chosen as the internal standard after determining the absence of thyme and that it separated well from other volatiles, possessed similar FID and MS response factors as most of the volatiles in thyme essential oil, was stable at high temperatures, and did not react with water. All of the aroma standards used for identification and quantification purposes were food grade.[29]

Sensory Evaluation with Trained Panel

Sensory evaluation with a trained panel was used to discriminate the intensities of the main aromatic characteristics of the thyme samples. Thyme was tested by eight panelists, aged 23 to 44 years (four female and four male, all members of the University Miguel Hernandez), with wide sensory evaluation experience (over 500 h) and trained in descriptive evaluation of fruits and vegetables.[30]

Thyme samples were assessed using an odor profile method. Initially, panelists discussed the odor attributes of thyme during two preliminary orientation sessions, each lasting 90 min, until they had agreed on their use of odor attributes. During these orientation experiments, panelists evaluated different coded samples of fresh and dried thyme from different geographical areas of Spain and commercial brands. Panelists agreed that the odor of thyme samples could be described using 10 attributes: fresh thyme, vegetable, herbaceous, balsamic, spice, hay-like, sweet, earthy, woody, and infusion. Samples with the highest and lowest intensities of these attributes were used as standards.

Measurements were performed in individual booths with controlled illumination and temperature.[30] The individual products were scored for the intensity of different odor attributes on a scale of 0 to 10, where 0 = *nonperceptible intensity* and 10 = *extremely high intensity*. Samples were coded with three-digit numbers and presented in 100-mL plastic beakers with lids, which stood at room temperature for 30 min prior to analyses.

Statistical Analysis

One-way analysis of variance (ANOVA) and Duncan's multiple range test were used for comparison of the experimental results. Homogenous groups and the least significant difference (LSD) were determined according to

Tukey's test (at a significance level of $p \leq 0.05$). Statistical analyses were performed using Statgraphics Plus 5.0 software (Manugistics, Inc., Rockville, MD).

RESULTS AND DISCUSSION

Drying Kinetics

According to experimental data obtained during CD, the loss of water content in thyme can be described by means of a two-term exponential model (Fig. 1):

$$MR = b_1 \cdot e^{-k_1 \cdot t} + b_2 \cdot e^{-k_2 \cdot t} \tag{2}$$

The mathematical form of this model indicates that the decrease in the moisture ratio, MR, can be divided into a constant rate period and a falling rate period (Fig. 2). The values of the drying constants, k_1 and k_2, as well as those of parameters b_1 and b_2 are shown in Table 1.

For CD (lines at the bottom of Fig. 2), the constant rate period lasted until the MR reached an approximate value of 0.75. However, only the falling rate period was needed to describe CD at 60°C where parameters b_2 and k_2 in Eq. (2) were zero; in this case, Eq. (2) can be simplified to a form of the Lewis equation. This simple exponential equation was also found to be the best for modeling hot air drying of oregano,[16] rosemary,[20] spearmint,[31] and betel leaves[32] and two-term exponential equation was one of the five models used to satisfactorily fit the experimental data obtained during hot air drying of purslane.[33]

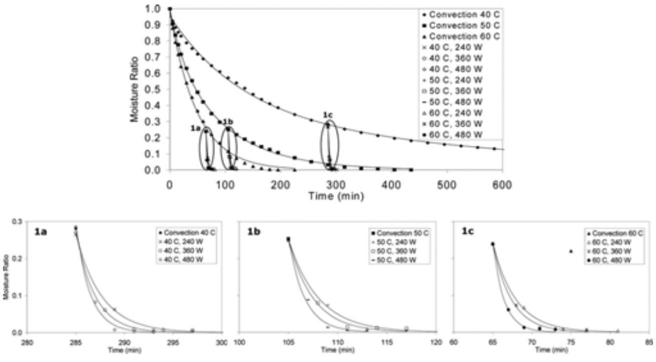

FIG. 1. Drying kinetics of thyme dehydrated using convective drying at temperatures of 40, 50, and 60°C and VM finish drying at (1a) 240 W, (1b) 360 W, and (1c) 480 W after convective predrying at different temperatures.

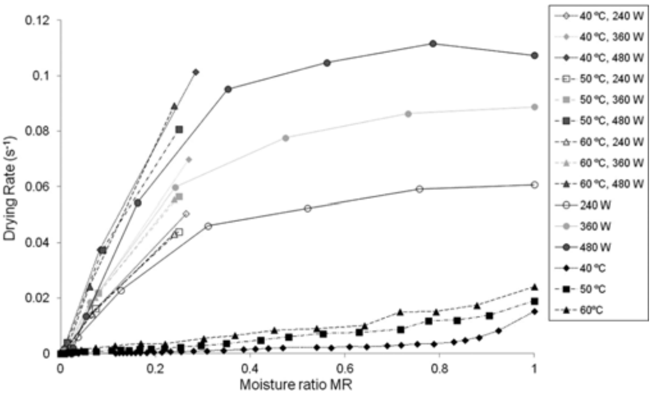

FIG. 2. Drying rate versus moisture ratio for thyme dehydrated by different drying methods.

During VMD (Fig. 3), two drying periods, divided by a critical point of the moisture ratio (K), were observed.[34] The critical point K was achieved at moisture ratios of 0.311, 0.242, and 0.162 kg kg^{-1} after 12, 9, and 8 min of drying at microwave powers of 240, 360, and 480 W, respectively. The decrease in moisture content during the constant rate period (until K was reached) was described by the following linear function:

$$MR = 1 - a \cdot t \tag{3}$$

and during the falling rate period (from point K until the end of the drying process), the water loss was described by an exponential function:

$$MR = b \cdot e^{-k \cdot (t - t')} \tag{4}$$

Similar drying kinetics were previously found for rosemary and oregano herbs dehydrated using a VM method.[21,35] Drying of okra (*Hibiscus esculenta* L.) using a microwave oven also presented these same two drying periods.[27] The presence of a constant rate period during drying of thin leafy spices can be explained by internal heating caused by microwaves penetrating the interior of the wet material. During this period of drying the relatively high temperature generated by microwaves inside the cellular structure contributes to the high water vapor pressure.[36] This pressure can maintain the removal of water vapor at a constant drying rate until the critical point K is reached. In the case of other plant materials with higher densities, such as garlic, microwave heating results in an increase in the drying rate until the critical point followed by a decrease in the drying rate beyond that point.[23] This increase in the drying rate is associated with an increase in the dried material temperature, which enhances diffusion of water from the interior of the material toward its surface.[13] Other factors influencing the absorption of microwave energy, which determines the drying kinetics, are the thickness and dielectric properties of the material.[37]

The experimental values of the parameters a, b, t' and drying constant k from functions (3) and (4), as well as the drying time, are summarized in Table 2. Parameter a is the slope of the straight line representing the drying

TABLE 1
Parameters of convective drying kinetics: b_1, b_2, k_1, and k_2 as well as drying time for different drying temperatures

	Drying kinetics					
	$MR = b_1 \cdot e^{-k_1 \cdot t} + b_2 \cdot e^{-k_2 \cdot t}$					
Drying temperature (°C)	b_1	k_1	b_2	k_2	R^2	Drying time (min)
40	0.5636	8.131×10^{-3}	0.3921	1.929×10^{-3}	0.9974	1,585
50	0.2306	42.25×10^{-3}	0.7641	10.45×10^{-3}	0.9995	435
60	0.9851	20.43×10^{-3}	0	0	0.9981	225

kinetics in the constant rate period; this parameter also indicates the drying rate in that period. Parameters b and t' are moisture and time coordinates of the critical point K, respectively. An increase in the microwave power from 240 to 480 W was related to increases in the values of parameter a and drying constant k from 0.0583 to 0.1054 and from 0.2426 to 0.5139, respectively. The values of parameter t' were 12, 9, and 8 min for microwave powers of 240, 360, and 480 W, respectively.

The drying time was the shortest when values of parameter a and drying constant k were the highest. An increase in the microwave power from 240 to 480 W reduced the drying time from 28 to 14 min. On the other hand, convective drying at 60 and 40°C lasted as much as 225 and 1,585 min, respectively.

In the combined method, VMFD drying kinetics for thyme also had an exponential character. An increase in the microwave power from 240 to 480 W at 40, 50, and 60°C resulted in a significant increase in the value of drying constant k from 0.3706 to 0.6658, 0.3245 to 0.5974, and 0.3338 to 0.6857, respectively (Table 3). Figure 2 shows that the drying rate of samples that were finish dried at the same microwave power in the range 240–480 W was almost constant despite the air temperature during the convective predrying step. However, the total drying time for thyme samples using the combined method (CPD-VMFD) was shorter when higher temperatures were applied during CPD (Figs. 1a–1c). This total drying time was additionally decreased by increasing the microwave wattage during VMFD (Table 3).

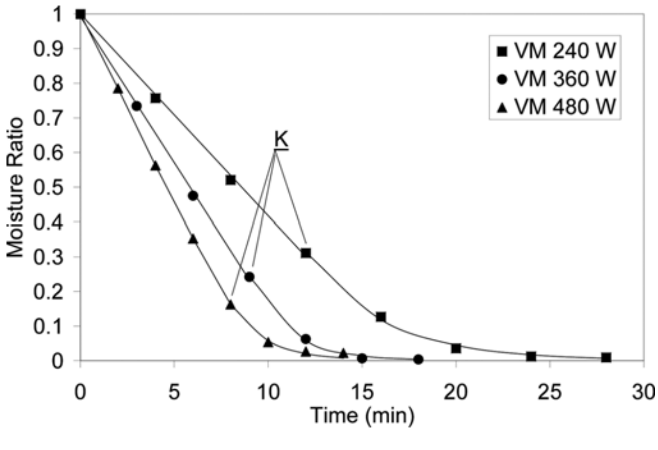

FIG. 3. Drying kinetics of thyme dried using VM at 240, 360, and 480 W (K = critical point).

Temperature

The temperature profiles obtained during VM drying indicate that the mean temperature of the dried material depends on both microwave power and duration. Namely, during VM the lowest mean temperature 43.5°C was found for the samples dried for 18 min at the medium microwave power level (360 W). The increase in microwave power to 480 W increased the mean temperature to 44.3°C despite the reduction in drying time of 4 min. On the other hand, microwave heating of the samples for the longest time (28 min) at 240 W increased their mean temperature to 45.7°C (Table 2). The same regularity was found for the VMFD samples after convective predrying at 40 or 50°C. However, for the VMFD samples after convective predrying at 60°C, the mean temperature of the samples depended on the microwave wattage. This may be related to the fact that samples predried at 60°C reached slightly lower moisture ratios before VMFD, indicated by the parameter b (from 0.2394 to 2399), than samples predried at 50°C (from 0.2497 to 0.2503) and 40°C (from 0.2648 to 0.2862; Table 3). This lower moisture ratio, strictly associated with lower moisture content, reduced the action capacity of microwaves driving the water dipoles to rotation within the material.[16]

Volatile Compounds in Fresh Thyme

Table 4 shows the profile of volatiles extracted from fresh Polish thyme by hydrodistillation. Hydrodistillation with a Deryng apparatus has been applied successfully in previous studies to different fruits and herbs, such as pomegranates,[38] rosemary,[20,21] basil,[19] and oregano.[16]

TABLE 2
Parameters of VM drying kinetics: *a, b, t′*, and *k* as well as drying time and sample temperature for different microwave powers

	Drying kinetics								
	$MR = 1 - a \cdot t$		$MR = b \cdot e^{-k \cdot (t-t')}$						
Power (W)	a	R^2	b	K	t'	R^2	Drying time (min)	Sample temperature (°C)
240	0.0583	0.9994	0.3128	0.2426	12	0.9970	28	45.7 ± 2.0a
360	0.0844	0.9991	0.2424	0.4717	9	0.9982	18	43.5 ± 2.9a
480	0.1054	0.9992	0.1617	0.5139	8	0.9949	14	44.3 ± 1.6a

Values followed by the same letter, within the same row, are not significantly different ($p < 0.05$), Tukey's multiple range test.

The main chemical groups of the volatile compounds in the Polish fresh thyme were as follows: monoterpenoids (representing 42.4% of the total concentration of volatiles), followed by monoterpenes (36.4%), sesquiterpenes (6.1%), and sesquiterpenoids (6.1%). Other compounds such as aldehydes, esters, and alcohols were present in minor concentrations. Monoterpenoids and monoterpenes represented almost 90% of the total volatiles in Polish thyme.

The total concentration of volatile compounds in the mixture of leaves, branches, and stems used in this experiment was 1,167 mg 100 g^{-1} db. A total of 33 compounds were tentatively identified by mass spectra, standards, and Kovats indexes. The most abundant compound found in fresh thyme was thymol (732 mg 100 g^{-1} db), as reported in previous studies.[25,39–41] Much lower values than those obtained for thymol were obtained for γ-terpinene (131 mg 100 g^{-1} db), *p*-cymene (56 mg 100 g^{-1} db), caryophyllene (23.9 mg 100 g^{-1} db), and α-terpinene (22.5 mg 100 g^{-1} db). The percentages and relative concentrations of these five compounds could be important in determining the quality of the different dried samples of thyme. It is important to remember that the main sensory descriptors for these compounds are[29] (1) thymol: woody, fruity, sweet, smoky, wine-like, spicy, earthy, coffee, and minty; (2) γ-terpinene: herbaceous and citrus; (3) *p*-cymene: weak and citrus; (4) caryophyllene: terpene odor, woody, and spicy; and (5) α-terpinene: berry, lemon, vegetable, woody, and pepper.

The composition and concentrations of essential oils from aromatic herbs depend on many factors, including climatic and soil conditions, stage of the vegetative cycle, seasonal variation, etc.[39] There is scientific evidence of the thyme essential composition from different geographical origins and with the employment of different isolation techniques. For instance, Usai et al.[41] found 40 different compounds in Italian thyme isolated by a Clevenger

TABLE 3
Parameters of VMFD kinetics: *b, t″*, and *k* as well as combined drying time and sample temperature for different drying conditions

Drying conditions		Drying kinetics					
		$MR = b \cdot e^{-k \cdot (t-t)}$					
Temperature (°C)	Power (W)	b	K	t''	R^2	Drying time (min)	Sample temperature (°C)
40	240	0.2648	0.3706	285	0.9988	301	42.8 ± 3.0ab
	360	0.2707	0.5020		0.9992	297	40.0 ± 2.2ab
	480	0.2862	0.6658		0.9961	293	44.3 ± 6.3ab
50	240	0.2501	0.3245	105	0.9970	121	46.5 ± 1.9ab
	360	0.2497	0.3945		0.9957	117	36.3 ± 4.6a
	480	0.2503	0.5974		0.9956	113	45.5 ± 4.4b
60	240	0.2398	0.3338	65	0.9981	81	38.3 ± 1.5b
	360	0.2399	0.4158		0.9977	77	39.0 ± 2.8ab
	480	0.2394	0.6857		0.9989	73	39.8 ± 3.3ab

Values followed by the same letter, within the same row, are not significantly different ($p < 0.05$), Tukey's multiple range test.

TABLE 4

Identification of essential oils found in thyme samples and concentration of fresh and freeze-, convective-, and vacuum–microwave-dried thyme leaves

							CD			VMD		
		Kovats indexes			Fresh thyme	FD	40°C	50°C	60°C	240 W	360 W	480 W
Compound	RT	Experimental	Literature	ANOVA[a]	Concentration (mg 100 g^{-1} db)							
3-Hexen-1-ol	5.13	859	850	**	0.70a[b]	0.49b	0e	0.08d	0.08d	0.14 cd	0e	0.20c
α-Thujene	6.75	929	932	*	16.5a	10.0b	14.9a	12.5ab	11.5b	15.4a	16.5a	14.0a
α-Pinene	7.07	946	939	*	7.86a	6.86ab	6.87ab	6.19ab	5.66b	7.22a	7.78a	7.35a
Camphene	7.6	965	954	**	4.34a	5.39a	2.53b	2.80b	2.33b	3.47ab	2.59b	4.61a
1-Octen-3-ol	7.95	977	982	**	6.57a	5.00b	5.05b	4.83b	4.81b	7.36a	5.93a	5.59ab
Sabinene	8.03	980	975	***	2.46b	5.00a	1.41c	1.27c	1.24c	2.22b	2.35b	2.16b
β-Myrcene	8.16	985	991	**	15.0b	9.80c	18.4a	15.2b	12.9bc	22.4a	17.2ab	13.9bc
β-Pinene	8.33	991	979	NS	1.88	1.47	1.84	1.69	1.47	2.64	2.10	1.96
3-Octanol	8.37	995	994	NS	1.76	1.37	2.93	1.53	1.47	22.4	1.85	1.37
α-Phellandrene	8.94	1,014	1,003	NS	3.52	2.25	3.33	2.88	2.56	3.89	3.83	3.04
α-Terpinene	9.19	1,021	1,017	***	22.5ab	14.7c	23.9a	20.8b	11.9c	24.0a	26.3a	21.1b
p-Cymene	9.46	1,032	1,015	***	56.0a	52.0a	48.2ab	42.1b	43.3b	54.9a	55.6a	52.5a
Limonene	9.57	1,035	1,029	NS	3.05	2.16	2.93	2.54	2.17	3.33	3.21	2.94
Eucalyptol	9.72	1,038	1,031	*	4.58a	2.94b	3.54b	3.39b	3.10b	4.44a	3.95ab	4.51a
γ-Terpinene	10.33	1,070	1,060	***	131b	97.3c	122b	114bc	95.3c	158a	145ab	134b
trans-Sabinene hydrate	10.78	1,077	1,070	**	14.9ab	8.63d	13.4b	11.5bc	10.9c	16.9a	16.3a	12.8b
Terpinolene	11.14	1,081	1,089	NS	1.17	0.39	1.01	0.76	0.78	1.25	0.99	0.98
Linalool	11.3	1,087	1,097	***	14.0ab	9.41c	12.5b	10.8c	9.53c	16.7a	15.1a	12.5b
Sabinene hydrate	11.72	1,093	1,098	*	2.46a	0.78b	2.32a	1.86ab	1.78ab	2.92a	2.72a	2.16a
Camphor	13.4	1,157	1,146	*	2.46ab	3.73a	1.11c	1.02c	0.93c	1.67bc	1.11c	2.06b
Borneol	14.04	1,178	1,169	***	12.9b	16.9a	5.96d	7.88c	5.04d	8.89c	6.05d	12.0b
α-Terpineol	14.5	1,194	1,189	NS	0.94	0.29	0.91	0.85	0.70	1.11	1.11	0.88
trans-Dihydrocarvone	14.65	1,205	1,200	NS	0.59	0.20	0.51	0.51	0.47	0.69	0.62	0.59
Thymol methyl ether	15.15	1,221	1,225	*	2.93bc	2.45c	3.54b	3.64b	1.78c	3.61b	4.32a	2.94bc
Carvacrol methyl ether	15.44	1,241	1,244	**	8.92b	5.49c	11.1a	8.90b	6.82c	8.33b	12.3a	7.45bc
Thymoquinon	16.09	1,248	1,250	NS	1.99	0.49	0.81	0.85	1.01	0.69	1.11	1.27
Thymol	16.97	1,278	1,277	***	732b	590c	571c	479d	451d	870a	757b	558c
Carvacrol	17.24	1,290	1,287	***	34.1b	24.9c	28.3b	22.6c	21.5c	43.1a	35.1b	38.9ab
Thymol acetate	18.41	1,339	1,350	***	5.63a	0.78c	3.94b	4.15b	3.10b	6.94a	6.91a	2.65bc
Caryophyllene	20.89	1,424	1,419	***	23.9b	16.1c	36.8a	22.1b	21.7b	30.6a	31.6a	16.6c
Germacrene D	22.46	1,487	1,485	**	9.39a	4.80b	10.1a	7.37b	6.82b	11.5a	11.6a	5.49b
Germacrene D-4-ol	24.96	1,560	1,567	*	4.11a	2.16b	2.83b	2.88b	2.33b	5.14a	3.95a	2.06b
trans-Cadinol	26.25	1,653	1,640	***	17.5b	42.0a	19.6b	18.0b	19.1b	17.1b	23.0b	21.4b
	Total			**	1,167ab	956b	1,000b	837c	765c	1,379a	1,224a	970b

Values followed by the same letter, within the same row, are not significantly different ($p < 0.05$), Tukey's multiple range test. RT = retention time.

[a] NS = nonsignificant *F* ratio ($p < 0.05$). Not significant at $^{*}p < 0.05$, $^{**}p < 0.01$, and $^{***}p < 0.001$, respectively.

[b] Treatment means of the ANOVA test (values are the mean value of three replications).

apparatus, with thymol as the major compound followed by *p*-cymene and γ-terpinene. Moreover, Rouatbi et al.[40] found 27 compounds in French thyme, with thymol and *p*-cymene as the most important compounds, which were isolated with superheated steam. Similar results were reported by Venskutonis,[25] who used a Likens-Nickerson apparatus to isolate 74 compounds from essential oils of Greek thyme, with thymol, *p*-cymene, and γ-terpinene as the major compounds. However, Viuda-Martos et al.[42] found 52 peaks in commercial essential oils from thyme and the predominant compounds were terpinen-4-ol, γ-terpinene, and *cis*-sabine hydrate. In general, it can be concluded that thymol, γ-terpinene, and *p*-cymene are predominant in the essential oils of fresh thyme.

Volatile Compounds in Dried Thyme

Table 4 shows the volatile compounds identified in fresh and dried thyme. The initial working hypothesis was that VMD should provide a final product of better quality than CD. However, the losses originated after VMD varied considerably from one species to another. Whereas in rosemary VMD produced greater volatile losses than CD, in sweet basil losses were greater with CD.[19,43]

In general, CD significantly reduced the total concentration of volatile compounds in thyme, and the best results were obtained after VMD, which did not provide statistically different concentrations of volatiles at 240 and 360 W (1,379 and 1,224 mg 100 g^{-1}, respectively) than those of the fresh material (1,167 mg 100 g^{-1}). The higher values of these two treatments compared to the fresh material meant that VMD at low powers led to dried material of the highest aromatic quality. However, the differences in the values were due to the heterogeneity of the plant material and the results were statistically equivalent.

FD is, in general, considered a control treatment, leading to high-quality products. However, in the current study, samples dried by FD presented lower total volatile contents (956 mg 100 g^{-1} db) than samples dried by VMD at 240 W (1,379 mg 100 g^{-1}) and 360 W (1,224 mg 100 g^{-1}) and similar to that of sample C dried at 40°C (1,000 mg 100 g^{-1}).

Venskutonis et al.[44] concluded that the total amount of volatile compounds in air-dried (30°C) and freeze-dried thyme samples were comparable, and the greatest changes were observed during storage. The concentrations of thymol, the predominant compound, were 647, 692, and 691 mg 100 g^{-1} db in fresh, air-dried, and freeze-dried thyme, respectively. Venskutonis[25] reported that the total concentration of volatile compounds in thyme significantly decreased when dried at 60°C. This total concentration was not changed during drying at 30°C and increased by 20% after freeze drying. However, the author did not explain this increase. Usai et al.[41] reported that air drying resulted in better retention of volatiles in thyme than freeze drying. However, FD preserved thymol and carvacrol better than CD.

Volatile losses increased with higher microwave powers and higher air temperatures. Consequently, the best results with regard to volatile composition were obtained for samples dried by VM at 240 W (1,379 mg 100 g^{-1}) and convectively dried at 40°C (1,000 mg 100 g^{-1}).

The changes with the treatment conditions for individual chemicals were quite similar to those previously described for the total concentration of volatile compounds in dried thyme. For instance, the concentration of thymol was 732 mg 100 g^{-1} in fresh thyme and changed to 870, 590, and 571 mg 100 g^{-1} for samples dried by VMD, FD, and CD, respectively. An increase in microwave power during VMD led to significant reductions in the thymol content from 870 mg 100 g^{-1} at 240 W to 558 mg 100 g^{-1} at 480 W.

According to Rao et al.,[45] the loss of volatile oil in herbs is related to energy input in the microwave oven. Our experimental results agreed quite well with this statement. Thyme samples dried using CPD-VMFD presented significant volatile losses as the treatment intensity (temperature or microwave power) increased. Samples predried at 40, 50, or 60°C and finish dried at 240 W presented total volatile concentrations of 1,127, 1,065, and 943 mg 100 g^{-1}, respectively (Table 5). In a similar trend, samples predried at 60°C and finish dried at 240, 360, and 480 W presented total volatile concentrations of 943, 830, and 731 mg 100 g^{-1}, respectively (Table 5).

