CHEMICAL ENGINEERING TRANSACTIONS

VOL. 102, 2023

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Laura Piazza, Mauro Moresi, Francesco Donsì

ISBN 979-12-81206-01-4; **ISSN** 2283-9216

DOI: 10.3303/CET23102014

Use of a Microwave Pilot Plant for Almond Disinfestation: Study on the Thermal Uniformity of the Treatment and Effect on Volatile Composition

Antonia Tamborrino, Carmine Summo, Antonio Berardi*, Davide De Angelis, Gianvito Ragone, Alessandro Leone

Department of Soil, Plant and Food Sciences, University of Bari Aldo Moro, Via Amendola 165/A, Bari, 70126, Italy
antonio.berardi@uniba.it

This paper outlines the experimental application of a continuous microwave-assisted (MW) industrial pilot plant for a post-harvest treatment on almond as disinfestation. The analysis of temperature uniformity and of the volatile profile on the unshelled almonds after the physical treatment were also investigated. The major problem during the production, storage and marketing of almonds is the contamination with insects or pests. Microwaves technologies is an alternative procedure to chemical one nowadays applied. The pilot plant has a treatment chamber with five generators of 1,5 kW/each installed along. A PLC operates on Electrical Power and flow rate to configure the operative parameter for the treatment condition. Samples of unshelled almonds from homogeneous batches have been treated with MW at different conditions. Insect mortality in three different life stages: 24-hours old eggs, 24-hours old larvae and mature larvae was evaluated after MW treatments. The uniformity of heating was studied as well as a volatile profile by SPME/GC/MS after the treatment. The results show that the optimal disinfestation effects on eggs and larvae are obtained by subjecting the almonds to a MW treatment at 25-rpm as spiral rotation speed equal to a 55.7 °C as temperature of the almond. The temperatures reached, during the treatment and the related time, were not sufficient for the development of oxidative aldehydes, secondary products of the lipid oxidation. An increase in volatile compounds, important for the characteristic almond flavour such as benzhaldeyde and 3-methylbutanol, has been observed.

1. Introduction

Almonds are products with a long shelf life, but many factors, including pests and insect contamination, can limit its marketability (Sen et al., 2010). These contaminants pose risks to human health and lead to reduced commercial value of products (Wang et al., 2013). Infested almonds are not easily detected by external inspection, leading to customer returns and loss of consumer confidence, and may result in legal or regulatory actions. Postharvest phytosanitary treatments are often required to completely control insect pests before the products are moved through marketing channels to areas where the pests do not occur (Heather et al., 2008).
The fumigants are extensively used around the world to control insect pests in stored commodities because of low cost, fast processing, and easy application. Methyl bromide (MBr) has been used since 1966 (Thompson, 1966) as an effective broad-spectrum fumigant. However, MBr is responsible for ozone depletion, which is why it was phased out globally under the "Montreal Protocol." This has led to the need to explore the use of alternative fumigants such as phosphine, which, to date, is the most widely used fumigant globally. Phosphine is used for the protection of stored products such as cereals, pulses, tobacco and nuts due to its low cost, the relative ease of application of its formulations and finally its acceptance as a residue-free treatment by international markets. In addition, phosphine decomposes rapidly after fumigation, making it atmospherically safer than methyl bromide. Given the concerns about the health risks of chemical pesticides and the resulting environmental pollution, there is interest in developing alternative non-chemical processing options to control pests while maintaining acceptable product quality. These include traditional hot air or water heating, controlled atmosphere and dielectric radio frequency (RF) and microwave (MW) heating. At present, the chemical fumigation method is widely used, and the efficient use of radio frequency and microwave methods for

