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DRYING OF PEARS IN CO_2 MODIFIED ATMOSPHERE

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Abstract. One of the biggest problem encountered in drying area of food processing are the losses in food quality. While drying process is held, there is an important damage done to vitamins, polyphenols and other important nutriments. Being easily affected by high temperature and oxygen exposure, our concern was to find out what will be the effect of convective drying in air flow and CO_2 modified atmosphere upon pears, "Conference" variety quality. Testing took place with temperatures between 60 and 100°C for both drying methods, one also used three different CO_2 concentration regimes for the modified atmosphere approach, namely 30, 60, and 80%. The usage of carbon dioxide instead of air inside the drying chamber is expected to reduce oxygen exposure of the product during drying process, thus reducing oxidative reactions. Using CO_2 as air substituent for convective drying showed good results from the organoleptic point of view by preserving a more natural pear color closer to the row material one, reduced damage done to ascorbic acid and total polyphenols concentration presumably thanks to reducing oxygen concentration and a slight drying duration reduction. There was deducted and established a mathematical model for the convective modified CO_2 drying atmosphere as well as a pilot drying installation was designed for combined dying methods equipped with a CO_2 recycling system.

Keywords: *pears, experimental drying plant, convection, drying kinetic curves, ascorbic acid, polyphenols.*

Rezumat. Una din cele mai grave probleme întâlnite la procesarea produselor alimentare și anume în domeniul uscării, este pierderea calității. În funcție de durata procesului de uscare pot fi grav denaturate vitaminele, polifenolii și alte nutrimente. Astfel cum, toate aceste substanțe, sunt mult afectate de expunerea la temperaturi înalte și oxigen, noi am avut ca scop să determinăm care va fi efectul uscării convective cu aer și în mediu modificat de CO_2 asupra calității perelor de soi „Conferința". Pentru ambele metode de uscare, testările au avut loc la temperaturi cuprinse între 60 și 100°C, iar pentru metoda de uscare cu CO_2 au fost utilizate și trei regimuri de concentrații 30, 60 și 80%. Prin utilizarea dioxidului de carbon în camera de uscare, ca substituent al aerului, se așteaptă o reducere considerabilă a proceselor oxidative prin reducerea concentrației de oxigen. Folosirea CO_2 ca substituent pentru uscarea convectivă a arătat rezultate bune din punct de vedere organoleptic și anume prin păstrarea unei culori a perelor aproape de cea a perelor proaspete, a redus nivelul de denaturare a acidului ascorbic și a conținutului total de polifenoli, fapt care probabil se datorează reducerii concentrației de oxigen și unei micșorării ușoare a duratei de uscare. A fost dedus și stabilit modelul matematic pentru uscarea convectivă în atmosferă modificată de CO_2 și proiectată instalația experimentală pentru uscarea combinată cu sistem de reciclare a CO_2.

Cuvinte cheie: *pere, instalația de uscare experimentală, convecție, curbele vitezei de uscare, acid ascorbic, polifenoli.*

1. Introduction

The human diet consists in a high percentage of fruits and vegetables. Pears, bring us a delicate taste and a sweet aroma as well as being characterized by a high digestibility, making them very popular [1]. The popularity of pears is due to their composition, containing polyphenols, minerals, vitamins, amino acids, sugars as well as an important quantity of water [2, 3].

Drying is the oldest method of food preservation and is used till our days as it brings a large gamma of benefits as reducing storage and transportation space as well as energy consumption. Through the time there were lots of scientist and researches that developed this conservation method introducing new drying types and regimes, that were meant to reduce food treatment time and assure an overall better final product quality. Such drying methods as microwave, vacuum, freeze were introduced for the food industry. As each method has its own advantages and disadvantages, there's a good decision to combine those and use their strong qualities to create new hybrid drying methods as convection with microwave, vacuum with microwave drying, etc.

One of the recent drying methods that was highlighted by researchers is modified atmosphere drying, in which the conventional drying agent – the air, is changed or mixed with an inert gas (carbon dioxide, nitrogen, etc.).