In general, the combination of CPD and VMFD resulted in high-quality dried thyme samples and significantly reduced the drying time compared to CD. In addition, the total concentrations of volatiles in samples dried by VMFD at 240 W, at all CPD temperatures assayed, were statistically equivalent to those of fresh thyme and of the best VMD treatments (240 and 360 W).

To summarize, the drying method that led to the highest total contents of volatile compounds was VMD at 240 W, proving that VMD is well suited for drying of thyme. The next best option is CPD (40°C) and VMFD (240 W).

Sensory Analyses with a Trained Panel

In general, the drying method significantly affected the intensities of the main sensory attributes of dried thyme. Attributes such as fresh, vegetable, pine, and herbaceous odor significantly decreased ($p < 0.01$) after drying compared to the fresh sample and are considered indicators of freshness (freshness attributes); the remaining attributes—balsamic, spicy, hay-like, sweet, earthy, woody, and infusion odor—increased after dehydration of the fresh herbs and are considered indicators of the drying process (dried attributes). Some of these experimental findings were related to the reduction in moisture content, which, for example, could be responsible for the increased woody odor and reduced vegetable odor.

TABLE 5
Concentration of thyme leaves affected by different conditions of combined drying

		CPD-VMFD								
		40°C			50°C			60°C		
		240 W	360 W	480 W	240 W	360 W	480 W	240 W	360 W	480 W
Compound	ANOVA[a]	Concentration (mg 100 g^{-1} db)								
3-Hexen-1-ol	*	0.34a[b]	0.00c	0.00c	0.11b	0.09b	0.08b	0.00c	0.08b	0.00c
α-Thujene	**	13.5a	14.3a	14.6a	14.2a	9.3b	12.1a	9.4b	12.4a	10.8ab
α-Pinene	NS	6.70	7.13	6.80	6.56	5.31	6.21	6.00	5.88	5.04
Camphene	NS	2.73	2.67	2.89	3.33	3.89	3.63	2.00	2.52	1.78
1-Octen-3-ol	*	5.45a	5.35ab	4.64ab	6.56a	4.96ab	4.76ab	4.95ab	4.71ab	3.56b
Sabinene	NS	1.93	1.88	2.27	1.94	1.06	1.29	1.71	1.76	1.56
β-Myrcene	***	17.5a	16.8a	15.1b	14.7b	10.2c	12.9c	13.9bc	14.5b	8.44d
β-Pinene	***	1.70b	1.78b	2.89b	1.72b	0.88b	1.45b	1.71b	15.38a	2.30b
3-Octanol	***	3.07b	1.68b	1.75b	1.83b	1.24b	1.69b	1.43b	15.38a	2.30b
α-Phellandrene	NS	2.95	3.37	3.20	3.12	2.12	2.50	3.05	2.86	2.52
α-Terpinene	***	24.7a	22.6a	22.9a	22.2a	13.3c	15.6bc	20.6a	19.3ab	17.9b
p-Cymene	NS	51.0	56.1	53.9	58.2	35.1	46.3	43.9	41.8	33.1
Limonene	NS	2.84	2.87	2.68	2.80	1.95	2.34	2.57	2.44	2.07
Eucalyptol	NS	4.20	3.66	3.51	3.98	3.19	2.98	3.33	3.28	2.52
γ-Terpinene	***	135a	122a	123a	125a	88.4c	101b	113ab	98.9b	98.5b
trans-Sabinene hydrate	**	15.5a	14.2a	13.4ab	14.4a	9.82b	10.9b	12.5ab	10.7b	9.19b
Terpinolene	NS	0.91	0.79	0.82	0.97	0.35	0.81	0.76	0.50	0.59
Linalool	*	10.3b	12.8a	12.9a	12.4a	9.03	10.6b	11.3ab	10.8b	9.26b
Sabinene hydrate	NS	2.61	2.38	2.27	2.47	1.59	1.77	2.10	1.68	1.56
Camphor	NS	1.14	0.89	1.03	1.29	2.04	1.77	0.48	1.18	0.67
Borneol	**	7.05ab	5.35b	6.29b	10.6a	12.5a	11.3a	4.76b	5.63b	4.00b
α-Terpineol	NS	1.14	0.89	0.93	1.08	0.80	0.65	0.86	0.42	0.67
trans-Dihydrocarvone	NS	0.45	0.59	0.52	0.54	0.44	0.40	0.48	0.25	0.37
Thymol methyl ether	NS	2.84	2.77	4.02	3.98	2.04	3.39	3.24	2.52	2.89
Carvacrol methyl ether	NS	8.75	8.22	10.0	8.49	6.02	7.26	7.33	6.97	7.33
Thymoquinon	NS	0.57	1.09	0.82	2.04	1.95	1.21	1.14	1.09	0.74
Thymol	**	697a	568b	621ab	654a	562b	457c	571b	470c	426c
Carvacrol	***	38.1a	30.4a	34.9a	31.1a	31.9a	20.8b	33.8a	23.4b	21.7b
Thymol acetate	***	5.68a	4.95a	6.19a	3.01b	0.97d	2.42c	4.38ab	2.77c	2.74c
Caryophyllene	**	26.9a	31.5a	28.6a	25.9a	16.0b	20.7b	28.4a	21.8b	23.0ab
Germacrene D	NS	9.89	9.90	10.2	9.03	5.22	7.18	10.6	7.90	8.96
Germacrene D-4-ol	NS	4.43	3.96	3.81	3.01	2.12	2.10	3.43	2.69	2.81
trans-Cadinol	***	19.7b	19.1b	2.9c	15.4b	29.5a	21.6b	19.0b	19.2b	16.1b
Total	**	1,127a	980a	1,021a	1,065a	875b	797b	943a	830b	731c

Values followed by the same letter, within the same row, are not significantly different ($p < 0.05$), Tukey's multiple range test.

[a] NS = nonsignificant *F* ratio ($p < 0.05$). Not significant at $^{*}p < 0.05$, $^{**}p < 0.01$, and $^{***}p < 0.001$, respectively.

[b] Treatment means of the ANOVA test (values are the mean value of three replications).

Figure 4 shows the descriptive sensory analysis profiles of different thyme samples. The descriptors selected were previously used for other dry herbs, such as parsley, bay leaf and spearmint,[46] and rosemary.[21] Fresh thyme was characterized by intense fresh (9.7), vegetable (9.1), and herbaceous (8.9) odor notes.

Generally, samples dried by FD are considered high-quality products and this was the case for freeze-dried thyme, which had high notes of some key descriptors; for example, fresh thyme, 6.7; vegetable, 7.4; and herbaceous, 6.1.

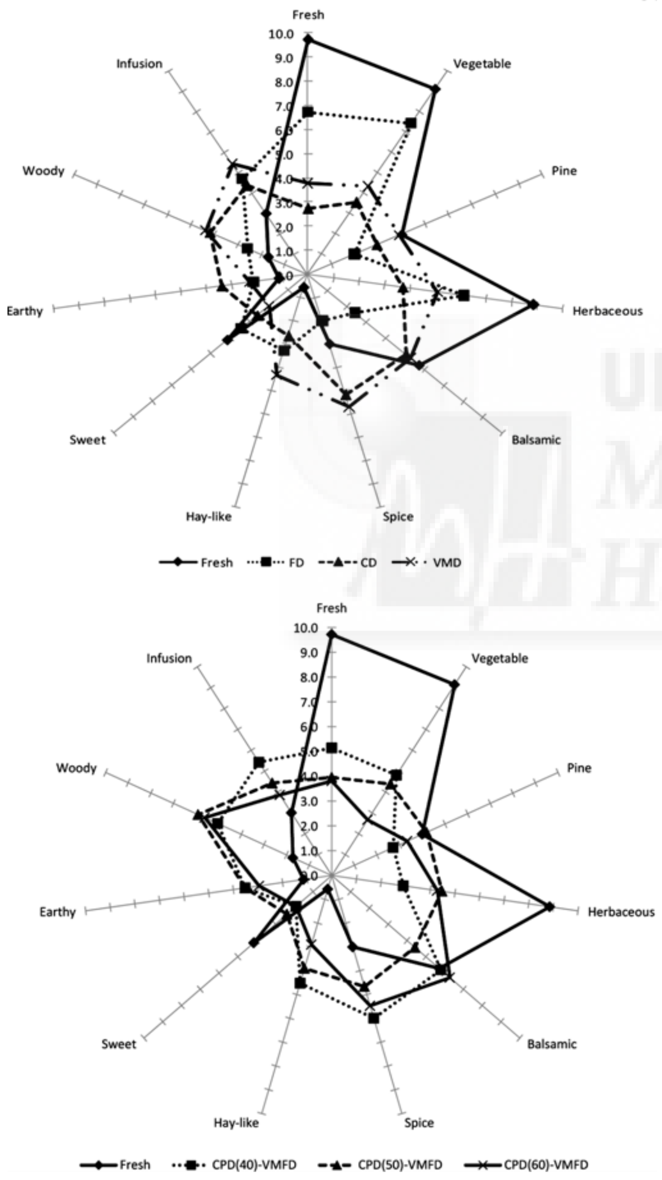

FIG. 4. Descriptive sensory analysis of fresh and dried thyme as affected by the drying method. Data presented for CD, VMD, and CPD are the mean of three different treatments at different temperatures or microwave powers.

Sensory data showed that samples dried by CD were characterized by the lowest scores of those attributes related to the freshness of thyme (fresh thyme, 2.7; vegetable, 3.5; pine, 3.0; and herbaceous, 3.7).

According to the freshness attributes, samples dried using VMD occupied an intermediate position between fresh and convective-dried samples, and the VMD scores were higher than those for samples dried by CD. However, samples dried by VM were also characterized by higher scores of the dried attributes (spice, hay-like, woody, and infusion) than convective-dried samples: spice (5.7 and 5.2 for samples dried by VMD and CD, respectively, compared to 3.0 in fresh thyme), hay-like (4.3 and 2.7 for samples dried by VMD and CD, respectively, compared to 0.6), woody (4.4 and 4.2 for samples dried by VMD and CD, respectively, compared to 1.7), and infusion (5.4 and 4.4 for samples dried by VMD and CD, respectively, compared to 3.0). The fact that VM-dried samples had high intensities of the dried attributes is not considered negative because these samples also retained high intensities of the freshness attributes.

An increase in the temperature of the hot air used during CPD in the combined method (CPD-VMFD) from 40 to 60°C at microwave powers of 240, 360, and 480 W resulted in significant ($p < 0.01$) decreases in the intensities of the fresh and vegetable attributes; however, no temperature-dependent trend was observed for other attributes such as pine and herbaceous. Samples dried at 40°C during CPD-VMFD presented the highest scores of the two most important attributes related to freshness—fresh thyme and vegetable—and therefore could be considered the best drying treatment.

CONCLUSIONS

The drying kinetics of thyme dehydrated using CD and CPD-VMFD were described with an exponential models, and for samples exclusively dehydrated by the VM method, the constant and falling rate periods were described by linear and exponential equations, respectively. The sample temperature was higher during VMD than in CPD-VMFD. In general, significant differences were found in the aroma quality of thyme dried by different methods. VMD at 240 and 360 W resulted in the highest total concentrations of volatile compounds; the combination of CPD and VMFD not only resulted in dried thyme samples of high sensory quality but significantly reduced the drying time compared to CD and resulted in high total concentrations of volatiles at 240 W, independent of the predrying temperature. The intensities of the key attributes related to freshness reached high scores in samples dried using VMD and CPD-VMFD at 40°C. Our final recommendation, based on the results from chemical as well as sensory analyses, is to use the combination CPD-VMFD; the best conditions assayed in this study were CPD at 40°C and VMFD at 240 W. The next best option was drying of thyme using VMD at 240 W exclusively.

NOMENCLATURE

a, b, b_1, b_2	Function parameters
K	Critical point of drying process
k, k_1, k_2	Drying constants (min^{-1})
M	Moisture content (kg kg^{-1} db)
M_0	Initial moisture content (kg kg^{-1} db)
M_e	Equilibrium moisture content (kg kg^{-1} db)
M_R	Moisture ratio
R^2	Coefficient of determination
T	Temperature (°C)
t	Time (min)
t'	Time coordinate of the critical point K (min)
t''	Time of convective predrying (min)

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PUBLICATION 4

Drying of garlic slices using convective pre-drying and vacuum-microwave finishing drying: kinetics, energy consumption, and quality studies

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ORIGINAL PAPER

Drying of Garlic Slices Using Convective Pre-drying and Vacuum-Microwave Finishing Drying: Kinetics, Energy Consumption, and Quality Studies

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Abstract Garlic slices were dehydrated by convective drying (CD) and by a combined method consisting of convective pre-drying followed by vacuum-microwave finishing drying (CPD-VMFD). Drying of garlic using VMFD led to samples with high values of lightness and slightly lower values of the coordinates *a** and *b**. The treatment CPD-VMFD significantly decreased the drying time from 630 min for CD to 49 min and contributed to an important energy saving compared with CD (54.4–86.3 %). The total drying time was shorter when vacuum microwaves were introduced earlier and microwave power was higher. The highest temperature (114 °C) was found for samples pre-dried to a moisture content of 60 % and then dried at 360 W while showing the lowest energy consumption (98±1 kJ g^{-1}). In general, the total antioxidant capacity increased after drying of garlic slices; however, the content of total phenolic compounds showed the opposite trend, and thus other compounds, such as allicin, should be involved in the antioxidant capacity of dried garlic. Garlic slices were CP dried until 30 % of moisture content followed by VMFD at 240 or 360 W showed the best results in terms of energy consumption and antioxidant capacity.

Keywords *Allium sativum* products · Antioxidant capacity · Drying methods · Specific energy consumption · Total phenolic compounds

Nomenclature

a, n	Function parameter (in kilograms per kilogram db)
CD	Convective drying
CPD	Convective pre-drying
db	Dry basis
Ec	Energy consumption in convective method (in kilojoules)
E_{VM}	Energy consumption in vacuum microwave drying (in kilojoules)
E'	Specific energy consumption (in kilojoules per gram)
Es	Energy savings (in percent)
exp	Experimental data
fw	Fresh weight
k, g	Drying constants (in minutes)
m	Mass (in grams)
M	Moisture content (in kilograms per kilogram db)
M_0	Initial moisture content (in kilograms per kilogram db)
M_e	Moisture content at equilibrium (in kilograms per kilogram db)
MR	Dimensionless moisture ratio
$\overline{\mathrm{MR}}$	Mean dimensionless moisture ratio
N	Power consumption (in kilowatts)
η_m	Efficiency of magnetrons
pre	Predicted data
R^2	Coefficient of determination
RMSE	Root mean square error
rpm	Revolutions per minute
t	Time (in minutes)
VM	Vacuum microwave
VMFD	Vacuum microwave finishing drying

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wb Wet basis

Introduction

Garlic (*Allium sativum* L.) is a semi-perishable spicy herb, which has been used worldwide as seasoning, spice and herbal remedy (Ahmad 1996). Garlic is known to possess a vast variety of biological functions, such as antimicrobial (Kim 2002), anticancer (Patel et al. 2004), anticardiovascular disorders (Gorinstein et al. 2007) and antioxidant properties (Nuutila et al. 2003; Bozin et al. 2008). These properties are related with the chemical composition of garlic, and more specifically with its content of phenolic and sulfur-containing compounds (Benkeblia 2004; Benkeblia 2005; Chung 2006; Bozin et al. 2008).

Due to the complex chemistry of garlic, variations in the processing can yield quite different chemical products. For instance, Maillard reactions which take place during drying of garlic may lead to important modifications such as changes in the antioxidant activity (Moreno et al. 2006) and the presence of Amadori compounds (Cardelle-Cobas et al. 2005). Fresh garlic is consumed worldwide and allicin is considered its predominant bioactive compound (Tsai et al. 2012). Allicin is a sulfur-containing compound responsible for the pungent odor of garlic which has important antioxidant properties and significant health benefits (Yong 2006). Currently, there are many garlic based products on the market, such as dried garlic powder and slices, garlic oil, or garlic mayonnaise.

Dehydration operations have been used for decades in food processing industries for efficient long-term preservation of final products. The basic objective in drying food products is the removal of water from fresh product reaching a level at which microbial spoilage is avoided.

Although convective drying (CD) is still the most popular method applied to fruits and vegetables, however, it has several disadvantages and limitations; for instance, degradation of important flavor and nutritional compounds as well as color alteration due to the temperature used during the process. The drying time can be greatly reduced (about 75 %) (Suárez et al. 2000; Sharma and Prasad 2004; Salazar-González et al. 2012), and the quality of finished food product can be improved (Men'shutina et al. 2005) by applying microwave energy to the material instead of drying by hot air. In this way, thermal degradation of essential nutrients is substantially reduced and preservation of food quality factors, such as color, is achieved (Suárez et al. 2000). For instance, hot air drying led to darker garlic slices than vacuum microwave (VM) dried samples (Rasouli et al. 2011; Cui et al. 2003). Drying using microwave energy under vacuum is a modern, efficient method of food preservation (Durance and Wang 2002). Lowered pressures induce faster evaporation of water from the food at relativity low temperature (Figiel et al. 2010), reducing thus the chemical, sensory, and nutritional alterations in dried products (Drouzas and Schubert 1996). The vacuum-microwave drying (VMD) method is not yet common in the food industry, although recently it has been investigated as a potential method for obtaining high-quality dried foodstuffs, including fruits, vegetables, and grains (Youngswatdigul and Gunasekaran 1996; Drouzas and Schubert 1996; Figiel 2009; Calín-Sánchez et al. 2012). Starting the dehydration in a VMD system, the intensive water evaporation from vegetables and fruits may exceed the vacuum pump capacity; this requires a reduction in the raw material mass or volume being subjected to drying or application of a large vacuum installation. This problem can be overcome by pre-drying the material using CD, which will drastically decrease the mass to be loaded in the VMD system (Hu et al. 2006). Pre-drying of plant materials by convective method before vacuum-microwave finishing drying (CPD-VMFD) can have a significant contribution to the fruit processing industry by reducing the total cost of dehydration and by improving the quality of the commercial dehydrated products (Hu et al. 2006).

Energy analyses have been conducted for different drying methods and conditions for products, such as carrots (Nazghelichi et al. 2010), mushrooms slices (Motevali et al. 2011a), sour pomegranates (Motevali et al. 2011b), and red pepper (Kowalski and Mierzwa 2011). However, this is the first study dealing with the estimation of the energy consumption associated with processing conditions during CPD-VMFD of garlic slices. Therefore, the aim of this study was to determine the best conditions of the CPD-VMFD of garlic slices, minimizing energy consumption and maximizing their antioxidant capacity.

Materials and Methods

Plant Material and Processing of Samples

Fresh garlic (*A. sativum* L.) bulbs were purchased from a local market in Wrocław (Poland); however, they came from a different Polish city, Krakow. Fresh bulbs were purchased in their optimal stage and were immediately transported to the Institute of Agricultural Engineering (Wrocław University of Environmental Life and Sciences).

Garlic bulbs had initial moisture content (M_0) of 1.19 g of water/g of dry matter. Bulbs were manually peeled, and individual cloves were cut into slices of 5 mm thick. Garlic samples of approximately 60 g were dehydrated until three levels of final moisture content were achieved using two drying protocols:

1. CD was conducted using drying equipment designed and built up in the Institute of Agricultural Engineering (Wrocław University of Environmental and Life Sciences). CD equipment enables simultaneous dehydration of six samples. Garlic samples were placed into trays of 10-cm diameter located at the top of the six pipes supplying the hot air produced by an electric fan. Convective method was operated at temperature of 60 °C with an air velocity of 1.4 ms^{-1}.
2. Combined drying (CPD-VMFD) consisted of CPD at temperature of 60 °C until *M* of 60, 30, or 15 % wet basis (wb), followed by VMFD with 240, 360, or 480 W (Fig. 1). VMDF was carried out in Plazmatronika SM 200 dryer (Wroclaw, Poland) connected to a vacuum system consisting of a vacuum pump BL 30P ("Tepro," Koszalin, Poland), a vacuum gauge MP 211 ("Elvac," Bobolice, Poland), and a compensation reservoir of 0.15 m^3 (Fig. 2). Garlic samples were placed in a cylindrical container of organic glass with volume of 6.8 L. The pressure in the container ranged from 4 to 6 kPa. To avoid local over-heating of fruits, the container rotated at a speed of 6 rpm, and additionally an electric fan was installed at the bottom of the dryer producing an air stream of 22 °C at a velocity of 1 ms^{-1}.

Drying Kinetics

The drying kinetics of garlic slices was presented as the decrease of moisture ratio MR *versus* time of drying *t*. Moisture ratio MR is defined by Eq. (1), where $M(t)$ is moisture content of garlic slices after time *t*, M_0 is the initial moisture content and M_e is equilibrium moisture content.

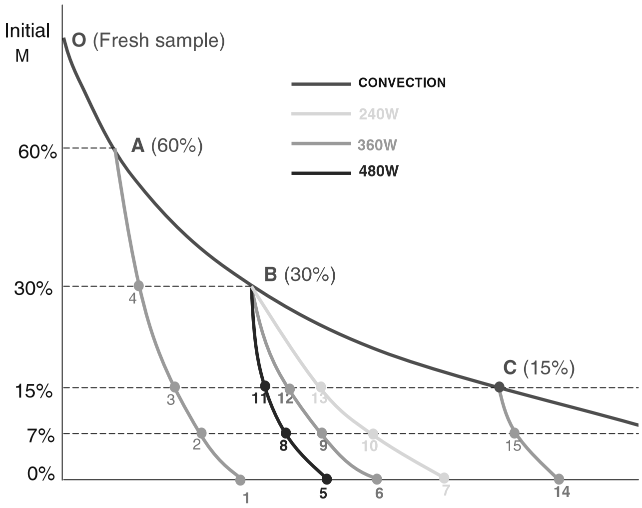


Fig. 1 Experiments of combined drying (CPD-VMFD) consisting of CPD at 60 °C until 60, 30, and 15 % of M (wb) followed by VMFD at 240, 360, and 480 W

$$MR = \frac{M(t) - M_e}{M_0 - M_e} \tag{1}$$

The equilibrium moisture content M_e is determined by the static method using saturated salt solutions (Babetto et al. 2011). However, this method is time consuming and *MR* usually is calculated from the simplified Eq. (2) assuming that the values of M_e are relatively small compared with $M_{(t)}$ or M_0 (Rasouli et al. 2011):

$$MR = \frac{M(t)}{M_0} \tag{2}$$

Therefore, MR for garlic slices was calculated from Eq. (2). The values of $M(t)$ were determined on the basis of mass losses of the garlic slices of initial moisture content M_0 determined by the vacuum oven method.

Basic and possible simple drying models (Table 1) were considered while fitting to the experimental points representing the decrease of MR with time. These models fulfilled the criteria of fitting for garlic slices dried using hot air (Rasouli et al. 2011). In our study, Newton, Page, and Verma models (Table 1) were applied to describe the drying kinetics of garlic slices entirely dehydrated in hot air. In the case of VMFD, the complex form of Verma equation was not appropriate because this phase of drying was relatively fast and did not concern the whole range of MR due to CPD. The last reason also required modifications of Newton and Page models by the introducing of parameter *a*. However, the modified form of Newton equation is known as Henderson–Pabis model. Therefore, only Henderson–Pabis model as well as modified version of Page model were used for describing the drying kinetics of VMFD (Table 1).

The drying models were evaluated according to coefficient of determination (R^2) and root mean square error (RMSE).

Determination of Moisture Content

The vacuum oven method was used to determine the moisture content (*M*) of the fresh and processed garlic slices. The slices were dried in vacuum dryer (SPT-200, ZEAMiL Horyzont, Krakow, Poland) for 24 h. The operating temperature was 70 °C. Moisture content was expressed in grams of water per grams of dry matter.

Temperature Measurement

Temperature was controlled because high values could be related to degradation of bioactive compounds.