Paper Received: 4 April 2023; Revised: 11 June 2023; Accepted: 29 July 2023
Please cite this article as: Tamborrino A., Summo C., Berardi A., De Angelis D., Ragone G., Leone A., 2023, Use of a Microwave Pilot Plant for Almond Disinfestation: Study on the Thermal Uniformity of the Treatment and Effect on Volatile Composition, Chemical Engineering Transactions, 102, 79-84 DOI:10.3303/CET23102014

disinfestation is still in the research stage. Microwaves have been tested on several agricultural commodities and some studies have been done on almonds (Patil et al., 2020; Mescia et al., 2022; Tamborrino et al., 2023). This type of heating is based on the conversion of the energy of an alternating electromagnetic field into heat by polar molecules acting on the material (Tamborrino et al., 2021). Many food molecules, such as water and fat, are electric dipoles, meaning they have a positive charge on one end and a negative charge on the other; therefore, they spin when they try to align themselves with the alternating electric field induced by the microwave beam. The rapid motion of molecules with dipoles creates friction and causes heat to dissipate in the microwave material treated. Microwave treatment is most effective on liquid water and is less effective on fats and sugars because of their molecular dipole moment (Sutar and Prasad, 2007). This is a type of volumetric heating that differs from conventional heating. Traditional heating occurs by convection or conduction, which requires the heat to spread across the surface of the material. Whereas for volume heating, the material can directly and internally absorb microwave energy, which is then converted into heat. In microwave pest control, insects are heated faster than the product they infested due to the high moisture content. Thus, insects can be heated to lethal temperatures while drier food is left untouched or slightly warmed. Although microwave heating has potential as a method of pest and insect control, no scientific research involving the use of MW conducted on industrial-scale sized plants are available and consequently no information on the impact of MW technology on the quality parameters of almonds have been carried out. Therefore, the first step of the research involved the evaluation of the effects of microwave treatments on the mortality of one of the most feared insects (*E. kuehniella*) during the almond's storage phase. The volatile compounds associated to the almond odour and flavour were analysed and finally the thermal uniformity on the treated almonds was evaluated using thermal images.

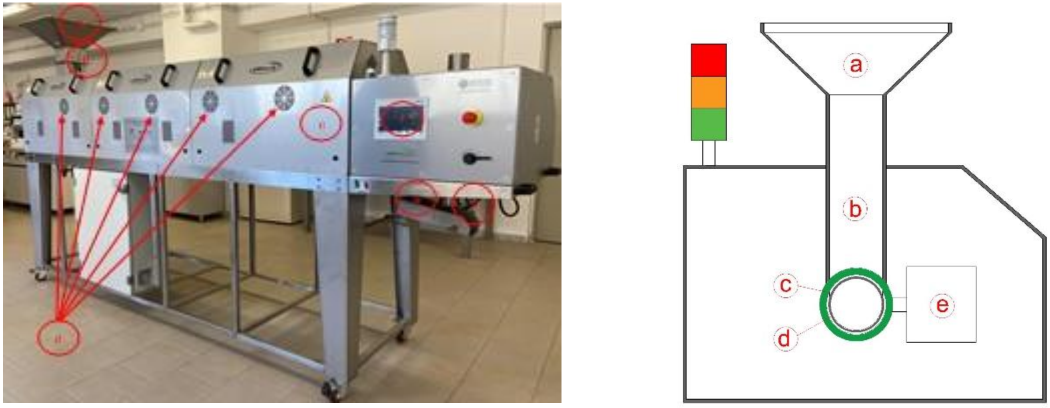
2. Materials and methods

2.1. Raw material

Almonds (*Prunus dulcis*) of the Filippo Ceo variety were used for the experimental assays. After harvesting, the almonds were hulled, sun dried, shelled and stored at controlled temperature (18°C) at Coop Contado (Toritto, Bari, Apulia, Italy).