Using the modified atmosphere drying method is a potential way to reduce oxidative processes during drying course. Reducing oxygen concentration inside the drying chamber, or even fully eliminating it, being replaced by another gas (carbon dioxide, nitrogen, etc.) has already proved to be a promising drying method. Several studies [4-6] were conducted in this context using as experimental material vegetal products (ginger, apples, strawberry, carrot, etc.) for whom were determined some important submitted to oxidative reactions components, such as gingerol, acid ascorbic, carotedoids, etc.

A group of scientists [4] experimented with different drying methods (freeze, vacuum, conventional and modified atmosphere convection) on ginger, namely they analyzed the effect of those specific drying methods upon 6-gingerol content preservation in dried ginger. For this goal the researchers had designed a closed circuit heat pump drying installation, adjusted for modified atmosphere drying. The results of the study represent the comparison between different drying methods dried ginger 6-gingerol content. As such, the highest content of gingerol was characteristic for vacuum (11 mg/g) drying method whilst modified atmosphere (carbon dioxide and nitrogen) was close enough to the same result (9.5 mg/g). The lowest 6-gingerol content was shown for conventional air drying (6 mg/g) [4].

The next study [5] was concentrated on analyzing the effect of freeze, conventional and modified atmosphere convection drying on ascorbic acid content in dried strawberries. The researchers have designed as well a close circuit drying installation, that allows the use of modified atmosphere. Analyzing the results, we can conclude that the highest losses of ascorbic acid were found to be in air dried strawberry samples (28 %), while the lowest were in freeze dried one (4 %). In terms of ascorbic acid losses, good result had also shown the modified atmosphere dried strawberry samples (6 %) [5].

The influence of drying atmosphere oxygen concentration on carotenoid and ascorbic acid retention ratio in dried carrot samples was researched [6] using a designed closed circuit experimental tunnel drier. The researchers experimented with different (5%, 10%, 15%, 20.9%) oxygen concentrations and established that retention ratio of ascorbic acid and carotene in dried carrot samples (70°C conventional and modified atmosphere convection) is inversely proportional to oxygen concentration, namely it increases 1.8 times for carotene and 1.7 times for ascorbic acid retention ratio.

The most undesirable drying results are the effect of browning of vegetal food, that is visible right away at the end of the process and important nutriments losses as a result of oxidation effects in general that happens throughout the drying procedure. This effect has been spotted and analyzed by diverse plants breeders, plants physiologists and food scientists. Some browning reaction are useful but their majority is not, as they lead to food quality diminution as result of organoleptic and nutritional properties alteration. The food browning of enzymatic nature brought by polyphenol oxidases has a significant economic effect on products like cereals, fruits and vegetables that should be well controlled [7-9].

The main goal of the study was to create a technology of drying vegetal food, namely "Conference" pears, in CO_2 modified atmosphere as well as designing a pilot drying installation for the same purpose. To accomplish that goal one formed the following objectives: optimizing the process of drying pears in CO_2 modified atmosphere, by mathematical modeling; elaboration of the experimental installation for drying pears in a CO_2 modified atmosphere; analysis of the quality parameters of dried pear fruits in a CO_2 controlled atmosphere in order to develop recommendations.

2. Materials and methods

2.1 Samples preparation

"Conference" variety pears belong to the family *Rosaceae*, genus *Pyrus*, species *Communis*, were selected from Republic of Moldova marketplaces according to [10] and prepared for the experiment.

The "Conference" pears were washed and cut in half circles (Figure 1) with a 0.005±0.0005 m thickness and a total pieces' weight of 100 ± 0.2 g. The drying was performed by two convective methods: in air flow and CO_2 modified atmosphere.

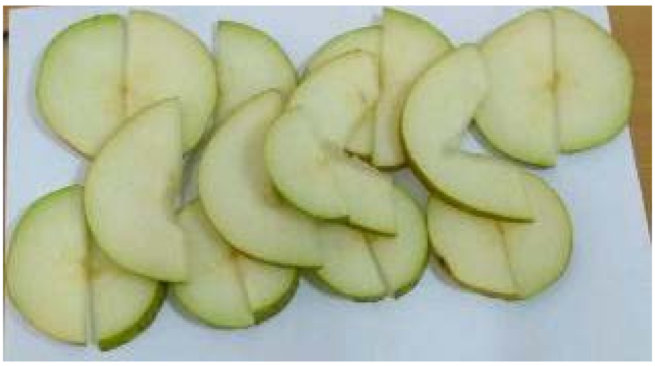


Figure 1. Preparation of half circles sliced "Conference" pears for drying.