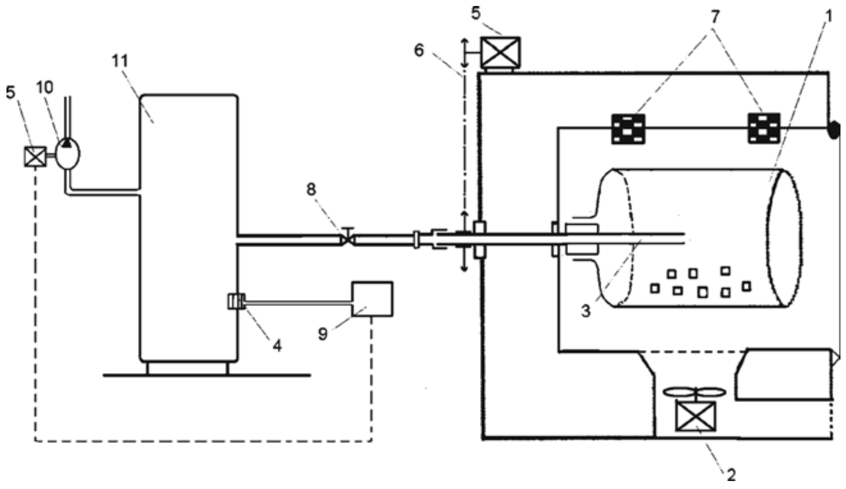


Fig. 2 Schematic diagram of vacuum-microwave dryer SM 200: *1*, vacuum-drum, *2*, fan, *3*, air pipe, *4*, vacuum sensor, *5*, electric motor, *6*, transmission chain, *7*, magnetrons, *8*, valve, *9*, vacuum gauge, *10*, vacuum pump, and *11*, compensation reservoir

Temperature readings were taken immediately after taking garlic slices out of the VM dryer using an infrared camera Flir i50. The maximum temperature observed was recorded with an accuracy of 0.1 °C. It is expected that the local temperature within material during drying could be higher; however, a direct measurement in the drying chamber under vacuum is not practically possible because the measuring elements are heated by the microwave emission.

Energy Consumption Calculation

Energy Consumption in Convective Method

Energy E_C consumed during CD (in kilojoules) was calculated according to Eq. (3):

$$E_C = \left(\frac{N_f}{6} + N_h\right) \times t \tag{3}$$

where N_f (in kilowatts) is power consumption by a fan blowing air to six pipes equipped with electric heaters of power consumption N_h (in kilowatts) and t is time of drying (in seconds).

Table 1 Mathematical models for fitting the drying curves of garlic slices

Model name	Equation
Newton	$\mathrm{MR} = \mathrm{e}^{-k \cdot t}$
Henderson–Pabis	$\mathrm{MR} = a \times \mathrm{e}^{-k \cdot t}$
Page	$\mathrm{MR} = \mathrm{e}^{-k \cdot t^n}$
Page (modified)	$\mathrm{MR} = a \times \mathrm{e}^{-k \cdot t^n}$
Verma	$\mathrm{MR} = a \times \mathrm{e}^{-k \cdot t} + (1 - a) \times \mathrm{e}^{-g \cdot t}$

MR dimensionless moisture ratio, *t* drying time (min)

Energy Consumption in VM Method

Energy E_{VM} consumed during VM drying (in kilojoules) was calculated according to Eq. (4):

$$E_{\mathrm{VM}} = \left(\frac{N_M}{\eta_M} + N_V + N_e\right) \times t \tag{4}$$

where N_M and η_M are output power (in kilowatts) and efficiency of magnetrons respectively, N_V is power consumption (in kilowatts) by vacuum pump and (N_e) is power consumption (in kilowatts) by electric engine rotating the container.

Determination of Specific Energy Consumption

The specific energy consumption (E') was calculated from the universal Eq. (5), which can be applied for both CD ($E'=E'_C$) as well as for combined drying consisted of CPD and VMFD ($E'=E'_{C\text{–VM}}$). This equation is the ratio of the sum of energy E_C and E_{VM} to the total mass of water removed from the fresh sample during drying by convective method (m_C) and VM method (m_{VM}):

$$E' = \frac{E_C + E_{VM}}{m_C + m_{VM}} \tag{5}$$

For entire ***CD*** the values of E_{VM} and m_{VM} equal to zero, while for combined drying the values of E_C and m_C result from the time of convective pre-drying. The specific energy consumption was presented versus the water content, which was changing during drying. The energy savings using CPD-VMFD with respect to CD was calculated as the ratio of the difference in E'_C and $E'_{C\text{-}VM}$ to E'_C (6):

$$Es = \frac{E'_C - E'_{C-\mathrm{VM}}}{E'_C} \times 100\% \qquad (6)$$

Color Measurement

Color of fresh and dried garlic samples was evaluated by a Konica Minolta Chroma Meter CR-200 Reflectance System (CIE$L^*a^*b^*$; Konica Minolta, Osaka, Japan). The device is a tristimulus colorimeter that measures four specific wavelengths in the visible range, specified by the *Commission Internationale de l'Eclairage*. Dried samples were crushed using an electric mill before measurement. The results were expressed as lightness (L^*), coordinate green-red (a^*), and coordinate yellow–blue (b^*). The measurements of color were conducted in triplicate.

Extraction and Determination of Antioxidant Capacity and Total Phenolic Compounds

Extraction

The same extraction protocol was used for the quantification of both antioxidant capacity and total phenolic compounds. The used method was described by Wojdyło et al. (2009). Briefly, 5 g of fresh or dried garlic slices were weighed. Twenty-five milliliters of ultrapure water were added with an extracting agent consisting of MeOH/H_2O (80:20) and HCl (1 %). The mixture was softly stirred and submitted to two consecutive sonication steps of 15 min each. After the sonication, the samples were left in tubes during 24 h at 4 °C. Finally, samples were centrifuged for 10 min at 15,000 rpm (centrifuge, MPW 360, Warsaw, Poland). Supernatants were collected and both antioxidant capacity and total phenolic compounds were measured in the next 24 h.

Measurement

Antioxidant capacity was measured as the radical scavenging capacity of free radicals by the ABTS spectrophotometric assay described by Re et al. (1999). Briefly, ABTS was dissolved in ultrapure water at 7 mM concentration. ABTS radical cation ($\mathrm{ABTS}^{\cdot+}$) was produced by reacting ABTS stock solution with 2.45 mM potassium persulfate. Then, the mixture was left to stand in the dark at room temperature for 16 h before use. For the study of garlic samples, the $\mathrm{ABTS}^{\cdot+}$ solution was diluted with ultrapure water to an absorbance of 0.700 (±0.02) at 734 nm. After the addition of 30 μL of supernatant to 3.0 mL of diluted $\mathrm{ABTS}^{\cdot+}$ solution ($A_{734\ \mathrm{nm}}=$ 0.700 (±0.02)), the absorbance was read exactly 6 min after initial mixing. All determinations were performed in triplicate. The results of the assay were expressed relative to μM Trolox/100 g of dry weight in terms of TEAC.

The total phenolic compounds assay was performed according to the method described by Wood et al. (2002) with slightly modifications. Briefly, two tubes were prepared for each extraction. In each one of the tubes, 2.5 mL of Folin-Ciocalteu reagent 1/10 (100 mL Folin+900 mL H_2O) were added. Later, 200 μL of the extract were added and then taken to a final volume of 500 μL with phosphate buffer (50 mM, pH 7.5). After 2 min, the reaction was stopped with the addition of 2 mL of Na_2CO_3 and the mixture was stirred again. Finally, the samples were placed in a warm water bath at 50 °C for 5 min before measurement. The absorbance was read at 760 nm in a spectrophotometer (UV–vis 2401 PC, Kyoto, Japan) and results were expressed as mg of gallic acid 100 g^{-1} dw.

Statistical Analysis

The program Table Curve 2D Windows v2.03 enabled mathematical modeling with the best parameters of fitting (R^2 and RMSE). The results obtained were evaluated by statistical analysis with the use of the SPSS (SPSS Science, Chicago, IL). In order to find out if the differences in the mean values estimated were statistically significant, the one-way analysis of variance was applied. Later, homogeneous groups were determined with the Duncan's multiple range test (at significance level α=0.05).

Results and Discussion

Drying Kinetics

Figure 3 shows the changes of the *MR* of garlic slices dehydrated by a combination of CPD at 60 °C followed by VMFD at three different power levels (240, 360, or 480 W), while Table 2 shows the constants of the mathematical modeling. In most cases, R^2 values were higher than 0.99,

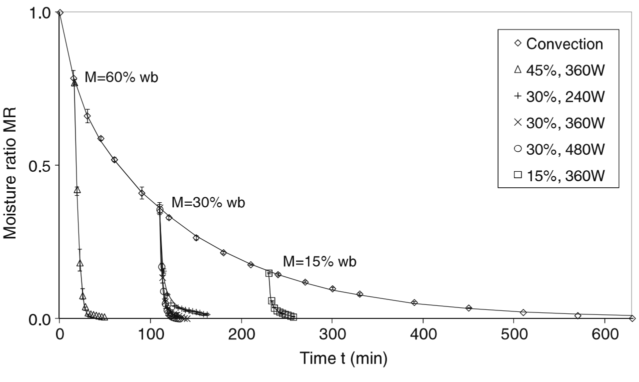


Fig. 3 Drying kinetics for garlic slices dehydrated using CD or combined drying (CPD-VMFD) consisting of CPD at 60 °C until 60, 30, and 15 % of M (wb) followed by VMFD at 240, 360, and 480 W

Table 2 Drying time, energy savings, and constants of the models describing the drying kinetics of garlic slices dried by: (1) convective method at air temperature of 60 °C and (2) vacuum microwave finishing drying at microwave power of 240, 360, or 480 W from different initial *M* (wb) (15, 30, and 60 %)

Drying conditions	Model	*a*	*k*	*n*	*g*	R^2	RMSE	Drying time (min)	Energy savings (%)
Convection	Newton		0.00947 i	0.7717 c		0.9788 b	0.044721 d	630 a	
	Page		0.02818 h			0.9993 b	0.008184 b		
	Verma	0.2204 c	0.06228 g		0.00704	0.9998 a	0.004396 d		
60 %–360 W	Henderson–Pabis	0.7813 a	0.23070 e	1.1753 a		0.9965 b	0.014591 b	49 e	54.42 d
	Page (modified)	0.7731a	0.16990f			0.9986a	0.009762b		
30 %–240 W	Henderson–Pabis	0.3342 b	0.15830 f	0.5295 d		0.9469 b	0.021331 a	162 c	63.23 c
	Page (modified)	0.3471 b	0.44101 b			0.9903 a	0.009535 b		
30 %–360 W	Henderson–Pabis	0.3597 b	0.30421 d	0.7474 c		0.9939 b	0.008845 b	140 d	74.15 b
	Page (modified)	0.3629 b	0.45071 b			0.9986 a	0.004464 d		
30 %–480 W	Henderson–Pabis	0.3541 b	0.34401 c	0.8925 b		0.9964 b	0.006719 c	134 d	75.38 b
	Page (modified)	0.3566 b	0.39861 c			0.9974 a	0.006071 c		
15 %–360 W	Henderson–Pabis	0.1418 d	0.20811 e	0.5121 e		0.9396 b	0.011192 b	266 b	86.25 a
	Page (modified)	0.1495 d	0.54201 a			0.9985 a	0.001872 e		

Values followed by the same letter, within the same column, were not significantly different ($p<0.05$), according to Duncan's test

and RMSE values were lower than 0.01; these values demonstrated that the selected models were appropriate to describe the drying kinetics of garlic slices. However, only the best models were fit to the experimental data (Fig. 3).

The Verma model, which in fact is an exponential equation of two terms (Table 1), was selected as the best to describe CD at 60 °C (Table 2). The mathematical structure of this model indicates that the reduction of the MR happened in two different drying periods. In the first period, the drying constant value (*k*) was 0.062, meaning that the decrease in the MR was faster than in the second period, which was characterized by the value of the drying constant *g*, 0.007. However, the range of moisture decrease in the first period was much lower than in the second period. These ranges equal to the values of coefficients *a* and (1-*a*), namely 0.2204 and 0.7796, respectively; the sum of both parameters amounts to the initial moisture ratio of the fresh garlic slices. The faster decreasing of MR in the first period of CD, indicated by the value of parameter *a*, was confirmed by the course of the drying rate shown in Fig. 4.

In the first period of CD, the drying rate decreased rapidly from the highest value of 0.0143 to 0.0082 min^{-1}; while during the second period, the drying rate gradually decreased from 0.0082 to 0.0002 min^{-1}. This drying behavior of garlic slices is in accordance with theoretical issues concerning water diffusivity (Crank, 1975). In this way, during the first period of drying, water easily evaporates from the surface of the dried material to the air by external diffusion (Yiotis et al. 2007). This process creates a moisture gradient inside the material, which enables transport of water to the surface by internal diffusion at slower rate typical of the second drying period (Roberts et al. 2008).

The presence of two drying periods with different drying rates (constant and falling) has been reported in many studies (Pabis 2007). In most cases, the best fitting to the experimental data was provided by Page model; this was the case of garlic (Sharma and Prasad 2004; Babetto et al. 2011), apples (Doymaz 2010), pomegranate arils (Kingsly and Singh 2007), and pumpkin slices (Alibas 2007). Also, Henderson–Pabis model was successfully used to describe drying kinetics of ginger (Thorat et al. 2012), strawberries (Doymaz 2008), as well as VMFD of beetroot (Figiel 2010) or oregano (Figiel et al. 2010).

On the other hand, the Verma model was successful in describing the drying kinetics of garlic slices (Madamba et al. 1996). This study confirmed the importance of the falling rate period, which was characterized by a low drying constant.

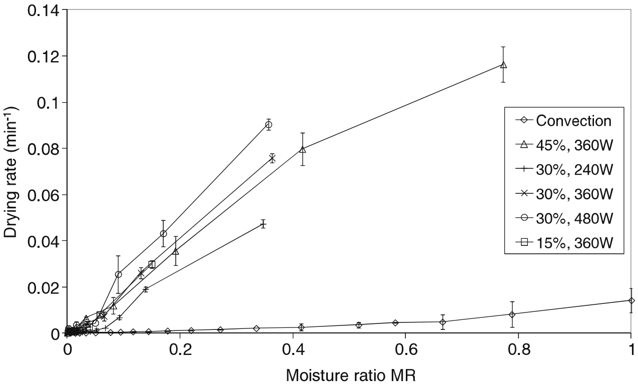


Fig. 4 Drying rate for garlic slices dehydrated using combined drying (CPD-VMFD) consisting of CPD at 60 °C until 60, 30, and 15 % of M (wb) followed by VMFD at 240, 360, and 480 W

In this study, the drying kinetics of VMFD was better described by the modified Page model than by the Henderson–Pabis model (Table 2). For both of these models, parameter *a* indicated the intermediate moisture content at which the VMFD was applied. The VMFD was faster at higher microwave powers. An increase in microwave power from 240 to 480 W increased the values of parameter *n* from 0.5295 to 0.8925 in modified Page model and drying constant *k* from 0.1583 to 0.3440 in Henderson–Pabis model (Table 2). The fast drying observed at high values of microwave power resulted from high drying rates (Fig. 4). Increasing the values of microwave power from 240 to 480 W increased the initial value of drying rate from 0.047 to 0.090 min^{-1} for samples pre-dried until 30 %.

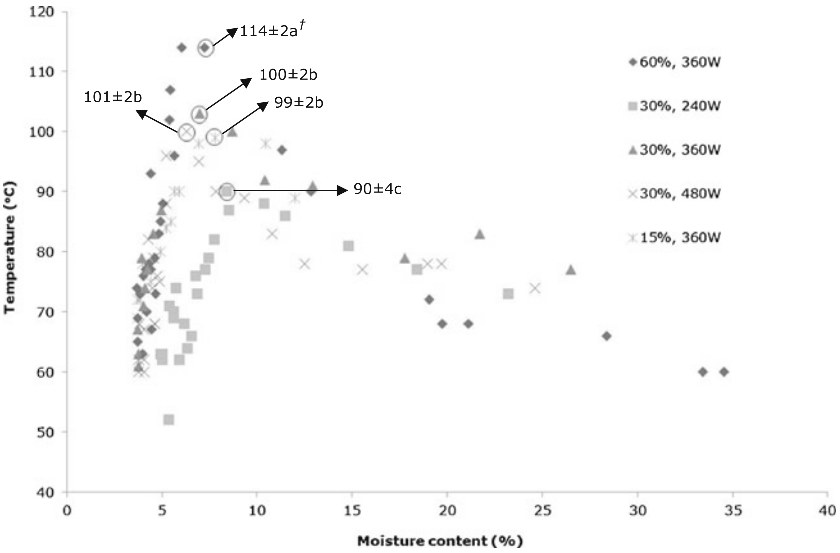
In the initial stage of CD, the loss of water was relatively fast; as the drying process advanced, the water loss decreased (Maskan 2000). The application of VMFD reduced considerably the total drying time (Table 2). The drying time for CD at 60 °C was 630 min; however, with the application of the combined drying, the total time was reduced to 49 min for the treatment CPD until 60 % of moisture content followed by VMFD at 360 W (60 %–360 W). With an earlier application of VMFD, the drying time was reduced approximately 5 times, from 266 min (15 %–360 W) to 49 min (60 %–360 W). Similar results were previously obtained in pears (Figiel et al. 2008) and beetroot (Figiel 2010). The high effectiveness of VM drying results from the way in which the microwave energy is transformed into heating energy. During VM drying the energy of microwaves is absorbed by the water dipoles (Tang 2005), which are located in the whole volume of the material being dried. This creates a large vapour pressure in the centre of the material, allowing rapid transfer of moisture to the surrounding vacuum and preventing structural collapse (Lin et al. 1998). As a consequence, the drying rate is considerably higher than in traditional methods of dehydration (Sharma and Prasad 2004).

Temperature

During the VMFD, an increment in the temperature was observed until a critical point of *M*. From this critical point of *M*, the sample temperature of dried garlic slices started to decrease (Fig. 5). The highest peak of temperature, 114±2 °C, was obtained for those garlic samples dried starting from the higher *M* (60 %). The lowest peak temperature, 90±4 °C, was obtained when the lowest microwave power was applied (240 W). The temperatures obtained in the case of CPD until 30 % of *M* followed by VMFD at 360 and 480 W and CPD until 15 % of *M* followed by VMFD at 360 W were similar and reached values close to 100 °C (Fig. 5). Drouzas and Schubert (1996) reported that during VMD, the highest temperature peaks were obtained in the *M* range of 0.5–0.8 kgkg^{-1} db; current results agreed and the highest temperatures were recorded in the range of 0.7–0.9 kgkg^{-1}.

Experimental results showed that the highest temperatures were obtained in dried garlic slices when CPD was applied during shorter times until higher moisture contents. This fact could be due to the garlic slices pre-dried until a *M* of 60 % required longer times of microwave application for the dehydration and this higher *M* percentage kept more microwave energy-producing higher temperatures. Also, VM finish-dried beetroot cubes (Figiel 2010) and rosemary samples (Szumny et al. 2010) reached relatively high temperatures at shorter times of CPD. However, in the case of beetroot cubes the highest temperature was obtained by the sample subjected to VMFD after the longest time of CPD. This unexpected

Fig. 5 Maximal temperatures recorded during the drying of garlic slices by CPD-VMFD. †$p < 0.05$, temperature values followed by the same letter, within the same column, were not significantly different according to Duncan's test



† Temperature values followed by the same letter, within the same column, were not significantly different (p <0.05), according to Duncan's test.

behavior might result from the different morphology of cellular system as well as differences in physical parameters of the dried material, such as heat conductivity, specific heat, and thus requires additional studies focused exclusively on the effect of VM drying conditions on the temperature profiles of different plant materials.

The falling in the temperature from the maximal point of temperature could be explained by two hypotheses: (1) creation of lower caloric energy due to decreasing the number of water dipoles activated by the microwaves (Tang 2005) and (2) evaporated water absorbs part of microwave energy reducing the temperature of the samples (Figiel 2009). Therefore, the temperature during VMFD was dependent ($p<0.05$) on the moisture content obtained after CPD in garlic slices; higher moisture contents involved longer processes of accumulation and dissipation of microwave energy leading to high temperatures independently of the microwave power. Similar results were obtained by previous researches with rosemary (Szumny et al. 2010) and basil (Calín-Sánchez et al. 2012).

Energy Consumption During Drying of Garlic Slices

The specific energy consumption profiles (Fig. 6) represent the amount of energy per 1 g of water removed from the fresh material while reducing the moisture content. The shape of the specific energy consumption profile showed an increment in the energy required during the last stages of the drying process. This behavior is typical in vegetal products with osmotic cellular structure to protect the vegetal tissues against water loss (Sarsavadia 2007). This profile also indicated that at the end of the drying process more time is required to remove the same amount of water at the targeted power than during the initial stages. However, at the beginning of the VMFD, the specific energy consumption (E') started to decrease due to the high effectiveness of the VM method. This behavior can be also explained by the form of Eq. 5. Namely, in the ratio of energy to mass of water removed from the sample, the values of E_c and m_c become constant as the CPD was completed and the contribution of m_{VM} to denominator was higher than the contribution of E_{VM} to numerator. Of course, at the end of VMFD the value of m_{VM} was getting lower in relation to E_{VM}, which resulted in a considerable increase of E'. Eventually, the final values of E' obtained for the dried product were lower when VMFD was applied earlier and values of microwave power were higher.

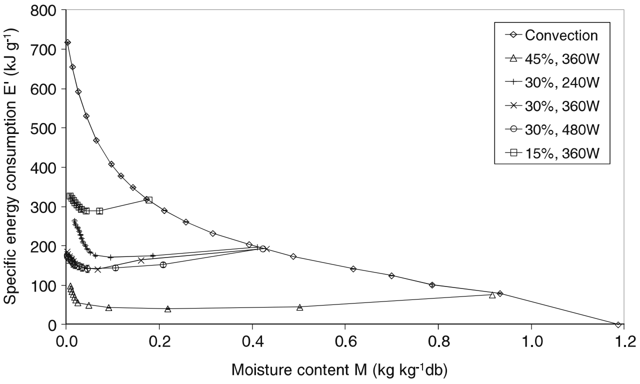


Fig. 6 Energy consumption of garlic slices drying, using CD and CPD-VMFD methods

CPD until 60 % of M followed by VMFD at 360 W led to the lowest value of specific energy consumption at the end of the drying process, 98±0.8 kJg^{-1}; this low value was associated with the fact that the VMFD was applied earlier with the highest initial M. In contrast, the highest energy consumption was estimated for the CD at 60 °C, 718±3 kJ g^{-1}. When the VMFD was applied with an initial M of 30 %, the values of E' ranged between 177±1 kJg^{-1} for 480 W and 264±1 kJg^{-1} for 240 W (Fig. 6). Finally, energy savings using CPD-VMFD with respect to CD were in the range from 54.42 to 86.25 % (Table 2).

Color Changes During Drying

All dried garlic samples showed significant ($p<0.001$) higher values of L^* (ranging from 72.1±0.4 to 76.1±1.2) than the fresh sample (64.7±1.2) (Table 3). Regarding the coordinate green-red, a^*, there were no significant differences between the fresh and CD-treated samples at 60 °C; however, the color of CPD-VMF dried samples shifted toward green colors, with values being close to 0. Finally, the coordinate blue–yellow, b^*, of all samples showed positive values and then the color of both fresh and dried garlic samples had an important yellow component. Fresh garlic and samples C dried at 60 °C had statistically equivalent b^* values, 21.6±0.3 and 22.2±0.3, respectively. Garlic slices dried by the combined method (CPD-VMFD) showed significant ($p<0.001$) lower b^* values than those

Table 3 Color parameters as affected by different drying methods

Drying conditions	Color parameters		
	L^*	a^*	b^*
Fresh	64.7±1.2 c[a]	2.68±0.51 a	21.6±0.3 a
60 °C	72.1±0.4 b	2.37±0.51 a	22.2±0.3 a
60 %–360 W	76.1±1.2 a	−1.15±0.21 c	13.3±1.1 c
30 %–240 W	74.3±1.1 a	0.12±0.03 b	18.1±0.2 b
30 %–360 W	75.4±0.2 a	0.09±0.03 b	19.4±1.8 b
30 %–480 W	75.2±0.4 a	0.06±0.03 b	18.3±0.3 b
15 %–360 W	76.0±1.0 a	0.09±0.03 b	16.1±1.5 b
ANOVA	***	***	***

Values followed by the same letter, within the same column, were not significantly different ($p<0.05$), according to Duncan´s test

*$p<0.05$; **$p<0.01$; ***$p<0.001$—level of significance

[a] Treatment means of the ANOVA test (values were the mean value of three replications)

obtained for both fresh and CD samples; these values ranged between 13.3±1.1 and 19.4±1.8 (Table 3).

These results suggest that CPD-VMFD produced brighter samples with colors shifted towards green and blue. These results agreed quite well with those previously obtained by Figiel (2009) and Sharma and Prasad (2004) in garlic dried under vacuum microwaves and microwaves, respectively.

Total Phenolic Compounds and Total Antioxidant Capacity of Dried Garlic Slices

Both the total phenolic compounds and the antioxidant capacity were significantly affected by the drying process (Table 4), as previously reported in strawberries (Wojdyło et al. 2009) and pomegranate (Calín-Sánchez et al. 2013). Total phenolic compounds significantly ($p<0.001$) decreased after the drying process and values ranged between 13.1±0.3 mg gallic acid 100 g^{-1} db for CPD-VMFD (60 %–360 W) and 79.7±7.6 mg gallic acid100 g^{-1} for the fresh samples. However, the CPD-VMFD method did not show significantly better results compared with CD. Thus, other factors such as time and energy consumption must be considered for taking the decision of selecting new alternatives to the traditional drying methods.