2.2. Microwave pilot plant

The microwave prototype was a horizontally developed machine with a feed section on one side and an unloading section on the opposite side as shown in Figure 1a, designed for the continuous treatment of solid and fractionated foodstuffs. The treatment cell consisted of a polypropylene tube with a metal spiral inside connected to an electric motor and reducer with the function of (i) mixing the product during treatment, making uniform the distribution of the electromagnetic field and (ii) transport the product from the infeed section to the outlet. The polypropylene pipe was contained in the reverberation chamber (Figure 1b) in which five magnetrons of 1.5kW each were positioned. The machine was equipped with a PLC Controller touch screen which allowed the operator to set the chosen operating parameters.



a

b

Figure 1: a: Microwave pilot plant: a) loading hopper, b) microwave filter, c) reverberant chamber with inner spiral, d) magnetrons with the power generator, e) discharge point, f) Programmable Logic Controller (PLC), g) thermometer. Microwave plant section, a) loading hopper, b) microwave filter, c) reverberant chamber with inner spiral, d) PTFE pipe, e) magnetrons with power generator

2.3. Experimental procedure

A plan of comparative trials of disinfestation of eggs, 48h-old larvae and mature larvae of *E. kuehniella* was performed at different spiral rotation speeds. In detail, seven different rotation speeds were investigated: from 15-rpm to 45-rpm. For each rpm, a homogenous batch of almonds was processed by inserting the target stage into transparent cellulose capsules into the treated mass. At the end of each treatment all the capsules were recovered from the treated almonds and their contents were inspected in the laboratory to determine the mortality rate of each sample.

2.4.Thermal uniformity of the treatment

The thermal uniformity of the almonds after the microwave's treatment was carried out by taking thermal images at regular time intervals. Thermal imager used was Testo 876, Testo SE & Co. KGaA, Lenzkirch, Germany. To describe the uniform temperature distribution, the coefficient of variation (COV) was used. COV expressed as:

$$COV = \frac{1}{T_a - T_0}\sqrt{\frac{\sum_{i=1}^{N}\left(T_i - T_a\right)^2}{N}} \tag{1}$$

where *Ti* and *Ta* are respectively the mesh point and average temperature after microwave heating, *To* is the initial average temperature and *N* is the number of mesh points.

2.5. Volatile compounds analysis

The volatile organic compounds (VOCs) of the almonds were analyzed by a headspace solid phase micro-extraction (HS-SPME) followed by GC-MS analysis using an Agilent 6580 gas-chromatograph equipped with an Agilent 5975 mass-spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA), according to a slight modification of the procedure reported by King et al. (2019). Briefly, 0.5 g of almonds, 4 ml of a saturated aqueous solution of NaCl and 150 μl of 160 ppm 1-propanol as internal standard were added into a glass vial. The extraction of volatile compounds was performed by exposing a 50-30 μm DVB/CAR/PDMS SPME fiber (Supelco, Bellefonte, PA, USA) in the vial's headspace for 40 min at 50°C. The fiber was desorbed for 2 min in the injection port of the gas-chromatograph in a split-less mode at 250°C. VOCs were separated through a capillary column HP-Innowax (60 m length × 0.25 mm i.d. × 0.25 μm film thickness). The oven temperature was kept at 35 °C for 5 min, then increased by 5 °C/min to 50 °C and kept in isothermal conditions for 5 min, then raised at 5.5 °C/min to 230 °C, with a final isotherm of 5 min. The mass detector was set as: quadrupole temperature 150°C, source temperature 250 °C, ionization energy 70 eV, and scan range 33–270 amu. The characteristic peaks of the almonds (King et al. 2019) were identified comparing the reference mass spectra of National Institute of Standards and Technology (NIST) and Wiley libraries. The quantification was carried out with the internal standard (1-propanol). The analysis was carried out in triplicate.