There were chosen several temperature regimes between 60°C and 100°C, drying agent velocity of 1.5±0.13 m/s for both drying methods and three concentrations for modified CO_2 atmosphere, namely 30%, 60% and 80% of CO_2.

2.2 Experimental drying installation

For the experimental part, one has designed and elaborated an experimental laboratory drying installation (Figure 2), that allows drying to take place through different methods, including conventional convection – using air, microwave drying and their combination, as well as the use of modified atmosphere by replacing air with different concentrations of carbon dioxide.

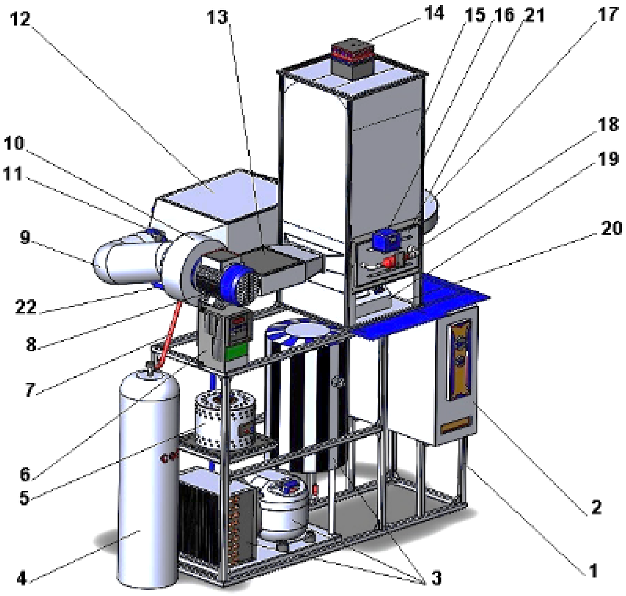


Figure 2. Experimental laboratory drying installation.
1 – carcass; 2 – control panel; 3 – cooling installation; 4 – CO_2 recipient;
5 – temperature controller; 6 – fan inverter; 7 – CO_2 income hose; 8 – electrical motor;
9 – intermediate pipe; 10 – centrifugal fan; 11 – pipe fastening; 12 – condenser;
13 – heat source; 14 – magnetron; 15 – drying chamber; 16 – CO_2 concentration indicator; 17 – drying agent recycling pipe; 18 – receiver; 19 – electronic scale;
20 – electronic scale space; 21 – lid.

The installation presents a drying chamber 15 which is installed on a metallic carcass 1 along with the heat source 13 and a centrifugal fan 10 which is driven by the electrical motor 8 and an inverter 6 which allows fan's velocity control. The gas, from the drying chamber may be recycled (Figure 3) through the recycling pipe 17, that is connected to the condenser 12, from which the gas is transferred into the drying chamber using the centrifugal fan 10 and the intermediate pipe 9. The installation allows drying using microwave energy. For this purpose, the installation is equipped with a magnetron 14 on the top of the drying chamber, that allows changing the height of the magnetron towards the product. For research purposes and data collection there is an electronic scale 19 installed under the working chamber 20. The drying chamber is hermetically closed using the lid 21 which holds the carbon dioxide concentration indicator 16 and receiver 18.

2.3 Total polyphenol content

The total polyphenol content was expressed in milligram of gallic acid equivalent (GAE) per 100 g of the researched product. Polyphenols content was established by optical density measurement of an extract that, in presence of the Folin-Ciocalteu reagent, absorbs at the wavelength of 765 nm. For the analysis 5 mL double distilled water, 1 mL of dried pears sample and 0.5 mL Folin-Ciocalteu reagent in a 10 mL volumetric flask were mixed.

After 3 minutes, 1.5 mL of 10% sodium carbonate was added and brought up to the mark with double-distilled water. The solutions are placed on the water bath at a temperature of 50°C for 16 min, after which it cools down to room temperature. Afterwards the absorbance is measured using a Hach Lange DR-5000 spectrophotometer [11].