A completely different situation was observed for the effect of drying on antioxidant capacity. Dried samples showed significant ($p<0.001$) higher antioxidant capacity compared with fresh garlic slices (Table 4) and values ranged between 11.3±0.1 and 89±1 μM Trolox100 g^{-1} for samples dried by CD and CPD-VMFD (intermediate stage of 30 %–240W), respectively.

The antioxidant capacity in several intermediate stages of the VMFD (8, 9, 10, and 11) was significantly higher ($p<0.001$) than at the beginning of the VMFD (Table 4), as previously reported by Manzocco et al. (2000). This behavior could be the result of two different factors: (1) some phenolic compounds have greater antioxidant capacity in some intermediate oxidation stages (Manzocco et al. 2000) and (2) thermal processing may induce the formation of new compounds with high antioxidant capacity (Manzocco et al. 2000); these compounds could be those formed by the Maillard reaction (Manzocco et al. 2000; Wojdyło et al. 2009; Calín-Sánchez et al. 2013).

The lack of positive correlation between antioxidant capacity and total phenolic content in could be attributed to the fact that not only phenolic compounds are the responsible of the antioxidant capacity of dried garlic.

Table 4 Total phenolic compounds and total antioxidant capacity of dried garlic slices

Drying conditions	Total phenolic compounds (mg gallic acid 100 g^{-1} db)	Total antioxidant capacity (μM Trolox 100 g^{-1} db)
Fresh	79.7±7.6 a[a]	35.6±0.1 k
60 °C	25.6±0.1 h, i, j	11.3±0.1 r
60 %–360 W	56.1±3.6 b	23.3±0.3 p
4	*52.8±3.1 b*	*32.2±0.1 m*
3	*33.8±0.2 e, f*	*13.4±0.1 q*
2	*28.6±1.2 g, h*	*13.2±0.1 q*
1	*13.1±0.3 k*	*51.4±0.51 g*
30 %–480 W	38.3±1.2 c, d	33.9±0.1 l
11	*34.7±1.4 d, e*	*38.5±0.7 c*
8	*28.6±2.4 g, h, i*	*60.5±0.2 d*
5	*23.5±2.5 j*	*24.2±0.1 o*
30 %–360 W	38.3±1.2 c, d	33.9±0.1 l
12	*24.2±1.4 i, j*	*38.5±0.1 i*
9	*16.7±2.4 k*	*85.7±0.6 b*
6	*16.4±1.6 k*	*54.9±0.2 e*
30 %–240 W	38.3±1.2 c, d	33.9±0.1 l
13	*33.4±3.4 e, f*	*39.1±0.7 i*
10	*28.8±2.4 g, h*	*52.9±0.1 f*
7	*24.6±2.2 h, i, j*	*89.2±1 a*
15 %–360 W	30.1±1.3 f, g	27.8±0.2 n
15	*32.07±2.5 e, f, g*	*36.5±0.2 j*
14	*27.9±1.9 g, h, i*	*45.9±1.0 h*
7 %	39.6±2.6 h, i, j	12.9±0.1 q
ANOVA	***	***

Values followed by the same letter, within the same column, were not significantly different ($p<0.05$), according to Duncan's test. Italic numbers (1–15) represent intermediate stages of VMFD and their exact position can be located in Fig. 1

*$p<0.05$; **$p<0.01$; ***$p<0.001$ —level of significance

[a] Treatment means of the ANOVA test (values are the mean value of three replications)

For instance, Li et al. (2007) reported an increase in the allicin during the thermal processing of garlic powder. Allicin and its derived products have been described as potent natural antioxidants (Yong 2006; Youji et al. 2006). The presence of allicin and its derived products could be responsible, at least partially, of the high antioxidant capacity of dried garlic slices.

Conclusions

Drying kinetics of garlic slices dried by the convective method was described by a two-term exponential model (Verma model), while drying kinetics of VMFD garlic was described by a one-term exponential function (modified Page model). The highest temperatures of the dried material were recorded when the VMFD was applied earlier. Drying of garlic slices by CPD-VMFD required less energy consumption than drying using the traditional CD. VMFD samples pre-dried until 60 % followed by VMFD at 360 W showed the lowest specific energy consumption of all studied drying treatments, 98±0.8 $\mathrm{kJg^{-1}}$. The energy savings of CPD-VMFD was very important compared with CD and ranged between 54.42 and 86.25 %. The total phenolic content was not significantly improved by the used of the combined drying method compared with the CD. However, a decrease in the *M* produced an increment in the antioxidant capacity of garlic slices. Dried garlic showed even higher antioxidant capacity than fresh samples. The highest antioxidant capacity was obtained for samples dried using CPD until 30 % of *M* and VMFD at 240 W. Results suggested that phenolic compounds and other chemical compounds, such as allicin, were responsible for the antioxidant capacity of dried garlic slices. Thus, the final recommendation considering both energy consumption and antioxidant capacity was that the best treatment for drying garlic slices was: CPD at 60 °C until a *M* of 30 % followed by VMFD at 240 or 360 W.

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PUBLICATION 5

Chemical composition, antioxidant capacity, and sensory quality of pomegranate (*Punica granatum* L.) arils and rind as affected by drying methods

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ORIGINAL PAPER

Chemical Composition, Antioxidant Capacity, and Sensory Quality of Pomegranate (*Punica granatum* L.) Arils and Rind as Affected by Drying Method

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Abstract The objective of this study was to evaluate the application of: (1) freeze drying, (2) convective drying (50, 60, or 70 °C), (3) vacuum–microwave drying (240, 360, or 480 W), and (4) a combined method of convective pre-drying and vacuum–microwave finish drying in the processing of pomegranate arils and rind. The quality parameters under study included sugars and organic acids, punicalagins and ellagic acid, total polyphenols, total antioxidant activity, and sensory quality. In general, drying led to a reduction in all studied parameters; however, the behavior of arils and rind was different. Vacuum–microwave drying at 240 or 360 W was the best drying treatment for arils, while rind required freeze drying or soft conditions of convective drying (50 °C). Further research is needed to obtain proper results with convective pre-drying and vacuum–microwave finish drying of arils and rind. With proper selection of the drying protocol, high-quality dried arils will be available for consumers; these arils will be characterized by high contents of fructose (25 g 100 g^{-1}), phytic acid (2.2 g 100 g^{-1}), punicalagins (0.57 mg g^{-1}), total polyphenols (1.6 mg eq gallic acid g^{-1}), high antioxidant capacity (0.6 mg eq Trolox g^{-1}), and high intensities of garnet color, sweetness, sourness, and fresh pomegranate aroma. Besides, dried rind with very high contents of active compounds (123 mg g^{-1} of punicalagins and 108 mg eq gallic acid g^{-1}) and high antioxidant capacity (26 mg eq Trolox g^{-1}) will be also available as functional material.

Keywords Antioxidant capacity · Descriptive sensory analysis · Drying kinetics · Organic acids · Polyphenols · Punicalagins

Nomenclature

db	Dry basis
d_b	Bulk density (kilograms per cubic meter)
wb	Wet basis
m	Mass (kilograms)
M_0	Initial moisture content (kilograms per kilogram dry basis)
V_b	Bulk volume (cubic meters)
ANOVA	Analysis of variance
AOC	Antioxidant capacity
CD	Convective drying
CPD	Convective pre-drying
DSA	Descriptive sensory analysis
dw	Dry weight
EA	Ellagic acid
FD	Freeze drying
HPLC	High-performance liquid chromatography
PC	Punicalagins
PG	Pomegranate

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TP	Total polyphenols
VMD	Vacuum–microwave drying
VMFD	Vacuum–microwave finish drying
VWP	Volume of woody portion

Introduction

Pomegranate (*Punica granatum* L.) is mainly cultivated in Iran, Afghanistan, India, Mediterranean countries, and to some extent in the USA, China, Japan, and Russia (Vardin and Fenercioglu 2003; Raisi et al. 2008). Spain is the greatest European producer (MARM 2010), and its production is mainly located in the southeastern provinces, mainly Alicante (Andreu-Sevilla et al. 2008).

The edible parts of pomegranates (PGs) can be consumed fresh; however, the unattractive external appearance of a high percentage (~20%) of fruits precludes their fresh consumption (Melgarejo and Salazar 2003).

Pomegranates are a well-known source of many valuable substances, such as hydrolyzable tannins (punicalagins and punicalins) (Gil et al. 2000), condensed tannins (proanthocyanidins) (Poyrazoglu et al. 2002), anthocyanins (Hernández et al. 1999), phenolic acids (gallic acid and ellagic acid) (Mousavinejad et al. 2009), and organic acids (malic acid) (Poyrazoglu et al. 2002). All these compounds show high antioxidant activity (García-Alonso et al. 2004) and induce health benefits against cancer, cardiovascular diseases, and other diseases (Sun et al. 2002).

Pomegranate juice is the most studied PG-based product (Tzulker et al. 2007; Calín-Sánchez et al. 2011a; Mena et al. 2011). Other authors have studied different alternatives for PG-based products such as jam (Melgarejo et al. 2011), wine (Zhuang et al. 2011), and dried arils, popularly called “anardana” in India (Singh et al. 2007).

Pomegranate peel (rind and carpellar membranes) is a richer source of antioxidants compared to edible arils (Li et al. 2006) and could be used as a nutraceutical supplement due to its elevated content of ellagitannins and ellagic acid (Espín et al. 2007), as well as a functional ingredient for juices (Navarro et al. 2011).

Dried arils and rind seem to be a proper PG-based product and co-product, respectively; however, up to this time there is no scientific literature on the influence of different drying methods on the chemical composition and activity of PG arils and rind.

Drying is one of the preservation methods ensuring microbial safety of biological products. Convective drying (CD) is still the most popular method applied to reduce the moisture content of fruits and vegetables. However, this method has several disadvantages and limitations; for instance, the high temperature used causes the degradation of important flavor and nutritional compounds, as well as color alteration. Freeze drying (FD) is also a popular drying method, but it is more expensive and its use is limited to high-price products, such as strawberries (Wojdyło et al. 2009).

The CD time can be greatly reduced (Sharma and Prasad 2004) and the quality of a finished product ensured (Men'shutina et al. 2005) by applying microwave energy to the dried material instead of hot air. Drying using microwave energy under vacuum (VMD) is a modern, efficient method of food preservation (Durance and Wang 2002) that can be used to significantly reduce the chemical, sensory, and nutritional alterations of the dried products (Drouzas and Schubert 1996). The low pressure also causes the so-called puffing effect, which is desirable to increase rehydration rate (Giri and Prasad 2007), create a crispy texture (Sham et al. 2001), and to maintain the appearance of the fresh product (Rahman 1999). Vacuum–microwave drying is not widely used in the food industry, although recent studies dealing with garlic (Figiel 2009) and herbs (Szumny et al. 2010; Figiel et al. 2010) have been reported. However, at the beginning of VMD, the intensive water evaporation from vegetables and fruits may exceed the vacuum pump capacity; this requires a reduction in the initial raw or setting up larger vacuum facilities. This problem can be easily overcome by using a convective pre-drying step that will drastically reduce the mass to be loaded in the vacuum–microwave (VM) system (Hu et al. 2006). The combination of convective pre-drying and VM finish drying (CPD–VMFD) may reduce the total dehydration cost and improve the quality of the commercial dehydrated product with a significant contribution to the fruit processing industry (Hu et al. 2006). Therefore, the main objective of this study was to determine the influence of different drying methods [CD, VMD, a combination of these two methods (CPD–VMFD), and FD] on the chemical composition, antioxidant capacity, and sensory quality of dried PG arils and rind.

Materials and Methods

Plant Material and Processing of Samples

Fresh pomegranate fruits (*P. granatum* L. cv. *Mollar de Elche*) were picked on 30 October 2010 in a commercial orchard in Elche (Alicante, Spain). *Mollar de Elche* is a late ripening cultivar with sweet arils and soft woody portion; this cultivar represents more than 95% of the pomegranate trees grown in Spain. Forty fruits were randomly harvested at commercial ripening (avoiding injured and sunburned fruits). Once in the laboratory, ten fruits remained at Miguel Hernández University facilities (Elche, Alicante, Spain) for analysis of fresh samples. The rest of the batch was express posted in a refrigerated package to the Institute of Agricultural Engineering (Wrocław, Poland). Pomegranate fruits were received after

1 day in perfect conditions and ready for the drying treatments. In all the samples under study, arils were manually separated and rinds including peel and carpellar membranes were treated separately. The rind was cut into 1-cm^2 squares just before drying.

Drying Methods

The initial moisture content (M_0) of the arils was 80.4% wet basis (wb) [4.1 kg kg^{-1} dry basis (db)] while M_0 of rind was 76.3% wb (3.2 kg kg^{-1} db). Pomegranate samples of approximately 60 g were subjected to four different drying protocols:

1. Convective drying (CD) was conducted using drying equipment designed and built up in the Institute of Agricultural Engineering (Wrocław University of Environmental and Life Sciences). Pomegranate samples were placed in a tray of 100-mm diameter. Convective method was operated at three different temperatures: 50, 60, or 70 °C with an air velocity of 0.8 ms^{-1}.
2. Vacuum–microwave drying (VMD) was carried out in Plazmatronika SM 200 dryer (Wrocław, Poland) connected to a vacuum system consisting of a vacuum pump BL 30P ("Tepro," Koszalin, Poland), a vacuum gauge MP 211 ("Elvac," Bobolice, Poland), and a compensation reservoir of 0.15 m^3. The dryer was operated at three different power levels: 240, 360, or 480 W. Pomegranate samples were placed in a cylindrical container of organic glass with a volume of 6.8 L. The pressure in the container ranged from 4 to 6 kPa. To avoid local overheating of fruits, the container rotated at a speed of 6 rpm, and additionally, an electric fan was installed at the bottom of the dryer producing an air stream of 22 °C at a velocity of 1 ms^{-1}.
3. Combined drying (CPD–VMFD) consisted of convective pre-drying (CPD) at temperature 60 °C for 90 or 150 min, followed by VM finish drying (VMFD) with microwave wattage of 360 W.
4. Freeze drying (FD) was carried out in a freeze drier OE-950 (Hungary) for 48 h at a pressure reduction of 65 Pa. The temperature in the drying chamber was −60 °C, while the heating plate reached 30 °C.

Bulk Density

The bulk density of dried samples was determined by calculating the ratio of their mass to their bulk volume (Eq. 1).

$$d_\mathrm{b} = \frac{m}{V_\mathrm{b}} \tag{1}$$

The samples were weighted with an analytical scale with an accuracy of 0.001 g, while the bulk volume V_b was measured with a 250-mL graduated cylinder. The cylinder was filled with the samples, and then, it was gently shaken to obtain the smallest volume of the samples.

Temperature

Temperature readings were taken immediately after taking the PG samples out of the VM dryer using an infrared camera Flir i50. The maximum temperature observed was recorded. It is expected that the local temperature within the material during drying was higher. However, a direct measurement in the drying chamber under vacuum is not practically possible because the measuring elements are heated by the microwave emission.

Extraction and Determination of Sugars and Organic Acids

Samples (4 g) were directly homogenized, while dried samples (2 g) were previously rehydrated with ultra pure water and phosphoric acid 0.1% (5 mL) and then homogenized. Both extracts were centrifuged at 15,000 rpm for 20 min. One milliliter of the centrifuged liquid was filtered using a 0.45-µm Millipore filter and then injected into a Hewlett-Packard high-performance liquid chromatography (HPLC) series 1100. The elution system consisted of 0.1% phosphoric acid with a flow rate of 0.5 mL min^{-1}. Organic acids were separated on a Supelcogel TM C-610H column (30 cm×7.8 mm i.d., Supelco, Bellefonte, PA, USA) and Supelguard column (5 cm×4.6 mm, Supelco) and detected using a diode-array detector set up at 210 nm. For sugar analyses, the same HPLC equipment, elution system, flow rate, and columns were used. The detection of sugars was performed using a refractive index detector (HP 1100, G1362A).

Standard curves for pure standards of organic acids (phytic, oxalic, citric, malic, quinic, and ascorbic acids) and for sugars (glucose, fructose, and sucrose) (Sigma, Poole, Dorset, UK) were used for quantification. Results for both organic acids and sugars were expressed as concentrations g 100^{-1} of dry weight (dw). Sugars and organic acids were determined in triplicate, and a model chromatogram for organic acids is shown in Fig. 1.

Identification and Quantification of Punicalagin Isomers and Ellagic Acid

Punicalagins and ellagic acid contents were determined separately in arils and rind. Two grams of arils and rind was diluted (5 mL of 80% MeOH+20% water+1% acetic acid) before its homogenization and then centrifuged at 15,000 rpm for 20 min. Supernatants were filtered through a 0.45-µm Millipore filter and then injected into a Hewlett-Packard HPLC series 1200 equipped with a diode-array

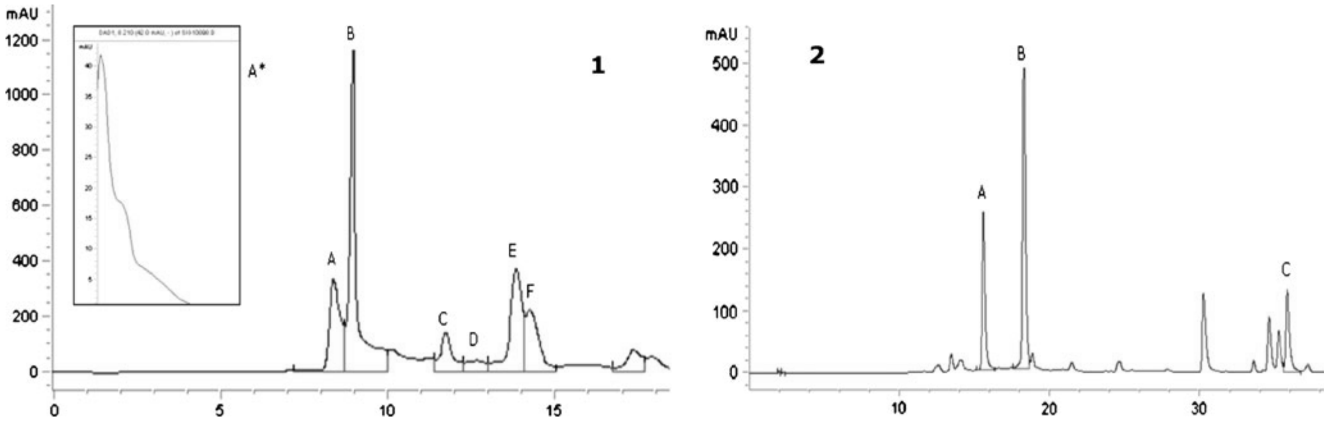

Fig. 1 Organic acid profile (*1*) (*A* phytic acid, *B* oxalic acid, *C* citric acid, *D* tartaric acid, *E* malic acid, *F* ascorbic+quinic acid) in pomegranate arils and phytic acid spectrum (*A**) and chromatogram (*2*) of punicalagins (*A* α-punicalagin and *B* β-punicalagin) and ellagic acid (*C*)

detector. Each sample (20 μL) was analyzed on a LiChroCART 100 RP-18 reversed-phased column (25× 0.4 cm, particle size, 5 μm; Merck, Darmstadt, Germany) equipped with a pre-column C_{18} (LiChroCART 4–4, LiChrospher 100 RP-18, 5 μm, Merck, Darmstadt, Germany) using a mobile phase of 1% acetic acid in ultra pure water (solvent A) and 1% acetic acid in MeOH (solvent B). Elution was performed at flow rate of 1 mL min^{-1} using a gradient starting with 1% B for 5 min, and increasing to 60% at 40 min. Punicalagins and ellagic acid detection was conducted at an absorbance of 360 nm.

For the identification of punicalagins and ellagic acid, spectrums and retention times were employed and compared with those obtained from the chemical standards. Standard curves for pure punicalagins (Chengdu Biopurify Phytochemicals Ltd. Sichuan, China) as well as for ellagic acid (Tocris Bioscience, Ellisville, MO, USA) were used for quantification. Results for individual isomer punicalagins (α and β) and ellagic acid were expressed as concentrations in milligrams per gram of dry weight. Punicalagin and ellagic acid were determined in triplicate, and a model chromatogram for punicalagins and ellagic acid is shown in Fig. 1.

Antioxidant Capacity and Total Polyphenols

The free radical scavenging activities using the radical 2,2-diphenyl-1-picrylhydrazyl method (DPPH) was evaluated according to that described by Brand-Williams et al. (1995) with some modifications (Llorach et al. 2004). Briefly, for each sample, 2 g of arils and 1 g of rind were homogenized in 5 mL of MeOH/water (80:20 *v*/*v*) and then centrifuged at 15,000 rpm for 20 min. Ten microliters of the supernatant was mixed with 40 μL of MeOH and added to 950 μL of a 0.094-mM DPPH solution. The absorbance at 515 nm was measured after 50 min of reaction; during this time, samples were sealed with parafilm to avoid evaporation losses. The decrease in absorbance was measured in a Uvikon XS spectrophotometer (Bio-Tek Instrument, Winooski, VT). Results were expressed as milligrams of Trolox equivalent 100 g^{-1} dw. Tests were run in triplicate.

Total polyphenols (TP) were quantified using Folin–Ciocalteu reagent (Singleton et al. 1999). Briefly, for each sample, 2 g of arils and rind was homogenized in 5 mL of MeOH/water (80:20 *v*/*v*)+2 mM NaF and then centrifuged at 15,000 rpm for 20 min. Absorption was measured at 760 nm using a spectrophotometer (ThermoSpectronic Heγios, UK). Results were expressed as milligrams of gallic acid per gram of dry weight.

Sensory Evaluation with Trained Panel

DSA with a trained panel was used to describe fresh and dried PG arils. A panel of seven panelists, ages 20 to 55 years (three females and four males) was trained in descriptive evaluation of fruits and fruit-based products. All panelists work at Miguel Hernández University and have a wide experience in sensory evaluation of fruits and herbs (Calín-Sánchez 2011b; Carbonell-Barrachina et al. 2012).

The study was carried out at UMH facilities (individual booths with controlled illumination and temperature) during three different sessions. In each session, the panelists tested all the PG samples; the sample order for each panelist was randomized. Approximately 4 g of fresh or dried arils was served at 21 °C together with the appropriate questionnaire; samples were served one at a time and waiting time was 5 min between samples. Water was provided to consumers for palate cleansing between samples.

In each questionnaire, the panelists were asked to evaluate the intensity of the following attributes of pomegranate arils: color (associated with arils of *Mollar de Elche* cultivar), volume of the woody portion (VWP) (visual perception of the volume of the woody portion), fresh PG odor and flavor (odor and taste of fresh arils from *Mollar de Elche* cultivar), burnt odor and flavor, caramel odor (associated with cooked sugars), sourness, sweetness, bitterness, crispiness (sound produced during chewing), adhesiveness (stickiness to teeth), and solubility (how fast the product dissolves in the saliva). The individual products were scored for the intensity of different aroma attributes on a scale of 0 to 10, where 0=no perceptible intensity and 10=extremely high intensity.

The panelists relied on their training experience to score products, which were presented coded with three-digit numbers in the test design. Sensory tests were run in triplicate.

Statistical Analysis

One-way analysis of variance (ANOVA) and multiple-range tests were used for comparison of the results. Homogenous groups and the least significant difference were determined according to Tukey's test (at significance level of $p \leq 0.05$). The statistical analyses were done using Statgraphics Plus 5.0 software (Manugistics, Inc., Rockville, MD, USA). Graphics were created using Sigma Plot 11.0 (SPSS Science, Chicago, IL, USA).

Results and Discussion

Temperature

During VM drying, an increase in the microwave power from 240 to 360 W resulted in increases in the temperature of rind and arils from 48 to 60.9 °C and from 49.4 to 61.6 °C, respectively. However, the further increase of the microwave power to 480 W reduced these mean temperatures to 55.3 and 52.0 °C, respectively. Similar patterns were found for the maximum temperatures reached during the VM drying process at 240, 360, and 480 W, with values being 55, 81, 69 °C and 70, 84, 72 °C for rind and arils, respectively. In general, an increase in microwave wattage increases simultaneously the temperature of samples (Drouzas and Schubert 1996; Figiel et al. 2010). The unexpected temperature of samples dried at 480 W could be due, among other reasons, to a drastic reduction in the drying time (from 72 to 28 min) and also to the high rate of water evaporating from the surface of this material to the surrounding atmosphere. Convective pre-drying always resulted in higher temperatures of the samples being dried compared to VMD at 360 W, reaching values as high as 87 °C in arils after 150 min of CPD.