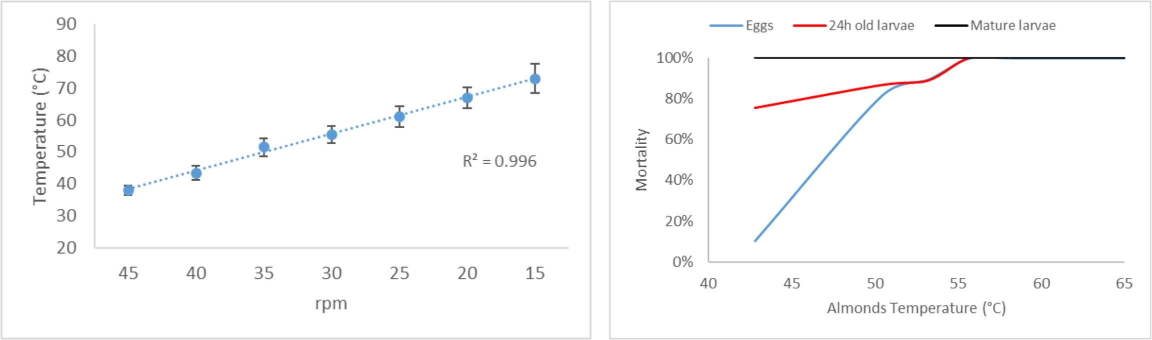
2.6. Statistical analysis

Two-sample t-test was carried out using Minitab 19 statistical software (Minitab Inc., State College, PA, USA) to determine whether the volatile compounds identified on the CTR and on the samples treated at 25-rpm were equal or not, at 95% confidence interval.

3. Results and discussion

3.1. Operative parameters and mortality

Figure 2a shows the rotation speed of the spiral versus the temperature of the almonds leaving the treatment chamber. The graph shows that as the rotation speed increases, the conveying capacity of the spiral increases and consequently, by decreasing the hourly throughput of the machine, the temperature of the outgoing almonds also decreases. The temperature is in the range 38 °C (45 rpm) to 73 °C (15 rpm). In figure 2b the mortality of eggs, 48h-old larvae and mature larvae of *E. kuehniella* is shown as a function of the temperature of the almonds after the treatment. The 100% mortality of eggs and 24h-old larvae is detected at a final almond temperature of at least 55.7 °C. In all test conditions 100% mortality of mature larvae was found.