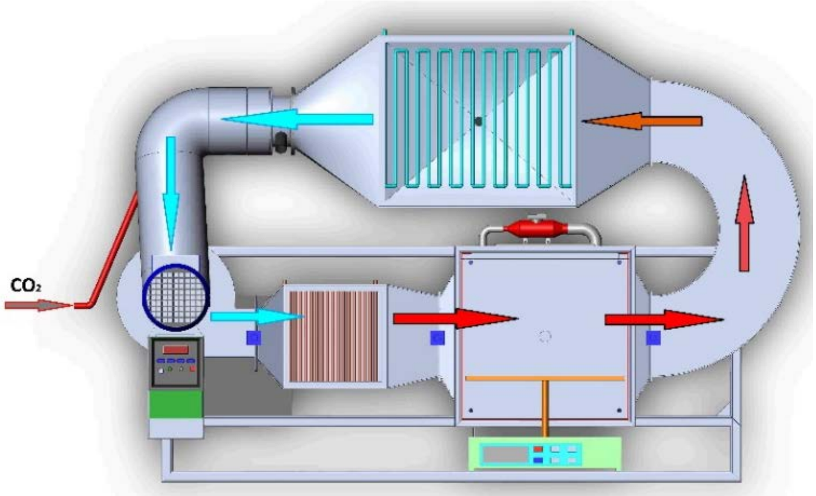


Figure 3. Experimental drying installation gas recycling system.

2.4 Vitamin C content

Using a mortar, 10 g of each analyzed “Conference” pear samples: fresh, convection-dried (air and CO_2), were separately crushed in the presence of 1% oxalic acid and quantitatively transferred to a 100 cm^3 volumetric flask and brought up to the mark with oxalic acid and mixed. The content of the flask was poured through filter material into a conical flask adding. 6 cm^3 of 2,6-dichlorophenolindophenol. The extinction is determined transferring the obtained solution to the cuvette and subjected to photocolorimetry at the wavelength 540 nm. For the second extinction: a few crystals of ascorbic acid are added to the cuvette with the analyzed solution (the color of 2,6-dichlorophenolindophenol disappears), the solution is stirred and photocolorimetry is performed again [12].

2.5 Mathematical modelling

For the drying process to be performed there was created a mathematical model which takes in account the changes of drying atmosphere by establishing boundary conditions adapted for carbon dioxide [13]:

$$(0{,}0008 \cdot t_a + 0.0149) \cdot \frac{\partial t(H,\tau)}{\partial \tau} + \left[\frac{Nu \cdot (0{,}0008 \cdot t_a + 0{,}0149)}{d}\right] \cdot [t_a - t(H,\tau)] - \\ -(1-\varepsilon) \cdot r` \cdot [0{,}167 \cdot \frac{0{,}13 \cdot 10^{-9} \cdot (-0{,}0004 \cdot t_a^2 + 0{,}8252 \cdot t_a + 163{,}69)}{d} \cdot \rho_{co_2} \cdot Re^{0.74} \cdot \\ \cdot Pr^{0.33} \cdot \left[\frac{l}{d}\right]^{-0.47}]\left(\theta(H,\tau) - \theta_p\right) = 0 \quad (1)$$

$$(0{,}0008 \cdot t_a + 0.0149) \cdot \frac{\partial \theta(H,\tau)}{\partial x} + \lambda_m \delta \cdot \frac{\partial t(H,\tau)}{\partial x} + [0{,}167 \cdot \\ \cdot \frac{0{,}13 \cdot 10^{-9} \cdot (-0{,}0004 \cdot t_a^2 + 0{,}8252 \cdot t_a + 163{,}69)}{d} \cdot \rho_{co_2} \cdot Re^{0.74} \cdot Pr^{0.33} \cdot \\ \cdot \left[\frac{l}{d}\right]^{-0.47}]\left(\theta(H,\tau) - \theta_p\right) = 0 \quad (2)$$

where t – moist body temperature, K; t_a – drying atmosphere temperature, K; τ – drying time, s; H – layer thickness, m; a_q, a_m – temperature and potential diffusion coefficients, m^2/s; ε – phase transformation criterion; r' – vaporization latent heat, kJ/kg; c'_T, c_q – specific mass, kg/kg·M and specific heat, J/kg·K capacities; ρ – moist body dry part density, kg/m^3; δ – moist body Sore coefficient, 1/K; ϑ – mass transfer potential (moisture), M potential units; λ_q, λ_m – thermal conductivity, W/m·K and mass conductivity, kg/m·s·M; *Re* – Reynolds criterion; *Pr* – Prandtl criterion; *Nu* – Nusselt criterion.