The maximum temperatures observed during drying of arils were higher than those for the rind, probably resulting from the higher internal pressure created by water inside the arils while microwaving. The cellular system of the arils is less permeable than that of the rind for the water vapor (Falade and Igbeka 2007) due to higher concentrations of compounds such as sugars and organic acids. Because of that, the cellular system of the arils is also more elastic and easily undergoes puffing at high inner pressure (Lin et al. 1998). The puffing usually increases the volume of the dried product (Lin et al. 1998; Figiel 2010) and in the same way decreases its density (Durance and Wang 2002).

Bulk Density

Pomegranate arils showed higher values of bulk density than PG rind for all treatments (Fig. 2). Pomegranate rind showed lower density after FD and CD than after CPD–VMFD and VMD, which confirms that puffing does not occur in this material. Additionally, the CPD–VMFD rind samples presented lower values than VMD samples due to the convective pretreatment. The temperature did not have significant effects on the density of rind dried by convection. FD rind samples exhibited the lowest value of bulk density (159 kg m^{-3}) due to their low shrinkage.

Lower density of the dried product is recommended to increase its attractiveness for consumers (Durance and Wang 2002). The density of PG arils was lower after CPD–VMFD and VMD than after FD and CD, proving that puffing occurs in arils. The density of VMD samples was additionally affected by the wattage showing lower values when higher wattages were applied. The increase in microwave wattage generally decreases the density of dried products by boosting of puffing, which directly increases the volume of these products (Durance and Wang 2002; Figiel et al. 2010; Figiel 2009). The lowest density of dried arils (333 kg m^{-3}) was obtained after application of 90 min of CPD–VMFD.

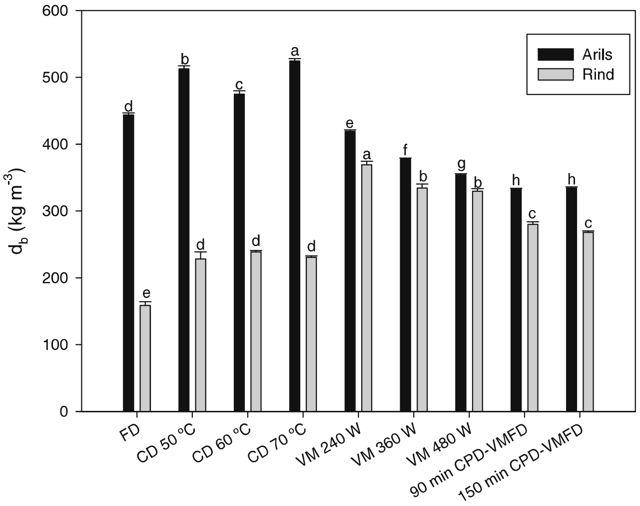

Fig. 2 Bulk density of pomegranate arils and rind as affected by the drying method. Values are the mean of three replications. Values followed by the same letter, within arils or rind, were not significantly different at $p<0.05$

Sugars and Organic Acids

Fructose and glucose were the main sugars of dried PG arils (Table 1). In the current study, fructose contents (ranging from 24.2 to 46.3 g 100 g^{-1} dw) were higher than those of glucose (ranging from 2.42 to 13.8 g 100 g^{-1}), as previously reported by Melgarejo et al. (2000) and Mena et al. (2011). The sugar analysis also revealed trace amounts of sucrose.

Arils sugars were more stable with softer drying conditions (low temperature and long time). Soft CD conditions (50 °C) provided the best results, followed by 150-min CPD–VMFD. An increase in the product temperature caused important degradation of fructose and glucose (~45%), mainly because of Maillard and browning reactions (Mota et al. 2010).

Table 1 Contents of sugars and organic acids in pomegranate arils as affected by the drying method

Treatment			
Sugars			
	Glucose (g 100 g^{-1} dw)		Fructose
Fresh	27.1±0.1 a		46.3±0.2 a
FD	14.7±0.1bc		24.8±0.1c
CD 50 °C	15.7±1.4b		27.8±2.6b
CD 60 °C	14.2±0.2c		24.2±0.3c
CD 70 °C	14.1±0.4c		24.2±0.6c
VM 240 W	14.4±0.2bc		24.8±0.3c
VM 360 W	14.8±0.1bc		25.7±0.1bc
VM 480 W	14.6±0.1bc		25.3±0.6bc
90-min CPD–VMFD	14.7±0.2bc		25.2±0.4bc
150-min CPD–VMFD	15.0±0.1bc		25.7±0.2bc
ANOVA	*		*
Organic acids			
	Phytic (g 100 g^{-1} dw)	Citric	Malic
Fresh	10.5±21a	0.52±0.09a	2.49±0.02a
FD	1.42±0.04d	0.04±0.01b	0.23±0.01ef
CD 50 °C	5.06±0.05b	0.03±0.01cd	0.18±0.01e
CD 60 °C	3.66 ±0.02cd	0.03 ±0.01bcd	0.20±0.01d
CD 70 °C	2.58±0.02e	0.03±0.01bc	0.20±0.01b
VM 240 W	2.22±0.02f	0.03±0.01cd	0.30±0.01d
VM 360 W	3.49±0.04d	0.02±0.01d	0.42±0.02c
VM 480 W	3.87±0.06c	0.02±0.01d	0.40±0.01c
90-min CPD–VMFD	3.65±0.15cd	0.03±0.01cd	0.36±0.01c
150-min CPD–VMFD	2.93±0.18e	0.03±0.01bcd	0.32±0.01d
ANOVA	*	*	*

Treatment means of the ANOVA test (values are the mean value of three replications). Values followed by the same letter within the same column were not significantly different, Tukey's multiple-range test

*$p<0.001$, significant

Phytic, malic, and citric were the main organic acids found in PG arils. Malic acid was reported as the major organic acid in pomegranate products by several researchers (Melgarejo et al. 2000; Poyrazoglu et al. 2002; Ozgen et al. 2008); however, this is the first manuscript reporting the presence of phytic acid (Fig. 1) and demonstrating that phytic acid is the main organic acid in PG arils (Table 1). Phytic acid content ranged from 1.42 to 10.5 g 100 g^{-1} dw, while malic and citric acid contents ranged from 0.18 to 2.49 g 100 g^{-1} and from 0.02 to 0.52 g 100 g^{-1}, respectively. The analysis of organic acids also revealed the presence of oxalic, tartaric, quinic, and ascorbic acid but in trace amounts.

In general, phytic acid is found in cereals, legumes, and oil seeds (Cheryan and Rackis 1980). Taking into account that the woody portion of PG arils represents about 15% of the aril (Melgarejo 2010) and that the total lipid content for sweet PGs ranges from 69 to 81 gkg^{-1} (Hernández et al. 2011), the presence of phytic acid in PG arils from *Mollar de Elche* cv. seems reasonable. In recent years, several benefits have been attributed to phytic acid: prevention of diabetes (Lee et al. 2006), renal calculi (Saw et al. 2007), Parkinson's disease (Xu et al. 2008), and cancer (Vucenik and Shamsuddin 2006) and high antioxidant activity (Harbach et al. 2007). All these properties will contribute to the health benefits and antioxidant capacity (AOC) of PG fruits.

The different behavior of the individual organic acids in PG arils made it difficult to make recommendations about the best drying method, and these conditions will depend on the aim of the final product. In general, soft conditions (CD and VMD) favored high contents of phytic and citric acids, while strong conditions favored high contents of malic acid. The general decrease of PG organic acids showed the high sensibility of this group of compounds to the temperature originated during drying, proving their role as reactants in the Maillard reaction (Nicoli et al. 1999).

Punicalagins and Ellagic Acid

The contribution of punicalagins and ellagic acid to the total antioxidant activity of PGs has been demonstrated and represents almost 87% of the total activity (Gil et al. 2000). PG rind is a richer source of punicalagins and ellagic acid than arils (Gil et al. 2000; Seeram et al. 2005). In the current study, the contents of the punicalagin isomers (α-PC and β-PC) and ellagic acid (EA) were significantly affected by the different drying methods in both rind and arils.

α-PC in rind ranged from 60.5 to 139 mg g^{-1} dw, while β-PC ranged from 54.1 to 143 mg g^{-1}, and EA from 1.07 to

2.49 mg g^{-1} (Table 2). The content of ellagic acid was significantly lower ($p<0.05$) than those of α- and β-PC in both fresh and dried PG arils. During rind drying, punicalagins were not hydrolyzed to EA, as previously reported during PG ripening (Schwartz et al. 2009) and PG juice manufacturing (Mena et al. 2011). β-PC showed higher contents than α-PC in fresh rind, as expected (Lu et al. 2008); however, in all nine treatments, α-PC was slightly more abundant than β-PC, proving the different thermal stability of the PC isomers.

Freeze drying was the treatment leading to the highest punicalagin contents during drying of PG rind. Besides and in general, VMD provided better results than CD and CPD–VMFD and soft conditions are recommended.

α-PC in arils ranged from 0.23 to 0.53 mg g^{-1} dw, while β-PC ranged from 0.34 to 0.57 mg g^{-1}, and EA from 0.012 to 0.061 mg g^{-1} (Table 2). The content of EA in arils was significantly lower ($p<0.05$) than those of α- and β-PC, as previously reported for PG rind. β-PC showed higher values than α-PC in both fresh and dried PG arils, showing a similar pattern to that previously described by Gil et al. (2000) and Mena et al. (2011) in PG juice.

During drying of PG arils, α-PC, β-PC, and EA contents decreased by 40%, 13%, and 4.5%, respectively. Soft conditions of CD led to the highest contents of both punicalagins, and reasonable contents were obtained after VMD at 240 or 360 W.

Antioxidant Capacity and Total Polyphenols

Lower AOC and TP were obtained for dehydrated samples compared to the fresh products (Table 3), with rind having values about one order of magnitude higher than arils (Li et al. 2006). AOC of PG rind ranged from 12.6 to 45.1 mg eq Trolox g^{-1} dw, while TP ranged from 57.3 to 125 mg eq gallic acid g^{-1} dw. PG rind showed the highest values of AOC and TP after FD ($p<0.05$), followed by soft conditions of both CD and VMD. This behavior could be the result of high temperatures decreasing the antioxidant activity of the products being dried, independently of the time required for the process. The CPD–VMFD did not improve the AOC and TP values of PG compared to CD and VMD.

AOC of PG arils ranged from 0.57 to 1.20 mg eq Trolox g^{-1} dw, while TP ranged from 1.57 to 7.57 mg eq

Table 2 Content of phenolic bioactive compounds in rind and arils of pomegranate as affected by the drying method

Treatment	α-Punicalagin (mg g^{-1} of dw)	β-Punicalagin	Ellagic acid
Rind			
Fresh	139±1a	143±1a	2.49±0.1a
FD	113±4b	98.7±2.2b	1.71±0.1bc
CD 50 °C	64.5±1.5ef	58.4±1.3ef	1.16±0.1fg
CD 60 °C	60.5±2.6f	54.1±2.5f	1.95±0.3b
CD 70 °C	65.8±1.7ef	58.7±1.8ef	1.13±0.1fg
VM 240 W	85.6±1.6c	74.6±1.5c	1.42±0.1de
VM 360 W	74.3±3.8d	67.3±3.5d	1.59±0.1cd
VM 480 W	70.5±0.3de	62.8±0.7de	1.27±0.1fg
90-min CPD–VMFD	62.3±2.8f	55.9±2.7f	1.36±0.1def
150-min CPD–VMFD	72.8±1.7d	65.9±1.6d	1.07±0.1g
ANOVA	*	*	*
Arils			
Fresh	0.53±0.01a	0.57±0.01a	0.061±0.01g
FD	0.27±0.01d	0.40±0.01c	0.032±0.01f
CD 50 °C	0.31±0.01b	0.50±0.01b	0.012±0.01cd
CD 60 °C	0.29±0.01c	0.50±0.01b	0.038±0.01de
CD 70 °C	0.23±0.01e	0.43±0.01c	0.036±0.01e
VM 240 W	0.23±0.01e	0.34±0.01d	0.042±0.01c
VM 360 W	0.28±0.01cd	0.40±0.02c	0.052±0.01b
VM 480 W	0.24±0.01e	0.34±0.03d	0.059±0.01a
90-min CPD–VMFD	0.24±0.01e	0.34±0.01d	0.048±0.01b
150-min CPD–VMFD	0.23±0.01e	0.34±0.01d	0.048±0.01c
ANOVA	*	*	*

Treatment means of the ANOVA test (values are the mean value of three replications). Values followed by the same letter within the same column were not significant different, Tukey's multiple-range test

*$p<0.001$, significant

Table 3 Antioxidant capacity (AOC) and total polyphenols (TP) of pomegranate rind and arils as affected by the drying method

Treatment	Rind		Arils	
	AOC (mg eq Trolox g^{-1})	TP (mg eq gallic acid g^{-1})	AOC (mg eq Trolox g^{-1})	TP (mg eq gallic acid g^{-1})
Fresh	45.1±0.1e	125±1a	1.20±0.02a	7.57±0.07a
FD	26.2±0.4b	118±1b	0.62±0.03def	1.93±0.01de
CD 50 °C	25.8±0.1bc	108±1d	0.70±0.01bc	2.05±0.05d
CD 60 °C	24.5±0.2d	105±1e	0.65±0.03cde	1.99±0.07de
CD 70 °C	12.6±0.1e	72.8±0.1f	0.68±0.02bed	2.01±0.04d
VM 240 W	25.4±0.4c	111±1c	0.57±0.02f	1.57±0.01f
VM 360 W	12.95±0.1e	69.2±0.1g	0.59±0.07ef	2.38±0.02c
VM 480 W	12.95±0.1e	57.3±0.4i	0.74±0.05b	2.51±0.03b
90-min CPD–VMFD	12.94±0.1e	63.4±0.6h	0.69±0.05bc	2.00±0.04de
150-min CPD–VMFD	12.56±0.1e	69.9±0.1g	0.72±0.02bc	1.87±0.03e
ANOVA	*	*	*	*

Treatment means of the ANOVA test (values are the mean value of three replications). Values followed by the same letter within the same column were not significant different ($p<0.05$), Tukey's multiple-range test

*$p<0.001$, significant

gallic acid g^{-1} dw. PG arils showed better results with low temperatures and consequently long times in CD; however, when VMD was applied, higher power leading to high temperatures and shorter drying time were recommended. The first trend (CD) was similar to that already described for the rind, while the second one (VMD) could be explained due to Maillard reactions producing compounds with high antioxidant capacity (Yilmaz and Toledo 2005). Finally, FD and CPD–VMFD did not improve the results associated to the best CD and VMD treatments of PG arils.

Sensory Analysis

In general, the drying method significantly affected the intensities of the main sensory attributes of dried arils (Table 4). Attributes such as color, fresh PG odor and aroma, sourness, and solubility significantly decreased after the drying process compared with the fresh sample, while the rest of the attributes, burnt odor and aroma, caramel odor and aroma, sweetness, bitterness, crispiness, and adhesiveness increased during the dehydration of the fresh fruits. Some of these experimental findings could be related to the reduction in the moisture content, which for example could be responsible for the increased adhesiveness and reduced solubility.

The color changes were linked with the Maillard reactions, which modify the initial pale red color (10 in the scale) of *Mollar de Elche* arils into a darker and intense brown color. Color ranged between 5 and 10, respectively; after the fresh sample, all the samples under CD showed better results (mean of 6.9±0.4) than VMD (6.1±0.3) and CPD–VMFD (6.3±0.4). FD was scored with the maximum values for fresh PG odor and aroma (3.6 and 5.7, respectively) after the fresh sample (10), and followed by VMD at 240 W (3.1 and 5.6, respectively). Fresh PG odor and aroma got lower scores as the temperature increased. Sourness decreased during the drying process while sweetness increased. Sweetness was scored from 4.0 in fresh sample to 6.4 in VMD at 240 W. Solubility obtained lower scores in dried products (ranging from 3.1 to 4.4) compared to fresh samples (5.0). Treatments using high temperatures or high microwave powers significantly increased crispiness from 3.3 (fresh samples) to 4.5 (CD at 70 °C) or 5.1 (VMD at 480 W), but at the same time they also increased adhesiveness. However, the highest scores for crispiness (5.6) and adhesiveness (6.3) were obtained for the samples dried by the combined method (150 min CPD–VMFD). The VWP of arils was also evaluated, and the best results were obtained for samples gently treated with hot air at 50 °C (3.9), while the worst result was found in samples dried using the CPD–VMFD (8.9). Caramel notes were clearly influenced by the temperature. Burnt odor and aroma were evaluated, and the following treatments led to unacceptable (too high) values: VMD at 480 W and both CPD–VMFD treatments. Bitterness scores were positively correlated with burnt notes. Finally and regarding sensory quality, the final recommendation to dry PG arils is to use FD or VMD at 240 W.

Conclusions

The chemical composition, functional properties, and sensory attributes of pomegranate and arils were significantly affected by their drying. In general, significant reductions in

Table 4 Descriptive sensory analysis of pomegranate arils as affected by the drying method

Property	Attribute	ANOVA	Fresh	FD	CD (°C)			VM (W)			CPD (min)-VMFD	
					50	60	70	240	360	480	90	150
Appearance	Color	*	10.0±0.2a	6.0±0.3f	7.0±0.4f	6.8±0.4c	7.0±0.06b	6.7±0.3d	6.3±0.3e	5.4±0.4h	5.9±0.4g	6.8±0.3c
	VWP	*	5.0±0.2c	7.0±0.3b	3.9±0.3d	4.3±0.3d	4.9±0.4c	4.4±0.3d	6.9±0.3b	5.5±0.3c	6.9±0.3b	8.9±0.1a
Odor	Fresh PG	*	10.0±0.4a	3.6±0.2b	2.1±0.2d	1.3±0.1e	0.9±0.1g	3.1±0.3c	3.1±0.2c	3.1±0.3c	3.1±0.3c	1.2±0.1f
	Burnt	*	0 a	0.8±0.1c	0.3±0.01f	0.4±0.01e	0.4±0.01e	0.3±0.01f	0.7±0.1d	2.6±0.1a	1.9±0.1b	0.7±0.1d
	Caramel	*	0 i	2.1±0.2e	0.7±0.1h	0.7±0.1h	1.8±0.1f	1.5±0.1g	3.6±0.2b	4.9±0.4a	3.1±0.2d	3.5±0.3c
Taste	Sweetness	*	4.0±0.1j	5.6±0.2c	4.9±0.4h	5.1±0.4g	4.7±0.2i	6.4±0.3a	5.5±0.4d	5.4±0.3e	5.9±0.3b	5.3±0.4f
	Sourness	*	4.5±0.2a	3.1±0.3e	2.9±0.2g	3.9±0.2d	2.0±0.1i	4.1±0.3c	3.1±0.2e	4.2±0.3b	3.0±0.2f	2.6±0.1h
	Bitterness	*	0 f	0.7±0.1 d	0.6±0.1e	0.6±0.1d	0.9±0.1c	0.4±0.01e	0.6±0.1d	3.7±0.2a	2.1±0.1b	0.9±0.1c
Aroma	Fresh PG	*	10.0±0.6a	5.7±0.4b	4.4±0.3e	4.3±0.3f	4.0±0.3g	5.6±0.3c	4.6±0.3d	3.1±0.2i	3.9±0.2h	4.3±0.2f
	Burnt	*	0 i	0.6±0.1f	0.4±0.01h	0.5±0.01g	0.8±0.1d	0.5±0.01g	0.9±0.1c	3.7±0.2a	2.6±0.1b	0.7±0.1e
Texture	Crispiness	*	3.3±0.3h	3.3±0.2h	4.0±0.3g	4.1±0.3f	4.5±0.4c	3.3±0.2h	4.4±0.3d	5.1±0.4b	5.6±0.2a	4.3±0.2e
	Adhesiveness	*	0 j	5.9±0.5b	3.3±0.2i	3.4±0.2h	4.6±0.3e	3.6±0.1g	3.9±0.2f	5.3±0.3c	5.0±0.4d	6.3±0.4a
	Solubility	*	5.0±0.2a	3.7±0.n	3.4±0.2f	3.2±0.2g	4.4±0.2b	4.0±0.3c	3.1±0.3h	3.2±0.1g	3.1±0.2h	3.6±0.2e

Treatment means of the ANOVA test (values are the mean value of three replications). Values followed by the same letter, within the same column, were not significant different ($p<0.05$), Tukey's multiple-range test

*$p<0.001$, significant

the contents of sugars, organic acids, and total polyphenols were associated with the drying process. Drying of both pomegranate arils and rind could be a good option to reduce the amount of wastes and create extra value in fruits with inappropriate appearance. Dried PG arils, after soft VMD (240–360 W), were a delicious, sweet, sour product with intense pomegranate aroma due to proper and equilibrated amounts of sugars and organic acid contents; besides, this product has significant antioxidant capacity (0.6 mg eq Trolox g^{-1}) mainly due to important contents of polyphenols (1.6 mg eq gallic acid g^{-1}) and punicalagins(0.57 mg g^{-1}). Dried PG arils can be stored for a long period and could be consumed as desserts, sweets, or even in salads. Dried PG rind is a suitable nutraceutical ingredient and food condiment, but in this case, soft conditions of CD are (50 °C) together with the most expensive FD. Surprisingly, CPD–VMFD was not an appropriate treatment neither for PG arils nor for rind under the conditions assayed. Due to this fact, further research is needed to find the proper combination of CPD and VMFD. Finally, it can be concluded that drying of rind and transformation of low-quality PG fruits into valuable dried arils with a long shelf life and wide range of application in modern healthy cuisine are appropriate options to fulfill the integral use of PG fruits and increase the income of farmers.

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PUBLICATION 6

Drying kinetics and energy consumption in dehydration of pomegranate (*Punica granatum* L.) arils and rind

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ORIGINAL PAPER

Drying Kinetics and Energy Consumption in the Dehydration of Pomegranate (*Punica granatum* L.) Arils and Rind

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Abstract The objective of this study was to evaluate the drying kinetics and energy requirements during convective drying (CD) (50, 60 or 70 °C), vacuum-microwave drying (VMD) (240, 360 or 480 W) and a combined method of convective pre-drying and vacuum-microwave finishing drying (CPD-VMFD) while processing pomegranate arils and rind. Drying kinetics of CD and VMD was described using seven basic drying models; however, VMFD was modeled only by the Henderson and Pabis equation. Pomegranate rind required less drying time (26–460 min) than arils (51–1,395 min) due to its higher porosity and lower sugar content. The drying time and the energy consumption were reduced when the air temperature and microwave wattage were increased. VMD required less energy than CD within the entire range of moisture content assayed. CD energy consumption can be reduced by its combination with VMD (CPD-VMFD), and this reduction was more important when the VMFD was applied earlier. VMD and CPD-VMFD are a good option for food drying industry in order to reduce both the drying time and the energy consumption while processing pomegranate arils and rind. Therefore, industries can optimise the drying process and consequently save their financial needs.

Keywords Drying kinetics · Drying time · Energy consumption · Energy efficiency · *Punica granatum*

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Nomenclature

a, b, c	Drying parameters
k	Drying constant (per minute)
m	Mass of the sample (gram)
M	Moisture content (kilograms per kilogram db)
M_e	Equilibrium moisture content (kilograms per kilogram db)
M_0	Initial moisture content (kilograms per kilogram db)
MR	Moisture ratio
$M(t)$	Moisture content after time of drying t (kilograms per kilogram db)
W	Mass of water (grams)
E_{C}	Energy consumed in convective method (kilojoules)
E_{C_m}	Specific energy consumed in convective method (kilojoules per gram fw)
E_{C_W}	Specific energy consumed in convective method (kilojoules per gram of water)
E_{ev}	Energy of water evaporation (kilojoules)
E_{VM}	Energy consumed in vacuum-microwave method (kilojoules)
E_{VM_m}	Specific energy consumed in vacuum-microwave method (kilojoules per gram fw)
E_{VM_W}	Specific energy consumed in vacuum-microwave method (kilojoules per gram water)
N_{f}	Power consumption by a fan (kilowatts)
N_{e}	Power consumption by an electric engine (kilowatts)
N_{h}	Power consumption by a heater (kilowatts)
N_{M}	Output power of magnetrons (kilowatts)
N_{V}	Power consumption by a vacuum pump (kilowatts)
η_{C}	Energy efficiency for convective method
η_{M}	Efficiency of magnetrons

η_{VM}	Energy efficiency for vacuum-microwave method
λ_{w}	Latent heat of water vaporisation (kilojoules per gram)
t	Time (minutes)
R^2	Coefficient of determination
ANOVA	Analysis of variance
CD	Convective drying
CEE	Cumulative energy efficiency
CPD	Convective pre-drying
fw	Fresh weight
db	Dry basis
wb	Wet basis
dw	Dry weight
K	Critical point
RMSE	Root-mean-square error
VM	Vacuum microwave
VMD	Vacuum-microwave drying
VMFD	Vacuum-microwave finishing drying

Introduction

The edible parts of pomegranates (*Punica granatum* L.), arils, are mostly consumed as fresh product; however, there is a huge amount of fruits whose quality is not good enough to be consumed as a fresh fruit due to the crop particularities, heterogeneous ripening and fruit physiopathies: sunburn or cracking (Melgarejo and Salazar 2003).