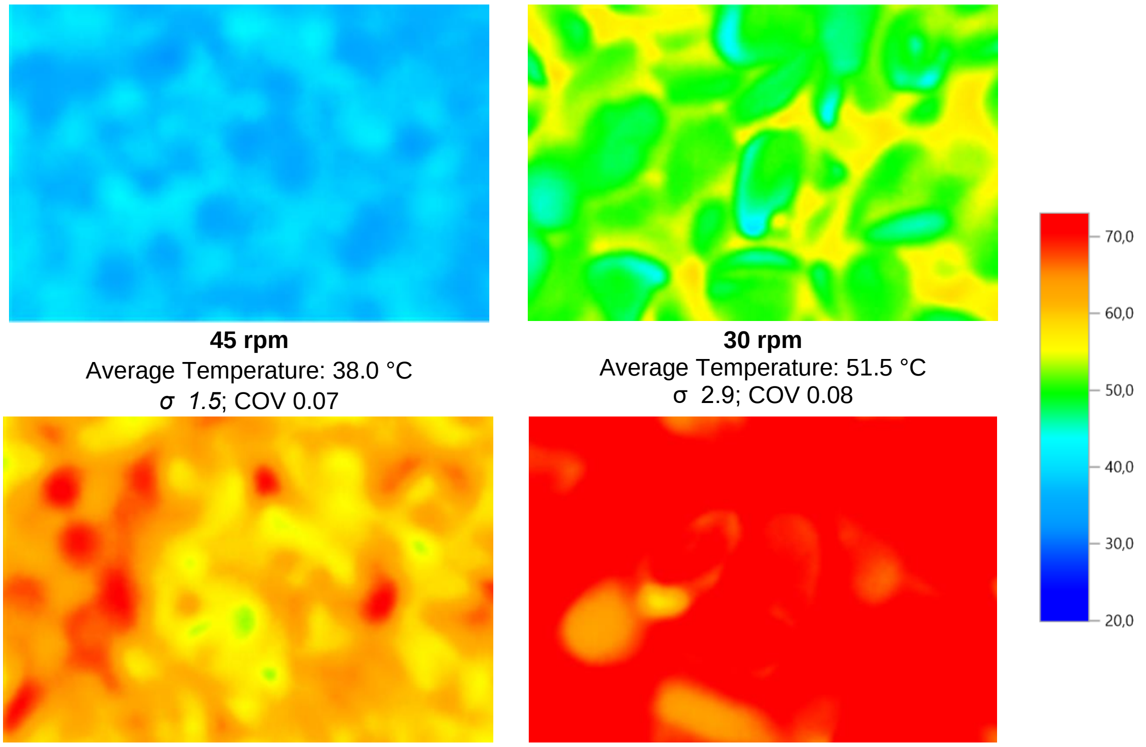


a b

Figure 2: a) Almond temperature versus the spiral rotation speed; b: Mortality trend versus almond temperature

3.2. Evaluation of the thermal uniformity of the microwave treatment

Figure 3 shows the thermal images for the different test conditions and reports mean temperature, standard deviation and COV (Coefficient of Variation). Albeit in a qualitative way, the images show a good uniformity of heating of the mass of almonds treated while the very low values on COV between 0.07 and 0.08 confirms the efficient heating uniformity of the prototype developed.



45 rpm
Average Temperature: 38.0 °C
σ 1.5; COV 0.07

30 rpm
Average Temperature: 51.5 °C
σ 2.9; COV 0.08

25 rpm
Average Temperature: 61.0 °C
σ 3.3; COV 0.08

15 rpm
Average Temperature: 72.9 °C
σ 4.9; COV 0.09

Figure 3: Thermal images for the different test conditions

3.3. Volatile compounds

The results of the volatile organic compounds determination are reported in Figure 4. In particular, the VOCs identified were principally belonging to the classes of alcohols and aldehydes, whereas no compounds related to the development of the Maillard reactions, e.g., furans, pyrroles, pyrazines (Xu et al. 2020) were identified. Hexanal and 3-methylbutanol were the major volatile compounds identified in the CTR sample. Hexanal is generally associated to green and grassy odour notes (Franklin and Mitchell, 2019), however, it may also be responsible for the development of oxidative flavours (Mexis et al. 2009; Franklin and Mitchell, 2019). 3-methylbutanol is characterized by a malty odour (Franklin and Mitchell, 2019) and it was previously identified when the almond VOCs were extracted with water, as it presumably derives from enzymatic reactions (Kwak et al., 2015). Benzaldehyde showed a concentration of 5.75 µg/gr, and it is one of the key odorant molecules in almond because it has a sweet/marzipan odour and a low threshold (Franklin and Mitchell, 2019).

As shown in Figure 4, the optimal microwave treatment, i.e., 25 rpm, affected the almonds VOCs profile. In particular, the hexanal concentration was almost completely reduced in the samples treated at 25 rpm, whereas the concentration of 3-methylbutanol showed a two-fold increase. Moreover, benzaldehyde was also detected in a significant higher concentration in the almonds treated at 25-rpm compared to the non-treated almonds. The reduction of hexanal was particularly important for the organoleptic quality of the almonds. In fact, the hexanal was negatively correlated with the marzipan/benzaldehyde flavour (King et al. 2019), and it confirms that the temperatures reached during the treatment (Figure 4) and the related time, were not sufficient for the development of oxidative aldehydes that represent the products of the secondary step of the lipid oxidation. Moreover, some alcohols such as the 1-Hexanol are in very low concentration, and they are metabolites of secondary oxidation reactions (Mexis et al. 2009). By contrast, it should be reminded that hexanal as well as other aldehydes derive from the lipoxygenase activity and/or from the auto-oxidation of linoleic acid (Beck et al. 2011) that might have been reduced in the treated almonds. This aspect was previously hypothesized by Patil et al. (2020). Furthermore, Qu et al. (2017) reported a decrease of lipoxygenase activity in wheat, after 20s microwave heating, corresponding to a temperature of 56°C.