2.6 Statistical processing of the results

To determine the error of a series of successive measurements of experimental data (ascorbic acid concentration, polyphenol concentration, etc.) standard deviations were calculated [14]. All calculations were performed using Microsoft Office Excel 2007 (Microsoft, Redmond, WA, USA). Data obtained in this study are presented as mean values ± standard error of the mean calculated from three parallel experiments.

3. Results and discussions

The speed of the drying agent plays an important role in the process of diffusion of moisture evaporated from the surface of the product into the surrounding environment. In the given case, the mathematical description of this phenomenon is strictly necessary for more efficient optimization of the drying process. The correct choice of the speed of the heating agent leads to the reduction of the energy consumption of the fans that ensure the parameters of the given flow and the consumption of thermal energy in the case of convection drying. In order to determine the optimal drying speed, the mathematical model of the speed of the drying agent at the mass transfer between the product and the environment was built. After performing the calculus, the following product temperature and humidity, for CO_2 environment formulas were deducted:

$$T = C_1 + A_1 e^{B_1 \tau} \tag{3}$$

$$U = C_2 + A_2 e^{B_2 \tau} \tag{4}$$

A, *B*, *C* – deducted coefficients which take in account drying process conditions and product characteristics

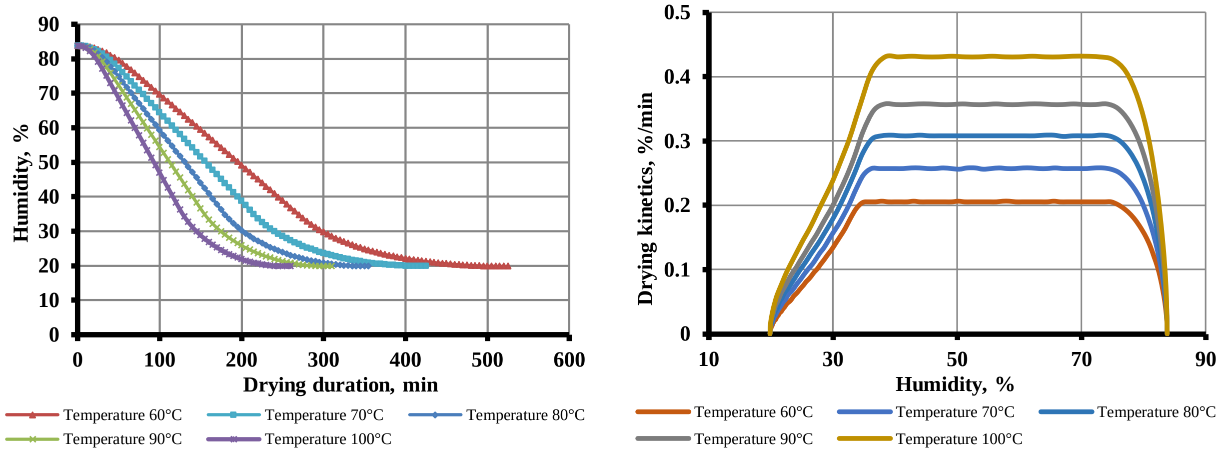
The mathematical model presented and the results of its verification for deviations, allows it to be used both for drying pears in a CO_2 modified environment and for air convection, more than that, the given model, after introducing some modifications, which would take into account thermophysical properties, would also find application in the determination of temperature and humidity during drying for other vegetable food products with a pear-like structure.

To carry out the experimental drying, the experimental drying installation with a modified CO_2 medium, with a closed cycle of the drying agent, with the possibility of changing the concentration of carbon dioxide inside the drying chamber and automatically taking over the experimental data during the drying process was designed and made (Figure 3).

In order to establish the influence of the environment modified by CO_2 on the drying process, experimental dryings of pears of the "Conferința" variety were carried out, both by the conventional method - with air, and in a modified environment. Drying took place at several thermal regimes and for CO_2 at several gas concentrations in the working chamber (30, 60 and 80%).

Based on the experiments drying process and drying kinetics curves were established for convective air drying (Figure 4) and convective 80% CO_2 modified atmosphere drying (Figure 5), from 60 to 100°C and 1.5±0.13 m/s drying agent velocity.