Pomegranates are a well-known source of many valuable substances, such as hydrolysable tannins (Gil et al. 2000), anthocyanins (Hernández et al. 1999) and phenolic acids (Mousavinejad et al. 2009); all these compounds show high antioxidant activity (García-Alonso et al. 2004) and induce health benefits against cancer, cardiovascular and other health diseases (Sun et al. 2002).

Due to the huge amount of non-commercial pomegranate fruits and the important health benefits of this fruit, researchers have intensively studied different options to develop or improve pomegranate-based products and co-products, such as juices, jams, wines and dried arils. On the other hand, pomegranate rind is a richer source of antioxidants than arils and could be used as a nutraceutical supplement due to its elevated contents of ellagitannins and ellagic acid (Espín et al. 2007). Thus, both dried arils and rind are considered proper pomegranate food and co-product, respectively (Calín-Sánchez et al. 2013).

Dehydration operations have been used for decades in chemical and food processing industries for efficient long-term preservation of final products. The basic objective in drying food products is the removal of water from solids down to a level at which microbial spoilage is avoided. Convective drying (CD) is still the most popular method applied to reduce the moisture content of fruits and vegetables; however, this method has several disadvantages and limitations; for instance, it has been demonstrated that the high temperature used during the process involves the degradation of important flavour compounds and nutritional ingredients, as well as negative colour alteration.

The drying time can be greatly reduced (Sharma and Prasad 2004) and the quality of the final products increased by using microwave energy (Men'shutina et al. 2005). Besides, drying with the microwave method under vacuum is a modern and efficient method of food preservation (Durance and Wang 2002), which belongs to swell-drying operations used for texturing of the food products (Mounir et al. 2012). Lowered pressures induce faster evaporation of water from the material at relatively low temperature (Figiel et al. 2010), which can reduce the chemical alterations within the dried product (Drouzas and Schubert 1996). The vacuum-microwave drying (VMD) method is not yet common in the industry, although investigations have already been conducted on tomatoes (Durance and Wang 2002) and garlic cloves and slices (Figiel 2009). However, at the beginning of vacuum microwave (VM) dehydration, the intensive water evaporation from the plant material may exceed the capacity of the vacuum pump. Therefore, a reduction in the amount of raw material subjected to drying or the application of a large vacuum installation is needed. This problem can be overcome by pre-drying the material using CD. As a result of pre-drying, the mass loads of VM equipment can be radically decreased (Hu et al. 2006). Pre-drying of the plant materials by convective method before VM finishing drying (CPD-VMFD) may reduce the total cost of dehydration and improve the quality of the commercial dehydrated product with a significant contribution to the fruit-processing industry (Hu et al. 2006).

Several authors have reported their findings on energy balances during drying of different materials such as carrots (Nazghelichi et al. 2011) or mushrooms (Motevali et al. 2011a). For instance, Kowalski and Mierzwa (2011) studied the drying of red bell pepper using convective, microwave and infrared heat sources applied separately and in different combinations to find the proper drying conditions (product of the best quality and minimum energy consumption). Motevali et al. (2011b) evaluated the energy consumed during drying of pomegranate arils by different drying systems, including hot-air convection, use of microwave pretreatment with convection drying, microwave drying, vacuum drying and infrared drying.

However, up to this time, there is no research literature on the influence of vacuum-microwave drying and convective pre-drying followed by vacuum-microwave finish drying on

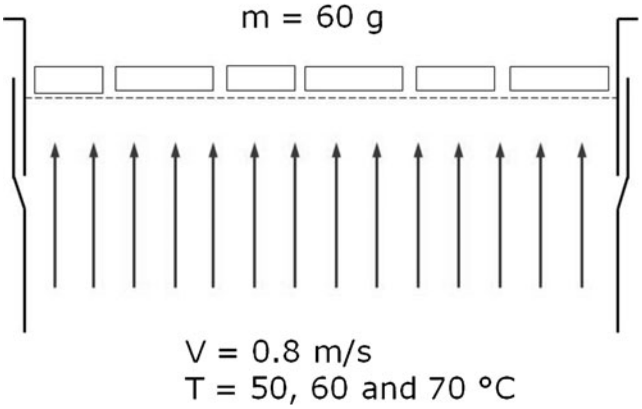


Fig. 1 Diagram of the convective drying conditions: mass, air velocity, air flux and temperatures

the energy requirements of pomegranate arils and rind. The energy input while drying is strictly associated with the drying kinetics of the material subjected to drying. Consequently, the main objective of this study was to determine the influence of drying parameters during CD, VMD and CPD-VMFD on the drying kinetics and energy profile of pomegranate arils and rind.

Materials and Methods

Plant Material and Processing of Samples

Fresh pomegranate fruits (*P. granatum* L. cv. *Mollar de Elche*) were picked on October 30, 2011 in a commercial orchard in Elche (province of Alicante, Spain). Thirty fruits were randomly harvested at commercial ripening. The fruits were express posted in a refrigerated package to the Institute of Agricultural Engineering (Wrocław, Poland); after 1 day, fruits were received in perfect conditions and ready for drying tests. The arils were manually separated, and the rind was cut into 1-cm squares just before drying.

The initial moisture content (M_0) of the arils was 80.4 % wet basis (wb) (4.1 kg kg^{-1} dry basis (db)) while M_0 of the rind was 76.3 % wb (3.2 kg kg^{-1} db). Pomegranate samples, ~60 g, were subjected to three different drying protocols which were successfully applied in pomegranate arils and rind in terms of nutritional, functional and sensory properties (Calín-Sánchez et al. 2013):

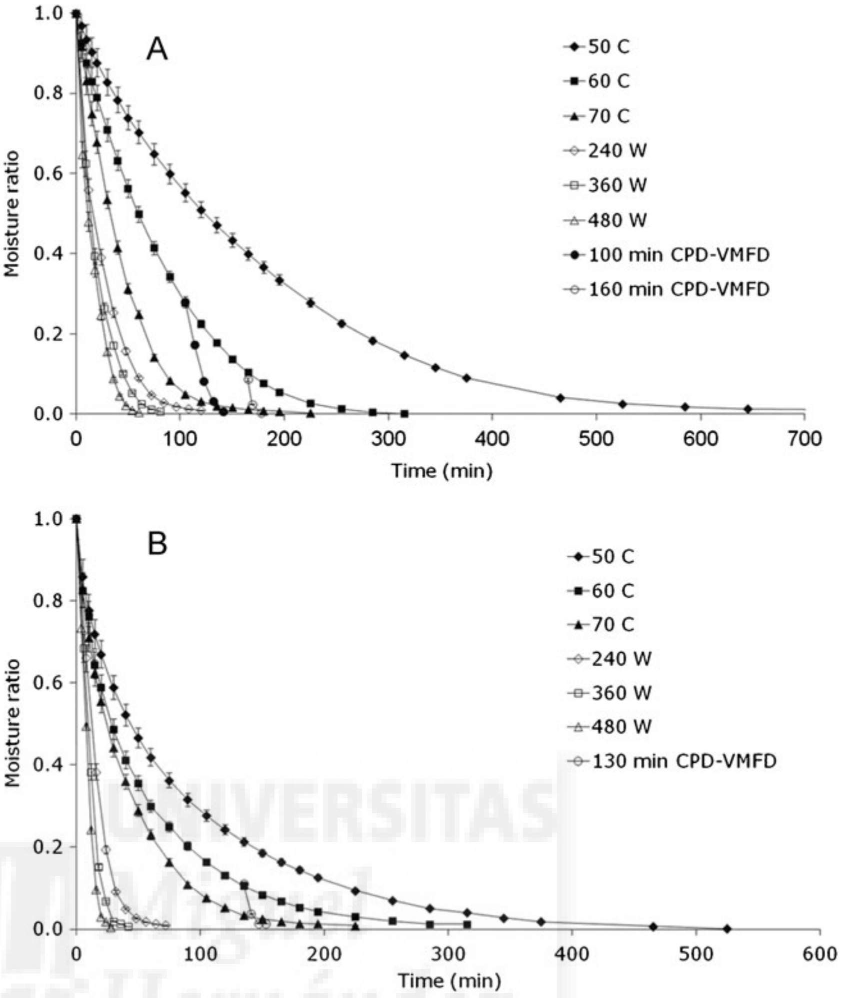
1. *Convective drying* (CD) was conducted using drying equipment designed and built up in the Institute of Agricultural Engineering (Wrocław University of Environmental and Life Sciences). Pomegranate samples were placed in a single layer on a tray of 100-mm diameter. The CD was operated at three temperatures: 50, 60 or 70 °C with an air velocity trough the sample of 0.8 m s^{-1} (Fig. 1). Average humidity and temperature of ambient air during CD were 52 % and 22 °C, respectively.
2. *Vacuum-microwave drying* (VMD) was carried out in a Plazmatronika SM 200 dryer (Wroclaw, Poland) connected to a vacuum system consisting of a vacuum pump BL 30P ("Tepro", Koszalin, Poland), a vacuum gauge MP 211 ("Elvac", Bobolice, Poland) and a compensation reservoir of 0.15 m^3. The dryer was operated at three power levels: 240, 360 or 480 W. Before drying, PG samples were spread out in a single layer on the bottom of a cylindrical container of organic glass with a volume of 6.8 L. The pressure in the container varied from 4 to 6 kPa. To avoid local overheating of fruits, the container rotated at a speed of 6 rpm.
3. *Combined drying* (CPD-VMFD) consisted of convective pre-drying (CPD) at a temperature of 60 °C, followed by VMFD with a microwave wattage of 360 W. The pre-drying times were 100 or 160 min for arils and 130 min for rind.

The process of drying was ended when the moisture content of pomegranate samples was lower than 0.06 kg kg^{-1} db. The final moisture content of the dried samples was determined in a vacuum dryer (SPT-200, ZEAMiL Horyzont, Krakow, Poland). The time of drying and operating temperature were 24 h and 60 °C, respectively. The drying time for pomegranate arils and rind dehydrated by particular methods was compared at a moisture content of 0.06 kg kg^{-1} db.

Table 1 Mathematical models applied to the experimental drying curves

Model name	Model equation	References
Newton	$\mathrm{MR}=e^{-k\cdot t}$	O'Callaghan et al. (1971)
Page	$\mathrm{MR}=e^{-k\cdot t^{a}}$	Page (1949)
Henderson and Pabis	$\mathrm{MR}=a\cdot e^{-k\cdot t}$	Henderson and Pabis (1961)
Logarithmic	$\mathrm{MR}=a\cdot e^{-k\cdot t}+b$	Dandamrongrak et al. (2002)
Two-term	$\mathrm{MR}=a\cdot e^{-k\cdot t}+b\cdot e^{-k_1\cdot t}$	Glenn (1978)
Sigmoid	$\mathrm{MR}=a+\frac{b}{1+e^{k\cdot(t-c)}}$	Figiel (2009)

Fig. 2 Drying kinetics of pomegranate arils (**a**) and rind (**b**) during CD, VMD and CPD-VMFD



Modelling of Drying Kinetics

The drying kinetics was determined on the basis of the mass losses of the pomegranate samples. The moisture ratio (MR) was determined from the following equation:

$$\mathrm{MR} = \frac{M(t) - M_\mathrm{e}}{M_0 - M_\mathrm{e}} \tag{1}$$

The equilibrium moisture content M_e was determined at the final stage of drying as the asymptotic value of the function fitted to the experimental points representing the moisture contents $M(t)$ using Table Curve 2D Windows v2.03 (Nawirska et al. 2009). The same software was used when fitting six drying models to the experimental points representing MR (Table 1).

The first five models have been widely used to describe drying kinetics of different plant materials such as grapes (Roberts et al. 2008), orange slices (Rafie et al. 2010), potatoes (Diamente and Munro 1993), ginger (Thorat et al. 2012), peach slices (Kingsly et al. 2007) and basil leaves (Calín-Sánchez et al. 2012). The sigmoid equation is a new model that was already used for description of drying kinetics of garlic slices (Figiel 2009). This equation is a very good tool for modelling drying curves with inflexion points. The advantage of the sigmoid equation is that its parameters have physical meaning; for instance, (1) parameter a is the asymptotic value of moisture ratio during drying, (2) parameter b is a theoretical interval of moisture ratio values, (3) parameter c corresponds to the time coordinate of the inflexion point in the drying curve; this point can thus be treated as the critical point K that divides the drying process into a period of increasing drying rate (above K) and decreasing drying rate (below K). Thus, the point K constitutes an extreme in the drying rate function (Figiel 2009). The k parameter is the drying constant. The lower the k values, the longer is the drying process.

The good fitting of a specific model to the experiment data was evaluated using (1) coefficient of determination (R^2) and (2) root-mean-square error (RMSE). The model fit is better, if the value of R^2 is closer to unity and the RMSE value is closer

Table 2 Constants (k, k_1, a, b and c) of the models describing the drying kinetics of pomegranate arils dried by CD at three air temperatures (50, 60 or 70 °C), by VMD at three microwave powers (240, 360 or 480 W) and by CPD-VMFD at two pre-drying times (100 or 160 min) at 60 °C and finished dried at 360 W

Drying conditions	Model name	Constants					Statistics	
		k	k_1	a	B	c	R^2	RMSE
CD 50 °C	Page	0.0058		1.000			0.9981	0.0142
	Henderson and Pabis	0.0058		0.988			0.9983	0.0132
	Two-term	0.0057	0.417	0.985	0.015		0.9983	0.0134
	Sigmoid	0.0060		0.015	7.080	−300.1	0.9991	0.0099
CD 60 °C	Page	0.0062		1.146			0.9989	0.0115
	Henderson and Pabis	0.0124		1.031			0.9953	0.0246
	Two-term	0.0124	0.013	0.939	0.092		0.9948	0.0246
	Sigmoid	0.0149		−0.023	2.675	−32.68	0.9998	0.0048
CD 70 °C	Page	0.0108		1.194			0.9996	0.0071
	Henderson and Pabis	0.0240		1.045			0.9952	0.0240
	Two-term	0.0334	0.048	2.267	−1.271		0.9997	0.0068
	Sigmoid	0.0347		0.002	1.873	3.677	0.9998	0.0051
VM 240 W	Page	0.0548		0.914			0.9968	0.0166
	Henderson and Pabis	0.0399		0.982			0.9954	0.0199
	Two-term	0.0375	0.707	0.947	0.058		0.9956	0.0191
	Sigmoid	0.0402		0.00171	262.9	−138.9	0.9938	0.0226
VM 360 W	Page	0.0505		1.004			0.9987	0.0111
	Henderson and Pabis	0.0511		0.998			0.9986	0.0111
	Two-term	0.0478	0.514	0.984	0.016		0.9953	0.0203
	Sigmoid	0.0492		−0.0137	119.1	−96.75	0.9988	0.0101
VM 480 W	Page	0.0604		1.012			0.9924	0.0263
	Henderson and Pabis	0.0623		0.998			0.9925	0.0262
	Two-term	0.0623	0.062	0.846	0.146		0.9899	0.0297
	Sigmoid	0.0556		−0.0401	910.4	−122.2	0.9939	0.0231
100 min CPD-VMFD	Henderson and Pabis	0.0632		0.298			0.9783	0.00134
160 min CPD-VMFD	Henderson and Pabis	0.1050		0.0994			0.9985	0.00168

RMSE root-mean-square error

to zero. Although six empirical models were used to adjust the experimental drying curves (Table 1), only four of them were chosen for the analysis because of their quality of fitting. Newton and logarithmic models were excluded from the discussion due to their poor quality of fitting, shown by their low values of R^2 and the high values of RMSE.

Energy Consumption

Energy Consumption in Convective Method

Energy E_C consumed during CD (kilojoules) was calculated according to Eq. (2) where N_f (kilowatts) is the power consumption by the fan blowing air to the six pipes equipped with electric heaters of power consumption N_h (kilowatts) and t is the drying time (seconds).

$$E_C = \left(\frac{N_f}{6} + N_h \right) \times t \tag{2}$$

Energy Consumption in VM Method

Energy E_{VM} consumed during VMD (kilojoules) was calculated according to Eq. (3) where N_M and η_M are output power (kilowatts) and efficiency of magnetrons, respectively; N_V is the power consumption (kilowatts) of vacuum pump; and N_e is the power consumption (kilowatts) of electric engine rotating the container.

$$E_{VM} = \left(\frac{N_M}{\eta_M} + N_V + N_e \right) \times t \tag{3}$$

Table 3 Constants (k, k_1, a, b and c) of the models describing the drying kinetics of pomegranate rind dried by CD at three air temperatures (50, 60 or 70 °C), by VMD at three microwave powers (240, 360 or 480 W) and by CPD-VMFD at pre-drying time (130 min) at 60 °C and finished dried at 360 W

Drying conditions	Model name	Constants					Statistics	
		k	k_1	a	B	c	R^2	RMSE
CD 50 °C	Page	0.0461		0.722			0.9989	0.0097
	Henderson and Pabis	0.0114		0.882			0.9854	0.0346
	Two-term	0.0093	0.089	0.737	0.255		0.9995	0.0061
	Sigmoid	0.0129		0.032	133.2	−390.5	0.9867	0.0329
CD 60 °C	Page	0.0415		0.789			0.9988	0.0106
	Henderson and Pabis	0.0153		0.913			0.9917	0.0274
	Two-term	0.0134	0.145	0.818	0.181		0.9999	0.0026
	Sigmoid	0.0169		0.026	91.54	−273.3	0.9922	0.0264
CD 70 °C	Page	0.0491		0.840			0.9987	0.0109
	Henderson and Pabis	0.0251		0.939			0.9949	0.0216
	Two-term	0.0226	0.229	0.858	0.143		0.9998	0.0045
	Sigmoid	0.0263		0.013	82.88	−169.9	0.9946	0.0221
VM 240 W	Page	0.0314		1.239			0.9995	0.0069
	Henderson and Pabis	0.0653		1.026			0.9919	0.0284
	Two-term	0.0700	0.300	0.994	0.001		0.9783	0.0455
	Sigmoid	0.1030		0.009	1.660	3.804	0.9999	0.0032
VM 360 W	Page	0.0277		1.444			0.9992	0.0098
	Henderson and Pabis	0.0916		1.041			0.9744	0.0543
	Two-term	0.1590	0.199	4.702	−3.703		0.9976	0.0154
	Sigmoid	0.0770		−0.073	181.5	−66.02	0.9744	0.0515
VM 480 W	Page	0.0333		1.511			0.9967	0.0196
	Henderson and Pabis	0.1170		1.054			0.9610	0.0679
	Two-term	0.0612	0.047	3.596	−2.566		0.9740	0.0526
	Sigmoid	0.0860		−0.143	362.6	−66.20	0.9700	0.0565
130 min CPD-VMFD	Henderson and Pabis	0.1440		0.114			0.9317	0.0840

RMSE root-mean-square error

Specific Energy Consumption

The specific energy consumptions (E_{C_m}) and (E_{C_W}) for CD [Eqs. (4) and (5)] as well as specific energy consumptions (E_{VM_m}) and (E_{VM_W}) for VMD [Eqs. (6) and (7)] were determined as the ratio of energy consumption to the initial mass of the sample m (grams) or as the ratio of energy consumption to the mass of water W (grams) removed from the sample during drying:

$$E_{C_m} = \frac{E_C}{m} \quad \left(\mathrm{kJ\ g^{-1}\ fw}\right) \tag{4}$$

$$E_{C_W} = \frac{E_C}{W} \quad \left(\mathrm{kJ\ g^{-1}\ water}\right) \tag{5}$$

$$E_{VM_m} = \frac{E_{VM}}{m} \quad \left(\mathrm{kJ\ g^{-1}\ fw}\right) \tag{6}$$

$$E_{VM_W} = \frac{E_{VM}}{W} \quad \left(\mathrm{kJ\ g^{-1}\ water}\right) \tag{7}$$

The value of energy consumption for drying a gram of the fresh sample has a practical meaning for a particular raw material, while the value of energy consumption related to the gram of water evaporated from the sample is more convenient when analysing energy requirements for different raw materials dried under different conditions.

Energy Efficiency

The energy efficiencies for CD (η_C) and VMD (η_{VM}) were determined as the ratio of energy necessary for evaporation of free water from the sample E_{ev} to the energy consumed while drying using the both methods, E_C and E_{VM}, respectively:

$$\eta_C = \frac{E_{ev}}{E_C} \times 100 \tag{8}$$

Table 4 Drying time for pomegranate arils and rind dried by CD at three air temperatures (50, 60 or 70 °C), by VMD at three microwave powers (240, 360 or 480 W) and by CPD-VMFD at different pre-drying times (100, 130 or 160 min) at 60 °C and finished dried at 360 W

Drying conditions	Drying time (min)			
	Arils		Rind	
	VMFD	Total	VMFD	Total
CD 50 °C		1,395±21 a		460±12 a
CD 60 °C		315±9 b		280±7 b
CD 70 °C		225±12 c		180±10 c
VM 240 W		108±9 f		64±1 e
VM 360 W		63±4 g		36±2 f
VM 480 W		51±4 h		26±1 g
100 min CPD-VMFD	40±3 a	140±3 e		
130 min CPD-VMFD			15±1	145±1 d
160 min CPD-VMFD	18±1 b	178±1 d		
ANOVA[a]	_***	_***	N.S.	_***

Treatment means of the ANOVA test (values are the mean value of three replications). Values followed by the same letter, within the same column, are not significantly different ($p<0.05$, Tukey's multiple-range test)

N.S. not significant

***$p<0.001$ (significant at this level)

[a] Not significant F ratio ($p<0.05$)

$$\eta_{\mathrm{VM}} = \frac{E_{\mathrm{ev}}}{E_{\mathrm{VM}}} \times 100 \tag{9}$$

Values of E_{C} and E_{VM} were calculated using Eqs. (2) and (3), while the value of E_{ev} was determined from Eq. (10) as a product of the mass of water evaporated from the sample W (grams) and the latent heat of vaporisation of water λ_{w} (kilojoules per gram).

$$E_{\mathrm{ev}} = W \times \lambda_{\mathrm{w}} \tag{10}$$

The latent heat of vaporisation of water λ_{w} was determined taking into account the temperatures of the samples at the final stage of drying. It was assumed that the temperature of CD samples is close to the temperature of the drying air, while the temperature of VMD samples was measured with the use of infrared camera. The values of λ_{w} for particular temperatures were similar, and the mean value of this parameter amounted to 2.36±0.02 kJ g^{-1}.

The energy efficiency is the most frequently quoted index in technical specifications (Kudra 2004), and therefore, this index enables comparison of drying effectiveness for different methods and various raw materials.

Statistical Analysis

The results obtained in the study were subjected to statistical analysis. Table Curve 2D Windows v2.03 (Jandel Scientific Software, USA) enabled mathematical modelling with the highest values of determination coefficient (R^2) and the lowest values of RMSE. One-way analysis of variance (ANOVA) was performed using Statistica v. 8.0 (StatSoft, Inc., Tulsa, USA) in order to find out whether the differences in the mean values were significant. Homogeneous groups were determined with the Tukey test at a significance level of $\alpha=0.05$.