Benzaldehyde derives from the hydrolysis in water or saliva of the diglucoside amygdalin (Franklin and Mitchell, 2019) and it might be hypothesized that the increase of benzaldehyde is related to a more fragile microstructure of the treated almond which facilitate the contact between amygdalin and water. Further studies could investigate this aspect to have a more comprehensive overview of the biochemical phenomena occurring during the microwave treatment.

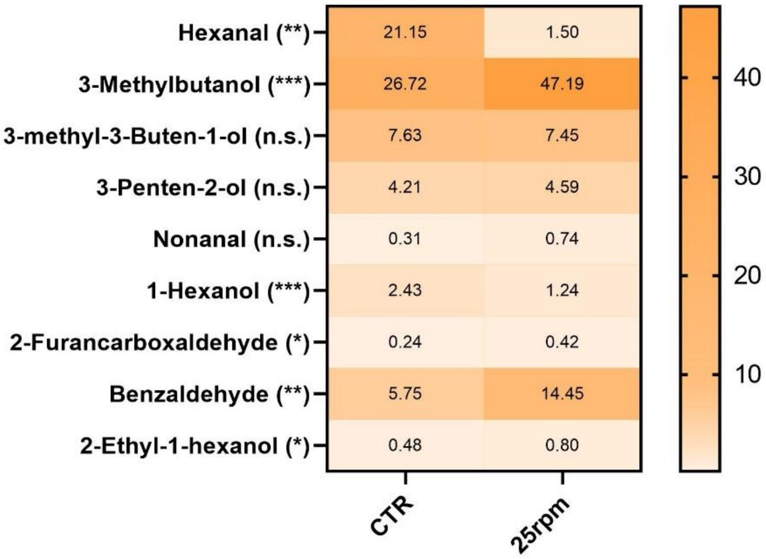


*Figure 4. Heat map describing the principal volatile organic compounds (µg/gr) detected in almonds. 2-sample t-test was carried out to calculate the significant differences between the CTR and the almond processed at 25 rpm. n.s.: not significant; *: p≤0.05; **: p≤0.01; ***: p≤0.001.*

4. Conclusions

The microwave industrial plant studied for disinfestation of shelled almond can be considered a promising technology for improving food safety and reducing the use of harmful chemicals in the agricultural industry. This industrial plant utilizes electromagnetic radiation in the microwave frequency range to target and destroy the cellular structure of pests and pathogens. As with any technology, it is important to carefully evaluate its potential benefits and limitations before implementation. The result of this study highlighted the eliminating of the investigates pests (*E. kuehniella*); In particular, the reached temperature of about 55.7 °C was enough to achieved 100 % mortality for eggs and 24-hours old larvae. In all tested process conditions, 100 % mortality of mature larvae was always achieved. The uniformity of the outlet almonds' surface temperature was investigated too. Overall, the COV (Coefficient of Variation) was used to evaluate the uniformity of the outlet almonds' surface temperature in a prototype microwave industrial plant for disinfestation. The low COV values obtained in this study (between 0.07 and 0.08) indicates that the temperature distribution across the surface of the almonds was relatively uniform, which suggests that the prototype was able to heat the almonds uniformly and consistently. The low COV values, combined with the thermographic images, provide strong evidence that the prototype microwave industrial plant for disinfestation was able to achieve efficient and uniform heating of the almonds. The volatile composition was significantly influenced by the microwave treatment, showing the decrease of hexanal and the increase of 3-methylbutanol and benzaldehyde. Although no compounds related to the lipid oxidation were identified, further studied might investigate the effect of the microwave treatment on the activity of the lipoxygenase and on the quality of the lipid fraction during the almond storage.