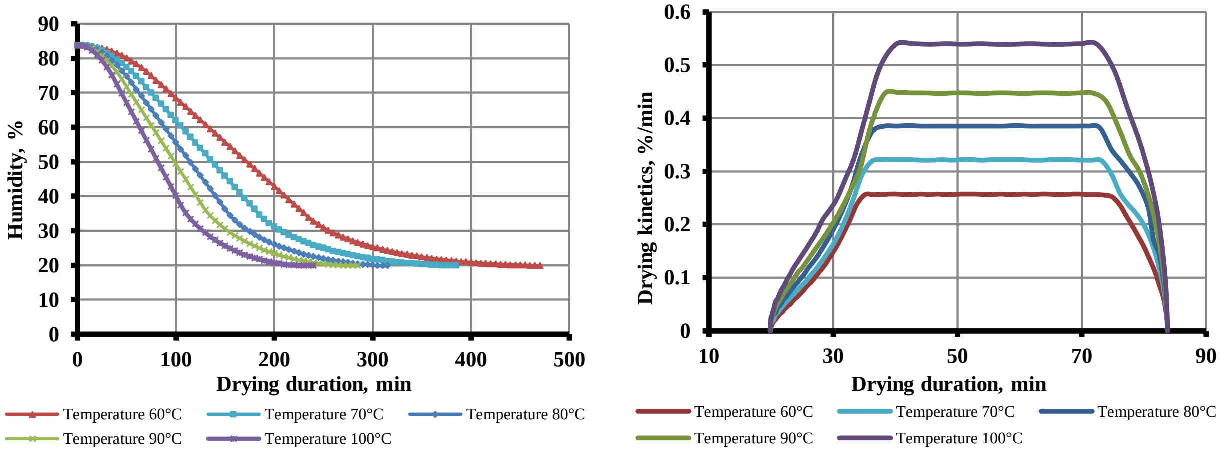
Analyzing Figure 4a and Figure 5a, an intensification of the drying process can be observed with the increase in the temperature of the drying agent. As a result of mass and heat transfer phenomena, at 60°C (air, convective regime), the drying time is 525 min, while at 100°C – 260 min, showing a 2.02 times diminution in drying duration. The same effect was reported by other researches [15-18].



a) b)

Figure 4. Drying process (a) and drying kinetics process (b) curves for dried "Conference" pears, by air flow method; drying agent air: 60, 70, 80, 90 and 100°C, drying agent velocity 1.5±0.13 m/s.

The drying kinetic curves for both methods (Figure 4b and Figure 5b) highlight all three stages of drying, in which the heating stage takes place up to 73-75% humidity, the constant drying stage – from 73-75% to 34 -38% and the speed reduction step – from 34-38% until equilibrium humidity is reached.



a) b)

Figure 5. Drying process (a) and drying kinetics process (b) curves for dried "Conference" pears, by CO_2 modified atmosphere method; drying agent CO_2: 60, 70, 80, 90 and 100°C; carbone dioxide concentration: 80%; drying agent velocity 1.5±0.13 m/s.

One can notice that temperature growth also shows an augmentation of drying process velocity, for example air drying constant drying stage velocity, for 60°C, 0.21±0.01 %/min, at 70°C – dU/dτ ≈ 0.26±0.01 %/min, at 80°C – dU/dτ ≈ 0.31±0.02 %/min, at 90°C – dU/dτ ≈ 0.36±0.02 %/min and at 100°C – dU/dτ ≈ 0.43±0.02 %/min, meaning an increase of 2.04 times from 60°C to 100°C. the same effect was mentioned by other authors [20, 21].

Drying kinetics curves for 80% CO_2 modified atmosphere (Figure 5 b.) has the same patterns as air drying one (Figure 4 b.) except higher values for the constant drying stage: 60°C, 0.25±0.01 %/min, at 70°C – dU/dτ ≈ 0.32±0.02 %/min, at 80°C – dU/dτ ≈ 0.38±0.02 %/min, at 90°C – dU/dτ ≈ 0.43±0.02 %/min and at 100°C – dU/dτ ≈ 0.54±0.03 %/min, showing an increase of 1.19 times for 60°C and 1.26 times for 100°C, that confirms the drying process acceleration namely while humidity is evaporated from the product surface.