Results and Discussion

Drying Kinetics

The MR changes versus the drying time of pomegranate arils and rind for CD, VMD and the combined CPD-VMFD are presented in Fig. 2. Tables 2 and 3 show the constants of the chosen drying models and the comparison criteria used to assess the quality of fit. The R^2 values ranged between 0.9317 and 0.9999, while the RMSE values ranged from 2.62×10^{-3} to 66.8×10^{-3}. These values show that there is a good agreement between the experimental data and the thin-layer modelling equations. This means that all chosen models could be used to describe the drying kinetics of pomegranate arils and rind. However, some of the models ensured the best fitting to the experimental points obtained while drying a particular raw material by a particular method. For instance, the sigmoid equation was found to be the best option for modelling of CD kinetics of arils due to the highest value of coefficient of determination ($R^2\geq0.9991$) and the lowest value of RMSE which is less than 9.91×10^{-3}. It can be seen from Tables 2 and 3 that the parameters a and c in the sigmoid equation adopted negative values; this experimental observation needs further explanation. The asymptotic value indicated by parameter a is the theoretical level of moisture ratio obtained over infinite time and is not achieved by the samples during the real time of drying. In turn, the negative value of parameter c means that the time coordinate of the inflexion point in the drying curve does not exist in the real time of drying and the whole process of drying occurs with the falling rate, which is typical for the exponential shape of the right side of the sigmoid curve. In the case of rind dried by CD, the two-term equation ensured the best fitting at $R^2\geq0.9995$ with a RMSE value lower than 6.12×10^{-3}. On the other hand, the use of the logarithmic equation for arils dried by VMD led to the highest values of R^2 (≥0.9947) and the lowest values of RMSE ($\leq2.11\times10^{-3}$). Finally, the best results in modelling of VMD kinetics of rind was assured by the Page model ($R^2\geq0.9967$ and $\mathrm{RMSE}\leq19.6\times10^{-3}$).

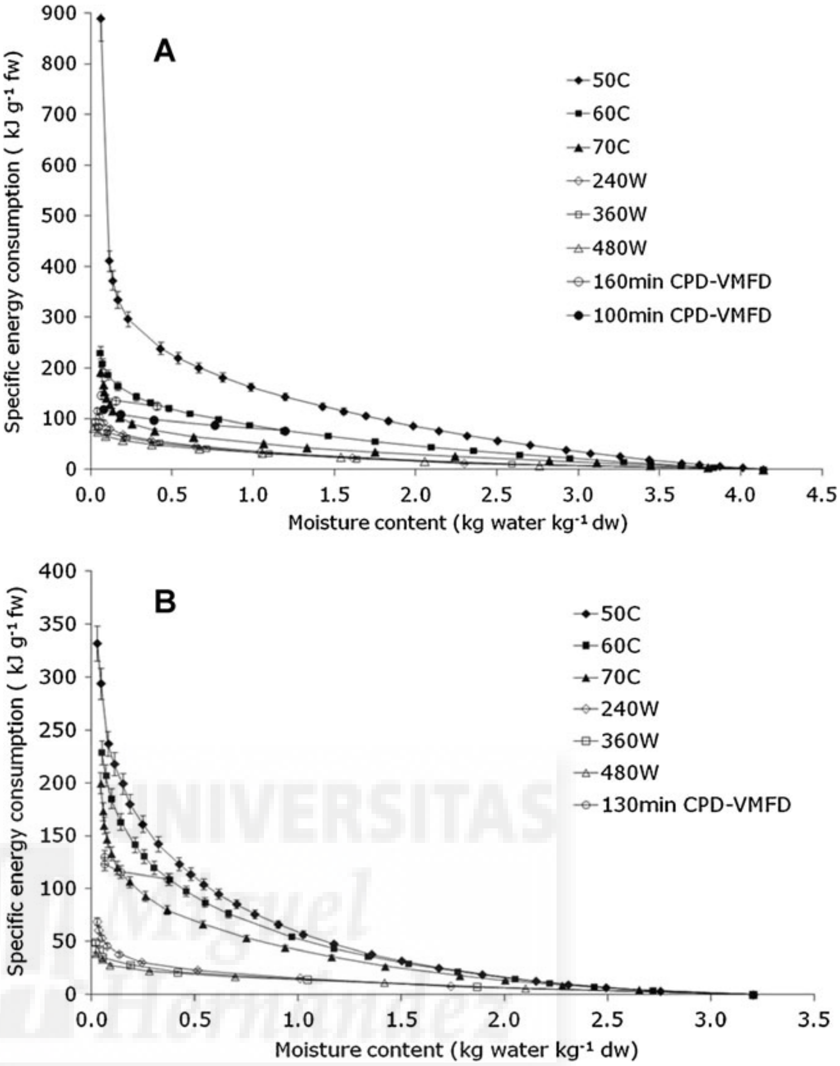


Fig. 3 Profiles of specific energy consumption during CD, VMD and CPD-VMFD of pomegranate arils (**a**) and rind (**b**)

Kingsly and Singh (2007) used four thin-layer drying models (Newton, Henderson and Pabis, Page and modified Page) to describe the drying kinetics of pomegranate arils dehydrated by convective method at 50, 55 and 60 °C. These authors found that the Page model was suitable to predict the moisture ratio due to its high values of R^2 (from 0.9942 to 0.9963) and its low RMSE (from 0.0007 to 0.0078).

The drying constants k and k_1 for pomegranate arils and rind were higher as drying air temperature or microwave wattage increased (Tables 2 and 3). Vacuum-microwave drying was conducted faster than CD. It was found that increasing the air temperature in CD from 50 to 70 °C decreased the drying time from 1,395 to 225 min in arils and from 460 to 180 min in rind. In VMD, an increase of microwave power from 240 to 480 W shortened the drying time from 108 to 51 min in arils and from 64 to 26 min in rind (Table 4). Previously, Kingsly and Singh (2007) confirmed that an increase in air temperature shortened the drying time of arils. So far, shortening of the drying time, as the result of the increase in VM wattage, has been described in tomatoes (Durance and Wang 2002) and edamames (Hu et al. 2006). The drying time of rind was always shorter than that of arils, mainly because pomegranate rind has lower initial moisture content than arils, porous structure and small amount of sugars, which strongly bind water molecules, while arils are rich in sugars (Calín-Sánchez et al. 2013) and their external membranes have low permeability for the water vapor (Falade and Igbeka 2007).

The combined method (CPD-VMFD) consisted of CPD for 100, 130 or 160 min and VMFD at 360 W. Therefore, CPD can be described in the same way as CD was, while VMFD required description of the drying kinetics using the Henderson–Pabis model (Table 1). The parameter a in this model corresponds to the MR obtained after CPD, and at the same time, its value equals the initial moisture ratio for VMFD (Tables 2 and 3). In arils, the increase in the pre-drying time from 100 to 160 min decreased the value of parameter a from 0.2980 to 0.0994. Increasing of pre-drying time also

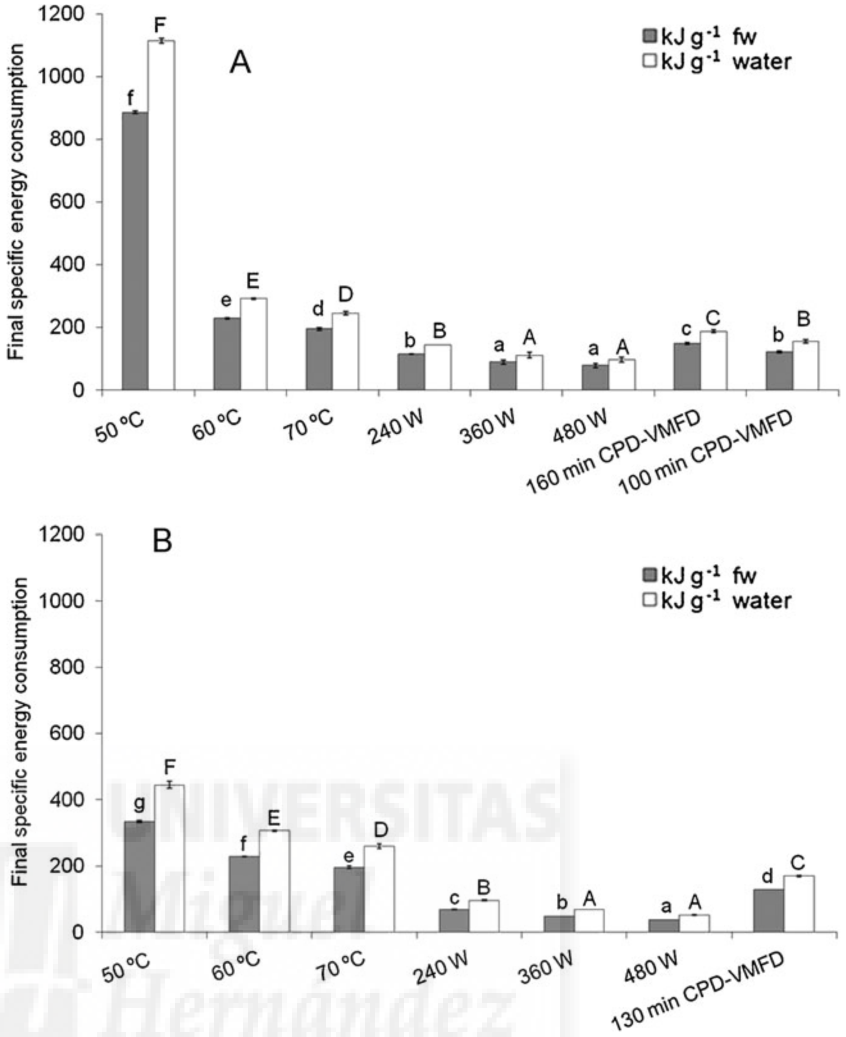


Fig. 4 Total specific energy consumption during CD, VMD and CPD-VMFD of pomegranate arils (**a**) and rind (**b**). *Different letters*, within the same type of bar, indicate significant differences ($\alpha = 0.05$) among mean values determined for grams of fw (*small letters*) and grams of water (*capital letters*)

significantly increased the drying constant k in arils during VMFD, from 63.2×10^{-3} to 105×10^{-3}.

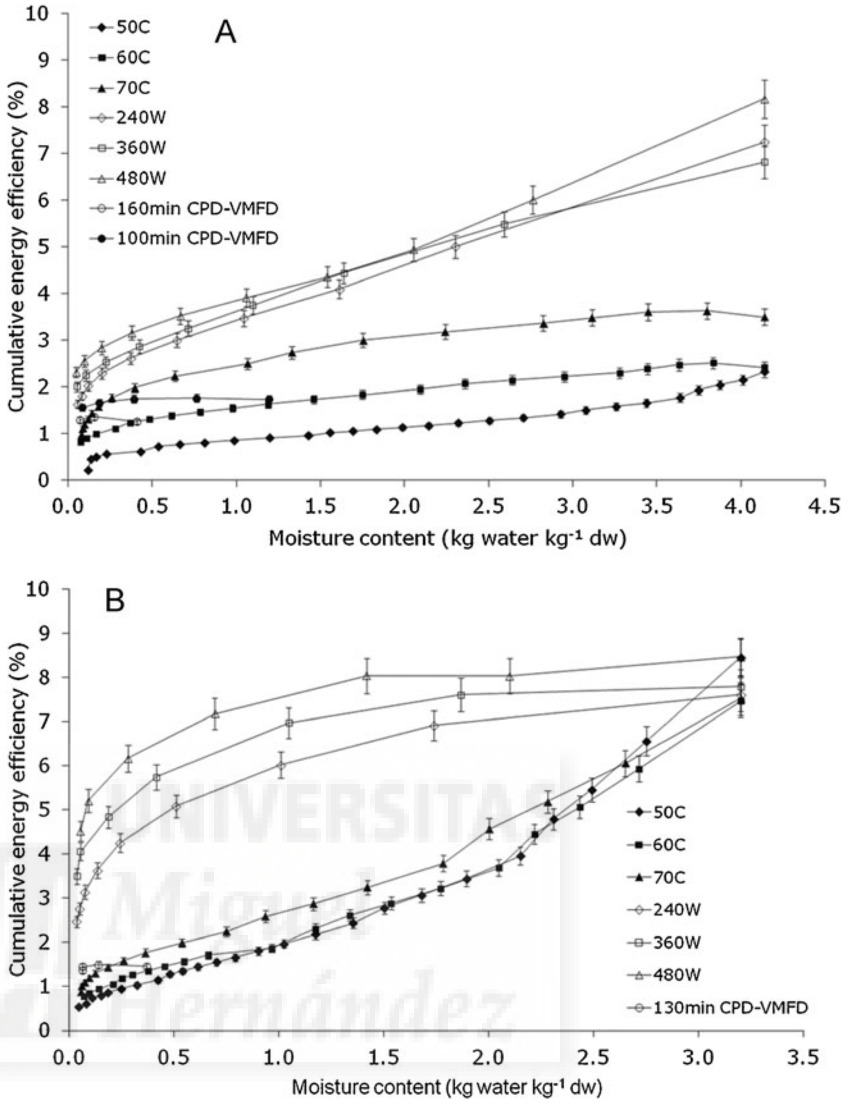
The total drying time of PG samples with combined method was calculated as the sum of the durations of CPD and VMFD. Eventually, the total drying time amounted to 140 and 178 min for arils pre-dried for 100 and 160 min, respectively, and 145 min for rind pre-dried for 130 min (Table 4).

It is worth of consideration that the moisture contents obtained after CPD of arils for 100 and160 min were 1.22 and 0.41 kg kg^{-1} db, respectively, while in the case of rind CPD, for 130 min, the moisture content reduced to 0.47 kg kg^{-1} db. These moisture content values ensured the soft texture of the biological material at the processing temperatures, which were definitely higher than the glass transition temperatures (Allaf 1982); this experimental finding enabled swelling process during VMFD as a result of the puffing phenomenon. Relatively early introduction of VMFD also prevented the appearance of a paradoxical effect, which is typical for the final stage of convective drying when thermal diffusivity significantly exceeds effective water diffusivity. This paradoxical effect is additionally enhanced by higher compactness resulted from shrinkage (Mounir et al. 2012).

Specific Energy Consumption and Efficiency of the Drying Process

The profiles of specific energy consumptions in CD, E_{C_m} (kilojoules per gram fresh weight (fw)), as well as in VMD, E_{VM_m} (kilojoules per gram fw), are shown in Fig. 3 for both arils (a) and rind (b). These profiles can be used to graphically calculate how much energy is required to reduce the initial moisture content of fresh material to certain moisture content. The shape of the specific energy consumption curves shows that the energy requirement increases drastically at the final drying stage. This shape is typical of all plant materials whose cellular structure has osmotic mechanism protecting the plant tissue against losses of water (Sarsavadia 2007). The shape of these curves also shows that drying should be ended as soon

Fig. 5 Cumulative energy efficiency during CD, VMD and CPD-VMFD of pomegranate arils (**a**) and rind (**b**)



as the needed moisture content is obtained, because successive drying only contributes to an unnecessary increase of the processing costs. The characteristic shape of the specific energy consumption curves corresponds to the shape of drying curves (Fig. 2) and results from the fact that at the final stage of drying, more and more time is required to remove the same portions of water from the dried material. It is clearly seen that VMD requires much less energy than CD for all assayed moisture contents. The high-energy consumption of the CD can be significantly reduced by using VMFD. Introduction of VMFD after CPD reduced the rate of specific energy consumption at the final stage of drying (Fig. 3); this effect was particularly effective when VMFD was applied earlier (Fig. 3a). It was found that the final specific energy consumption for arils and rind dehydrated exclusively by CD at 60 °C was 228 and 229 kJ g^{-1} fw, respectively. Applying VMFD after 160 min of CPD reduced the final specific energy consumption for arils by 80 kJ g^{-1} fw. This reduction reached 107 kJ g^{-1} fw when VMFD was introduced after 100 min of CPD (Fig. 3a). On the other hand, applying VMFD after 130 min of CPD reduced the final specific energy consumption for rind by 100 kJ g^{-1} fw (Fig. 3b).

Another aspect worth of consideration was the effect of the power of the drying equipment. Namely, higher temperatures in CD and higher microwave wattages in VMD led to lower-energy consumption of the drying process (Fig. 3). The increase in drying temperature from 50 to 70 °C reduced the final specific energy consumption from 886 to 195 kJ g^{-1} fw and from 334 to 196 kJ g^{-1} fw in arils and rind, respectively. On the other hand, increasing the microwave power from 240 to 480 W decreased the final specific energy consumption from 115 to 78.2 kJ g^{-1} fw and from 68.8 to 48.9 kJ g^{-1} fw in arils and rind, respectively (Fig. 3). The results of the final specific energy consumptions with their standard deviations are presented in Fig. 4. The presentation of specific energy consumption profile in kilojoules per gram fw is more

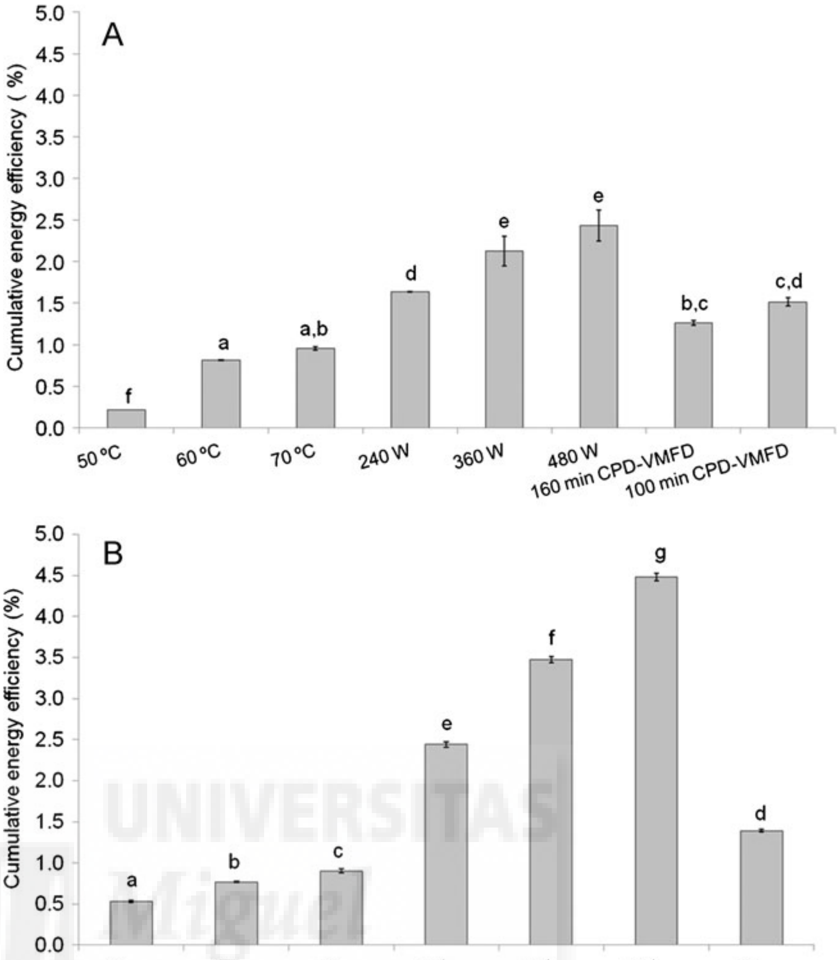


Fig. 6 Total energy efficiency during CD, VMD and CPD-VMFD of pomegranate arils (**a**) and rind (**b**). *Different letters* indicate significant differences ($\alpha = 0.05$) between mean values

convenient from the practical point of view. However, presenting the final specific energy consumption in kilojoules per gram water gives the possibility to compare the obtained results with those reported by other authors dealing with drying of different materials. Usually, the increase in drying temperature decreases the energy consumption while drying plant materials (Motevali et al. 2011b). Some reports confirm that increasing microwave wattages also has a positive effect on the energy consumption while drying (Soysal et al. 2006; Sharma and Prasad 2006).

The shapes of the specific energy consumption curves (Fig. 3) were directly related to the profiles of cumulative energy efficiency (CEE) (Fig. 5) determined for arils and rind. The values of CEE decreased during drying with the lowering of moisture content. This decrease was especially intense at the final period of drying when the specific energy consumption increased sharply. The values of CEE obtained for VMD were in general higher than those for CD (Fig. 5); as the drying process advanced, the differences in the CEE values increased, because the effectiveness of VMD was almost constant until the final moisture content was reached. The use of VMFD after CPD allowed maintaining relatively high values of CEE at the final period of drying.

The increase in drying temperature from 50 to 70 °C in CD increased the final values of CEE from 0.21 to 0.95 % and from 0.53 to 0.90 % in arils and rind, respectively. At the same time, increasing the microwave power from 240 to 480 W in VMD increased the final values of CEE from 1.63 to 2.44 % and from 2.44 to 4.48 % in arils and rind, respectively (Fig. 6).

The values of CEE were very low because the drying experiment was performed under laboratory conditions; for instance, the amount of raw material used was very small and the material was spread in a single layer on the tray or placed in a vacuum drum made of organic glass, which absorbed the microwave energy to some extent. However, these results showed clear tendencies on the influence of the drying method on the energy balance or requirements; these energy trends and also quality aspects (Calín-Sánchez et al. 2013) should be considered when drying pomegranate arils or rind under industrial conditions.

Conclusions

Based on the experimental results reported for both pomegranate arils and rind as affected by the drying method, the following conclusions can be reached:

1. The best options (highest values of R^2 and lowest of RMSE) for modelling drying kinetics for CD of arils, CD of rinds, VMD of arils and VMD of rind were the sigmoid equation, two-term equation, logarithmic equation and Page model, respectively.
2. Pomegranate rind needed much lower drying times than arils, particularly while VMD and CD at 50 °C, mainly due to its lower initial moisture content, higher porosity and lower total sugar content.
3. VMD required less energy than CD within the entire range of moisture content assayed in both arils and rind. The high level of energy required by CD can be reduced by the CPD-VMFD combination; this energy reduction was more important when the VMFD was applied earlier.
4. Higher temperatures in CD and higher microwave wattages in VMD led to lower-energy consumptions.
5. Finally, it can be stated that the best drying treatment in terms of time of drying, energy consumption and efficiency is the VMD of pomegranate arils and rind. However, CPD-VMFD can be a good option for food drying industry in order to maintain the good quality of the final product with reduced investment costs due to decreasing the mass loads of VM equipment.

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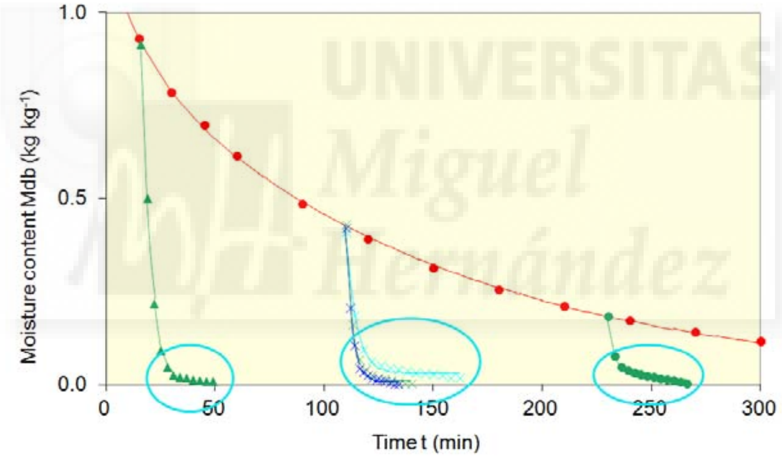
Chapter 5.- Results and Discussion



5. RESULTS AND DISCUSSION

Dehydration of fruits, vegetables and aromatic herb is still a field needing further research to clearly define the best methods for specific foods according to the quality of the dried product and the total economic cost. This PhD dissertation tends to describe some of these modern and efficient drying techniques and their effects on the global quality (chemical and nutritional composition, bioactive and volatile compound content and sensory evaluation) of vegetables and on the energy consumption and consequently the total cost of dehydration. It is important to mention that the energy input while drying is strictly associated with the drying kinetics of the material being dried. The following lines will try to show a summary of the main data obtained throughout the current Ph.D. dissertation and their discussion.

5.1. Drying kinetics

5.1.1. Drying kinetics of aromatic herbs

In the first of the manuscript, an assisted drying technique for microwave drying was applied. Microwave drying was complemented by different levels of vacuum and different powers of microwaves. This technique was applied to **rosemary** leaves (*Rosmarinus officinalis* L.).

The next two manuscripts focused on other aromatic herbs: **sweet basil** (*Ocimum basilicum* L.) and **thyme** (*Thymus vulgaris* L.). In these experiments assisted and combined techniques were used. In both cases, convective pre-drying (CPD) followed by vacuum-microwave finishing drying (VMFD) were used; the study was conducted at different CD temperatures, different vacuum levels and different microwave powers. According to experimental data obtained during convective drying of **basil** and **thyme**, it was stated that the loss of water content can be described by means of a two-term exponential model function (31):

$$MR = b_1 \cdot e^{-k_1 \cdot t} + b_2 \cdot e^{-k_2 \cdot t} \qquad (31)$$

The mathematical structure of this model indicated that the decrease in the moisture ratio occurred in two phases, which were characterized by the way the drying rate changed with the moisture ratio (*MR*). The first phase lasted while the process was characterized by a fast change of the drying rate with the *MR*. The faster decrease in the drying rate in the first phase was associated with values of the drying constant k_1 being higher than those of k_2.