Acknowledgments

The authors have contributed to the same extent to the present study.
The authors would like to thank Dr. Domenico Tarantino for the technical and laboratory support.
This work was supported by PSR Puglia 2014-2020, sottomisura 16.2, Progetto “Almond Management Innovations (Approcci per una Mandorlicoltura biologica) – AMÌ”, “PSR Puglia 2014-2020, sottomisura 16.2 – prog. AMI’ – CUP: B99J20000110009, D.d.S. n. 94250025148.

References

Beck, J.J., Mahoney, N.E., Cook, D., Gee, W.S. 2011, Volatile analysis of ground almonds contaminated with naturally occurring fungi. Journal of Agricultural and Food Chemistry,59(11), 6180-6187.

Franklin, L. M., Mitchell, A. E. 2019, Review of the sensory and chemical characteristics of almond (Prunus dulcis) flavor. Journal of Agricultural and Food Chemistry, 67(10), 2743-2753.

Heather, N.W., Hallman, G.J., 2008, Pest Management and Phytosanitary Trade Barriers. Columns Design Ltd. Readind, UK. 226 pp.

King, E. S., Chapman, D. M., Luo, K., Ferris, S., Huang, G., Mitchell, A.E., 2019, Defining the sensory profiles of raw almond (Prunus dulcis) varieties and the contribution of key chemical compounds and physical properties. Journal of agricultural and food chemistry, 67(11), 3229-3241.

Kwak, J., Faranda, A., Henkin, J. M., Gallagher, M., Preti, G., McGovern, P.E., 2015, Volatile organic compounds released by enzymatic reactions in raw nonpareil almond kernel. European Food Research and Technology, 241, 441-446.

Mescia, L., Lamacchia, C. M., Berardi, A., Leone, A., Tamborrino, A., 2022, Continuous microwave pilot plant for almond disinfestation: Preliminary tests. Paper presented at the Mediterranean Microwave Symposium, 2022-May.

Mexis, S. F., Badeka, A. V., Chouliara, E., Riganakos, K. A., Kontominas, M. G. 2009, Effect of γ-irradiation on the physicochemical and sensory properties of raw unpeeled almond kernels (Prunus dulcis). Innovative Food Science and Emerging Technologies,10(1), 87-92.

Qu, C., Wang, H., Liu, S., Wang, F., Liu, C. 2017, Effects of microwave heating of wheat on its functional properties and accelerated storage. Journal of Food Science and Technology, 54, 3699-3706.

Sen, F., Meyvaci, K.B., Turanli, F., Aksoy, U., 2010, Effects of short-term controlled atmosphere treatment at elevated temperature on dried fig fruit. Journal of Stored Products Research, 46, 28e33.

Sutar, P.P., Prasad, S., 2008, Microwave drying technology-recent developments and R&D needs in India, in proceedings of the 42nd ISAEAnnual Convention, pp. 1–3, Kolkata, India.

Tamborrino, A., Berardi, A., de Lillo, E., Ragone, G., De Benedictis, M., Tufariello, M., Santino, A., Leone, A., 2023, Using a continuous microwave system for postharvest almond disinfestation, Postharvest Biology and Technology, Volume 201, 112369, ISSN 0925-5214, https://doi.org/10.1016/j.postharvbio.2023.112369.

Tamborrino, A., Veneziani, G., Romaniello, R., Perone, C., Urbani, S., Leone, A., Servili, M., 2021, Development of an innovative rotating spiral heat exchanger with integrated microwave module for the olive oil industry. LWT. 147, 111622, https://doi.org/10.1016/j.lwt.2021.111622.

Thompson, R.H., 1966, A review of the properties and usage of methyl bromide as a fumigant. Journal of Stored Products Research, 1, 353–376

Wang, S., Tang, J., Johnson, J.A., Cavalieri, R.P., 2013, Heating uniformity and differential heating of insects in almonds associated with radio frequency energy. Journal of Stored Products Research, 55, 15e20.

Xu, Y., Liao, M., Wang, D., Jiao, S., 2020. Physicochemical quality and volatile flavor compounds of hot air-assisted radio frequency roasted almonds. Journal of Food Processing and Preservation, 44(4), e14376.