The small reduction in drying time for the CO_2 modified atmosphere compared to air drying, which is most likely explained by an intensification of mass transfer from the product to the medium, and less by mass transfer within the product. This phenomenon can also be related to the reduction of the vapor pressure of the drying product while the CO_2 is washed, a fact noted by other researchers [6].

After performing the experiments there was determined the total polyphenols content and ascorbic acid concentration for dried "Conference" pears samples. Basing on the Figure 6. One can identify the effect of drying upon total content of polyphenol in dried "Conference" pears by both methods of air and CO_2 convection.

Analyzing the diagram from Figure 6., one can observe an augmentation of total polyphenols content with temperature increase. The same effect was mentioned by other scientists [15, 19, 22], and is presumably caused by shorter exposer of polyphenols to temperature action, as a result of reduced drying time at higher temperatures. identify an evolution of the polyphenol content as CO_2 concentration augments, if taking the same temperature of 60°C, we'll have 28.03±1.45 mg GAE/100 g of plant for air drying; 36.77±1.90 mg GAE/100 g of plant for 30% CO_2 drying; 40.73±2.11 mg GAE/100 g of plant for 60% CO_2 drying and 42.34±2.19 mg GAE/100 g of plant for 80% CO_2 drying respectively.

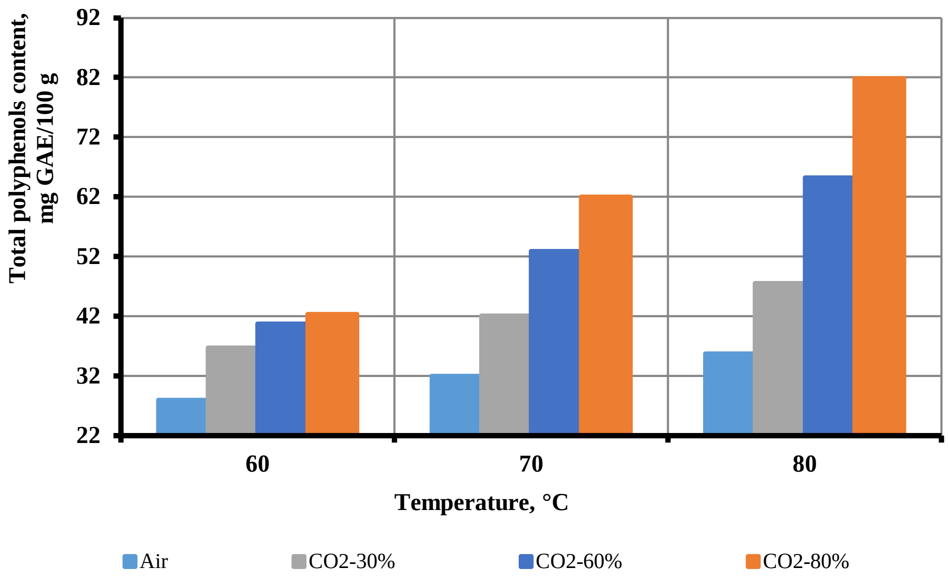


Figure 6. Total polyphenol content in dried pears, "Conference" variety, by air flow and CO_2 modified atmosphere methods. Drying agent temperature (air and CO_2): 60 and 80°C; Carbone dioxide concentration: 30, 60 and 80%.

If compared, the same CO_2 concentrations will show a boost for the temperature of 80°C: 35.79±1.85 mg GAE/100 g for air drying; 47.59±2.46 mg GAE/100 g for 30% CO_2 drying; 65.25±3.38 mg GAE/100 for 60% and 81.90±4.24 mg GAE/100 g for 80% CO_2 drying which shows an increase of total polyphenols preserved of 1.27 times for air drying environment and 1.93 times for 80% CO_2 drying atmosphere. The increase in total polyphenols content in CO_2 modified atmosphere, as noticed by other researchers [5], is due to the even more reduced drying time, as such decreased product temperature exposure, as well as the reduced concentration in oxygen, that presumably reduce the probability that oxidative reactions will occur.