During vacuum-microwave drying (VMD) of **rosemary**, **basil** and **thyme**, two drying periods, divided by a critical point (*K*), were observed. The critical points, *K,* were achieved at different moisture ratios and different drying times. The decrease in moisture content during the first drying phase (until *K* was reached) was described by a linear function (32):

$$MR = 1 - a \cdot t \qquad (32)$$

while during the second drying phase (falling drying rate stage: from point *K* until the end of the drying process), the water loss was described by an exponential function which represents the Henderson-Pabis drying model (33):

$$MR = b \cdot e^{-k \cdot (t - t')} \qquad (33)$$

A similar drying kinetics was previously found in oregano dehydrated by the VM system (Jałoszyński et al., 2008).

Parameter *a* is the slope of the strait line representing the drying kinetics in the first drying phase; this parameter represents the value of drying rate in that phase. Parameters *b* and *t'* are moisture and time coordinates of the critical point *K*, respectively. An increase in the microwave power was associated with increases in the values of parameter *a*, the drying constant *k*, and *b*. The values of parameter *t'* were lower as the wattages increased.

In the combined method (CPD-VMFD), which was used in both **sweet basil** and **thyme**, the drying kinetics had also an exponential character. An increase in the microwave power resulted in a significant increase in the value of the drying constant *k*. In general, the slopes of the VMD drying rate curves plotted *versus MR* coordinate axes were much higher than those of the CD drying rate curves due to the big difference in the drying rate values. Therefore, as the result of the big jump in the drying rate values, the drying rate curves for combined method were not continuous in pre-established moisture content at which convective pre-drying was replaced by VM finish drying.

The total drying time for **sweet basil** and **thyme** dehydrated by the combined method (CPD-VMFD) decreased as the temperature of the CPD stage increased. This total drying time was additionally decreased by increasing the microwave wattage during VMFD.

5.1.2. Drying kinetics of garlic and pomegranate

While modeling drying of **garlic slices** (*Allium sativum* L.) and **pomegranate arils** and **rind**, most of the R^2 (coefficient of determination) values were higher than 0.99 and RMSE values were lower than 0.01; these values demonstrated that the selected models were appropriate to describe the studied drying kinetics. The Verma model, which in fact is an exponential equation of two terms, equation (34), was selected as the best one to describe the CD of **garlic slices**.

$$MR = a \times e^{-k \cdot t} + (1-a) \times e^{-g \cdot t} \qquad (34)$$

The mathematical structure of this model indicates that the reduction of the *MR* happened in two different drying periods. In the first period, the drying constant value, *k*, was higher, meaning that the decrease in the *MR* was faster than in the second period, which was characterized by a lower value of the drying constant *g*. However, the range of moisture decrease in the first period was much lower than that of the second period. These ranges equal to the values of coefficients *a* and (1–*a*), while the sum of both parameters amounts to the initial moisture ratio of the fresh garlic slices. The faster decrease of *MR* in the first period of CD, indicated by the value of parameter *a,* was confirmed by the behavior of the drying rate. This drying behavior of garlic slices agreed with theoretical issues concerning water diffusivity (Crank, 1975). In this way, during the first period of drying, water easily evaporated from the surface of the dried material to the air by external diffusion (Yiotis et al., 2007). This process created a moisture gradient inside the material, which enabled transport of water to the surface by internal diffusion at a slower rate typical of the second drying period (Roberts et al., 2008).

Regarding **pomegranate** (*Punica granatum* L.) **arils**, a sigmoid equation (35) was found to be the best option for modeling of CD kinetics; this goodness was reflected in the highest value of R^2 and the lowest value of RMSE. In the case of **rind** dried by CD the two–term equation (36) ensured the best fitting.

$$MR = a + \frac{b}{1 + e^{k \cdot (t - c)}} \qquad (35)$$

$$MR = a \cdot e^{-k \cdot t} + b \cdot e^{-k_1 \cdot t} \qquad (36)$$

The drying constants *k* and k_1 for **pomegranate arils** and **rind**, respectively, increased as the drying air temperature or the microwave power increased. Vacuum–microwave drying was conducted faster than CD. It was found that increasing the air temperature during CD, decreased the drying time in both **arils** and **rind**. In VMD, an increase in the microwave power shortened the drying time in **arils** and **rind**. The drying time of **rind** was always shorter than that of **arils**, mainly because **pomegranate rind** has a porous structure and small amounts of sugars (which strongly bind water molecules), while **arils** are rich in sugars and their external membranes have low water vapor permeability (Falade and Igbeka, 2007).

Regarding the combined method (CPD–VMFD), CPD of **garlic slices** and both **pomegranate arils** and **rind** can be described in the same way as CD; however, VMFD required different modeling that isolated VMD drying kinetics. In the **garlic** study, the drying kinetics of VMFD was better described by the modified Page model (37). For this model, the parameter *a* indicated the intermediate moisture content at which the VMFD was applied. The VMFD was faster at higher microwave powers. Besides, an increase in microwave power increased the values of parameter *n*.

$$MR = a \times e^{-k \cdot t^{n}} \qquad (37)$$

Regarding the **pomegranate** drying kinetics, VMFD required description of the drying kinetics using the Henderson–Pabis model (38).

$$MR = a \cdot e^{-k \cdot t} \qquad (38)$$

The parameter *a* in this model corresponded to the *MR* obtained after CPD and at the same time, its value equaled the initial moisture ratio for VMFD.

5.2. Temperature

5.2.1. Aromatic herbs temperature while VMD and CPD-VMFD

In general, it can be stated that the temperature profile is different depending on the material being dried and it is influenced by both the wattage and the microwaving exposure (Szumny et al., 2010; Drouzas and Schubert 1996). It was found that increasing the microwave power during VMD of **sweet basil** samples slightly increased the maximum temperature of the samples; however, differences were not statistically significant. On the other hand, an increase in the microwave power during VMFD significantly increased the maximum temperature of the samples. It can also be stated that the temperature of hot air used during CPD had no significant effect on the temperature of the VMFD samples. Nevertheless, the temperatures found during VMD were higher than those recorded while VMFD due to longer expositions to microwave radiation. In the case of **thyme** a similar general trend was observed but with slight differences. During the VMD the lowest mean temperature was found for the samples dried at the medium level of microwave power. The increase in microwave power increased the mean temperature despite the reduction in drying time. On the other hand, microwave heating of the samples for the longest time at the lowest wattage increased their mean temperature. The same trend was found for the samples VM finish dried after convective pre-drying at low and medium temperatures. However, for the samples VM finish dried after CPD at the highest temperature, the mean temperature of the samples depended first of all on microwave wattage. This may be related to the fact that samples pre-dried at the highest temperature reached a bit lower values of moisture ratio before VMFD. This lower moisture ratio, strictly associated with lower moisture content, reduced the action capacity of microwaves, driving the water dipoles to rotation within the material (Figiel et al., 2010).

5.2.2. Pomegranate and garlic temperature while VMD and CPD-VMFD

During the VM drying the increase in microwave power from lowest to the medium wattage increased the mean temperature of **rind** and **arils**. However, a further increase in the microwave power reduced these temperatures. As mentioned before, the increase in microwave wattage increased the temperature of samples; however, **pomegranate arils** and **rind** experimented a huge decrease in the drying time for the highest microwave power, which resulted in a significant decrease of the energy absorbed by the samples and consequently in a reduction of their temperature. Another factor that could contribute to the decrease of the dried material temperature is the high water evaporating rate from the surface of this material to the ambient (Figiel et al., 2010). Regarding the combined method, both **pomegranate arils** and **rind** showed that the application of CPD increased the mean temperature of the samples treated with vacuum-microwaves, particularly for longer pre-drying times.

The case of garlic slices was quite different due to the different cellular system which is more permeable than that of **pomegranate arils**. The behavior of the **garlic slices** showed a trend in which the highest temperatures were obtained in dried **garlic slices** when CPD was applied during shorter times until higher moisture contents. This could be due to the fact that **garlic slices** pre-dried until high moisture content required longer times of microwave application for the dehydration; thus, this higher moisture captured more microwave energy producing higher temperatures. Also VM finish-dried beetroot cubes (Figiel, 2010) reached relatively high temperatures at shorter times of CPD. However, in the case of beetroot cubes the highest temperature was obtained by the sample subjected to VMFD after the longest time of CPD. This unexpected behavior might result from the different morphology of cellular system as well as differences in physical parameters of the dried material such as heat conductivity, specific heat, and thus requires additional studies focused exclusively on the effect of VM drying conditions on the temperature profiles of different plant materials.

5.3. Energy consumption in dehydration of garlic and pomegranate

Several authors have studied the energy balances during drying of fruits and vegetables, such as carrots (Nazghelichi et al., 2006) and mushrooms (Motevalli et al., 2011a). For instance, Kowalski and Mierzwa (2011) studied the drying of red bell pepper using convective, microwave and infrared heat sources applied separately and in different combinations to find the proper drying conditions. Motevalli et al. (2011b) evaluated the energy consumed during drying of pomegranate arils by different drying systems, including hot-air convection, microwave pretreatment with convection drying, microwave drying, vacuum drying and infrared drying. The energy input while drying is directly linked to the drying kinetics of the material subjected to drying.

Specific energy consumption profiles can be used to graphically calculate how much energy is required to reduce the initial moisture content of a fresh material to certain moisture content. **Garlic slices** and both **pomegranate arils** and **rind** followed the same pattern of specific energy consumption. The shape of the specific energy consumption curves showed that the energy requirement increased drastically at the final drying stage. This shape is typical of all plant materials, because their cellular structure with osmotic mechanisms protects the plant tissue against water losses (Sarsavadia, 2007). The shape of these curves also showed that drying should be ended as soon as the targeted moisture content is reached, because further drying will only contribute to an unnecessary increase of the processing costs. The characteristic shape of the specific energy consumption curves corresponds to the shape of drying curves and results from the fact that at the final stage of drying more and more time is required to remove the same portion of water from the dried material. It was clearly seen that VMD required much less energy than CD at all assayed moisture contents. The high energy consumption of the CD can be significantly reduced by using VMFD. The application of VMFD after CPD significantly reduced the rate of specific energy consumption at the final stage of drying; this effect was more evident when VMFD was applied earlier.

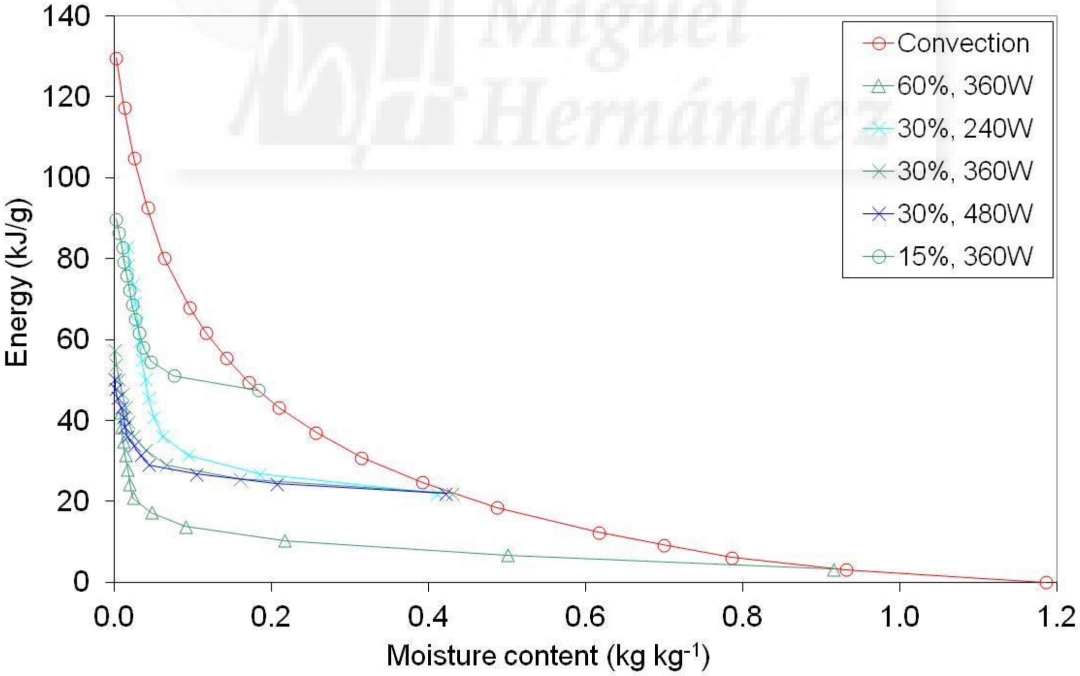


Figure 2: Energy consumption of garlic slices during dehydration (Calín–Sánchez et al., 2012)

5.4. Volatile compounds in dried aromatic herbs

The losses of volatile compounds observed during convective, microwave, vacuum microwave and convective pre-drying followed by vacuum microwave finishing dryings were species dependent. For instance, Szumny et al. (2010) reported the loss of rosemary volatile compounds after convective drying; however, the optimization of the working conditions of VM-drying led to concentrations of **rosemary** total volatiles close or even higher than those previously reported by Szumny et al. (2010). The loss reduction in the contents of the volatile compounds initially found in fresh **sweet basil** essential oils increased with the air temperature and microwave power during CD and VMD, respectively (Díaz-Maroto et al., 2004). According to Rao et al. (1998), the loss of volatile oil in herbs is related to energy input in the microwave oven. Consequently, the best results from a volatile composition point of view were obtained for samples convectively dried at the lowest temperature and at the lowest microwave power. The initial working hypothesis was that VMD should provide a final product of better quality than CD. Regarding **thyme** volatile composition, CD significantly reduced the total concentration of volatile compounds, while the best results were obtained after VMD; in this last treatment no significant effects of the microwave power were observed. The losses originated during VMD varied considerably from one species to another, as previously mentioned.

Regarding the combined drying, there were different trends among the species; however, this novel technique was always considered as the best one or being in the first positions. For instance, in the case of **sweet basil**, the CPD-VMFD was the best drying option; however, it is important to mention that this method presented significant volatile losses as the treatment intensity (temperature and/or microwave power) increased. In the case of **thyme**, the combination of CPD and VMFD resulted in dried products of high quality and significantly reduced the drying time compared to CD. Besides, the total concentrations of volatiles in dried samples by VMFD at the lowest wattage, at all CPD temperatures assayed, were statistically equivalent to those of fresh **thyme** and of the best VMD treatments.

5.5. Total phenolic compounds and total antioxidant capacity of dried garlic slices and pomegranate arils and rind

Both the total phenolic compounds content and the antioxidant capacity were significantly affected by the drying process, as previously reported in strawberries (Wojdylo et al., 2009). However, very different behaviors were found in different plant materials. On one side, phenolic compounds from **garlic slices** significantly decreased after the drying process; however, the CPD–VMFD method did not show significantly better results compared with CD. Thus, other factors such as time and energy consumption must be considered for taking the decision of selecting new alternatives to the traditional drying methods in **garlic slices**. A completely different situation was observed for the effect of drying on antioxidant capacity of dried **garlic slices**. Dried samples showed significant higher antioxidant capacity compared with fresh **garlic slices**. The antioxidant capacity in several intermediate stages of the VMFD was significantly higher than at the beginning of the VMFD, as previously reported by Manzocco et al. (2000). This behavior could be the result of two different factors: (i) some phenolic compounds have greater antioxidant capacity in some intermediate oxidation stages (Manzocco et al., 2000) and/or (ii) thermal processing may induce the formation of new compounds with high antioxidant capacity (Manzocco et al., 2000); these compounds could be those formed by the Maillard reaction (Wojdylo et al., 2009; Manzocco et al., 2000).

The lack of positive correlation between antioxidant capacity and total phenolic content could be attributed to the fact that not only phenolic molecules are the responsible compounds of the antioxidant capacity of dried **garlic**. For instance, Li et al. (2007) reported an increase in the allicin during the thermal processing of garlic powder. Allicin and its derived products have been described as potent natural antioxidants (Yong, 2006; Youji et al., 2006). The presence of allicin and its derived products could be responsible, at least partially, for the high antioxidant capacity of dried **garlic slices**.

On the other hand, **pomegranate arils** showed that lower values of antioxidant capacity and total phenolic compounds were found in dehydrated samples compared to the fresh products; **rind** had values about one order of magnitude higher than **arils** (Li et al., 2006). **Pomegranate rind** showed the highest values of antioxidant capacity and total phenolic compounds after soft drying conditions (low temperature and wattage). This behavior could be the result of high temperatures decreasing the antioxidant activity of the products being dried, independently of the time required for the process. The CPD-VMFD did not improve the antioxidant capacity and total phenolic compounds compared to CD and VMD. **Pomegranate arils** showed better results with low temperatures and consequently long times in CD; however, when VMD was applied, higher power lead to high temperatures and shorter drying time were recommended. The first trend (CD) was similar to that already described for the **rind**, while the second one (VMD) could be explained due to Maillard reactions producing compounds with high antioxidant capacity (Yilmaz & Toledo, 2005). Finally, CPD-VMFD did not improve the results associated to the best CD and VMD treatments of **arils**.

5.6. Sensory evaluation of aromatic herbs and pomegranate arils as affected by dehydration

Sensory evaluation with trained panel was used to quantitatively discriminate the intensities of the main aromatic characteristics of rosemary, basil, thyme and pomegranate samples. In general, samples were tested by a panel of 7 or 8 panelists, ages 24 to 48 years (3 female and 4 male, all members of the University Miguel Hernandez), with sensory evaluation experience and trained in descriptive evaluation of fruits and vegetables (Meilgaard et al., 1999; AENOR, 1997). **Descriptive Sensory Analysis** (DSA) has been successfully used for comparing appearance, flavor and texture attributes in many different foods (Vázquez-Araújo et al., 2008; Alasalvar et al., 2003).

All the samples were assessed using odor or full profile methods (Meilgaard et al., 1999). It is important to highlight that odor is defined as the perception of volatile compounds while the food is outside the mouth. Panelists agreed in 10-11 odor attributes for the case of **aromatic herbs** (as previously reported by Díaz-Maroto et al., 2007): fresh herb, vegetable, pine, herbaceous, balsamic, spice, hay-like, sweet, earthy, woody and infusion, while an agreement was reached for 13 attributes in the case of **pomegranate arils**, but divided into appearance (color and volume of woody portion); odor (fresh, burnt and caramel); taste (sweetness, sourness and bitterness); aroma (fresh and burnt); texture (crispiness, adhesiveness and solubility). DSA of dried **pomegranate arils** was described for the first time.

In general, the drying method significantly affected the intensities of the main sensory attributes of dried aromatic herbs. Assisted microwave **rosemary** drying with different levels of vacuum (VMD), implied: (i) decreases of some attributes, mainly related to the "freshness" of samples: fresh, vegetable, pine, herbaceous, and balsamic, but (i) increases of some others, mainly related to the "dried character" of samples: hay-like, earthy, woody and infusion. Samples dried using soft vacuum and microwave showed much better sensory profiles (closer to those of fresh rosemary) than samples dried using intense VM drying conditions (high power and intense vacuum). Similarly, drying of fresh **sweet basil** implied decreases of some attributes: fresh, floral and herbaceous, but increases of some others: spicy, hay-like, sweet, earthy, woody and infusion. The effects of the microwave power during VMFD on the sensory quality of dried sweet basil were more important than those of the temperature of the hot air during the CPD, with higher temperatures and microwave powers resulting in dried products of lower sensory quality (lower intensities of fresh notes and higher intensities of dried notes). The decrease in the typical attributes of fresh sweet basil, such as fresh, floral and herbaceous during the drying process could intensify the spicy odor observed in the dried samples. **Thyme** sensory data showed that samples dried by CD were characterised by the lowest scores of those attributes related to the freshness of thyme, while samples dried using VMD ranked in an intermediate position among fresh and convective-dried samples, and the VMD scores were higher than those samples dried by CD. However, thyme samples dried by VM were also characterised by higher scores of the dried attributes but simultaneously these samples also retained high intensities of the freshness attributes. Thyme dried using the lowest temperature of CPD and different powers of VFD presented the highest scores of the two most important attributes related to freshness, showing results very close to the fresh thyme. Finally, the drying method significantly affected the intensities of the main sensory attributes of **pomegranate dried arils**. Attributes such as color, fresh **pomegranate** odor and aroma, sourness and solubility in mouth significantly decreased after the drying process compared with the fresh sample; however, some other attributes (burnt odor and aroma, caramel odor and aroma, sweetness, bitterness, crispiness and adhesiveness) increased during the dehydration of the fresh **arils**. Some of these experimental findings could be related to the reduction in the moisture content, which for example could be responsible for the increased adhesiveness and reduced solubility. The color changes were linked with the Maillard reactions, which modify the initial pale red color, which is characteristic of the fruits of *Mollar de Elche* **pomegranates**. The combined method (CPD–VMFD) did not improve the desirable attributes of **arils** compared with CD, while VMD at the lowest power gave the best results. An increase in the microwave power let to undesirable attributes, such as burn.

Chapter 6.- Conclusions

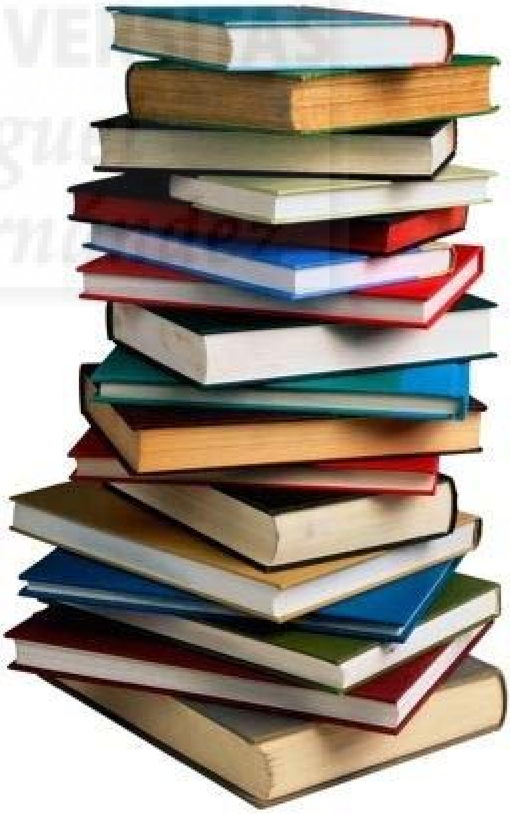
6. CONCLUSIONS

1. Unfortunately, the optimal drying technology is different for each of the materials studied in this Ph.D. thesis and specific conditions must be recommended.
2. The higher the vacuum intensity in the drying system for a specific microwave power and the higher the power intensity, the lower the concentration of total **rosemary** volatile compounds.
3. The higher the vacuum intensity and the microwave power, the shorter the time needed to dry the rosemary samples. The best conditions were 72-74 kPa and 360 W (39 min were needed to dry samples) and 240 W and 0 kPa (56 min were required) compared to 180 min required for convective drying of rosemary.
4. Convective pre-drying followed by vacuum-microwave drying is recommended for **sweet basil** according to the total amount of volatile compounds. An increase in the intensity of the treatment (higher microwave power) resulted in small decreases of total volatiles concentrations, while an increase in the temperature of the hot air used for convective drying resulted in high reductions of total volatiles.
5. The best option to dry sweet basil is convective pre-drying at 40 ºC followed by vacuum-microwave drying at 360 W; this conclusion is based on a relatively short drying time (≈ 250 min) and a high concentration of total volatiles, as well as good sensory profiles.
6. Vacuum-microwave drying of **thyme** led to high concentrations of total volatile compounds; however, the combination of convective pre-drying at 40 ºC followed by vacuum-microwave drying at 240 W present a sensory profile typical of high-quality dried thyme as well as a saving of time and energy.
7. The best drying system for **garlic** slices is convective pre-drying at 60 ºC up to a 30 % of moisture content followed by vacuum-microwave drying at 240 or 360 W; this conclusion is based on energy consumption.
8. Combined techniques of drying do not improve the quality of **pomegranate arils and rind** regarding the chemical composition, antioxidant capacity and sensory quality. Thus vacuum-microwave drying (240-360 W) is recommended for **arils** according to obtained

results, while convective drying at 50 ºC is appropriated for retaining all the bioactive compounds of the pomegranate **rind**.

9. The best drying treatment for pomegranate arils and rind, in terms of drying time, energy consumption and efficiency, is vacuum-microwave. However, convective pre-drying followed by vacuum-microwave finishing drying (CPD-VMFD) might be a good option for food drying industry in order to obtain a final product of good quality with reduced investment costs.

Chapter 7.- References



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