From Figure 7 one can observe the degradation process of vitamin C which is easily affected by high temperature exposure, as well as oxygen presence. Researches also noticed that diminution in ascorbic acid is closely connected to moisture content of the product to be dried [15, 23], so lower temperatures are not recommended, for a rich vitamin C dried product. Beginning with a fresh "Conference" pear concentration in ascorbic acid of 44.05±2.47 mg/100 g DW (dried weight), for air convective drying, versus 43.86±2.41 mg/100 g DW, for CO_2 modified atmosphere drying, one can notice the deterioration process intensifying with drying process length.

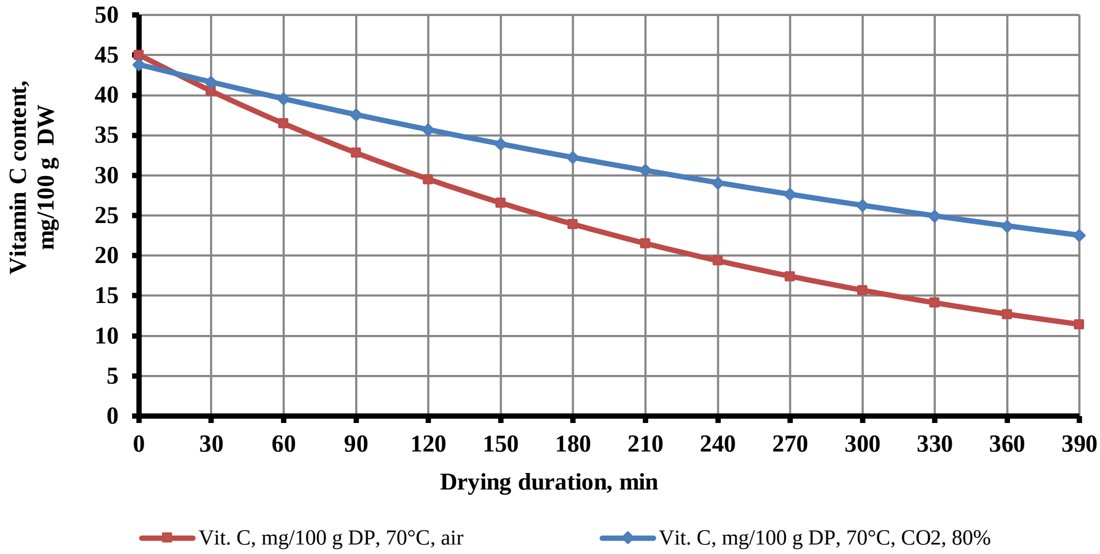


Figure 7. Ascorbic acid concentration for dried pears, "Conference" variety by air flow and CO_2 modified atmosphere methods (Carbone dioxide concentration: 80%; t= 70°C).

As such at 390 min the losses in Vitamin C represents 77 %, or 11.45±0.63 mg/100 g DW for air dried pears and 50%, or 22.74±1.24 mg/100 g DW for modified atmosphere one. There is a boost of 27%, or 1.98 times to preserved ascorbic acid. As mentioned by other sources [5, 15] that effect can be explained by the reduction of oxidative processes of ascorbic acid during drying process, that is possible to achieve with oxygen concertation reduction in the drying chamber when using CO_2 modified atmosphere.

4. Conclusions

This study was meant to investigate the effect of different types of drying agents, namely air and carbon dioxide for half-circle sliced pieces of "Conference" pears convective drying, with a temperature range of 60 – 100°C, and three CO_2 concentration: 30%, 60%, 80%.

The resulting data allowed to conclude that the above mentioned boost to polyphenols and ascorbic acid content can be explained as an effect of CO_2 modified atmosphere, as it allows to diminish oxygen presence thus reducing the oxidative action inside the drying chamber during heat treatment. There is as well a correlation between the augmentation of drying temperature and lower levels of damage to nutriments in dried products which is presumably due to the fact that drying temperature elevation means shorter drying duration which reduce polyphenols and Vitamin C temperature and oxygen exposure thus preserving them better.

In conclusion, one can recommend to maintain the quality of dried vegetable products, it is recommended to apply the drying method in a CO_2 modified environment, with the speed of the drying agent of 1.5 ± 0.13 m/s; temperature of the thermal agent of 70°C; concentration of carbon dioxide in the working chamber of 80%.

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Conflicts of Interest: The author declares no conflict of interest.

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