

Controlled temperature grinding under modified atmosphere for Almond (*Prunus Dulcis*) paste production

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Abstract

The quality of the raw material and the processing conditions have a great influence on the nutritional properties of finished products. This research is focused on almond paste production and aims at developing a new production process to deliver the high nutritional content of the raw almonds into the finished product. Raw almonds are composed mainly of fats (approx. 50%) and proteins (approx. 25%), and are particularly rich in omega 6 fatty acids, and are hence exposed to denaturation and oxidation phenomena during the traditional grinding/homogenization process. The study involved the analysis of six different local cultivars based upon the main nutritional indicators (protein content, vitamins, and fatty acids) which resulted in the determination of the cultivar *tuono* as the one with the best nutritional properties. The further step consisted in establishing an innovative production process involving controlled atmosphere and refrigerated grinding with the aim of preserving the nutritional value of the raw material. Finally an experimental comparison of the product obtained with the proposed production process and the traditional method showed an average incremental gain of 27% and 21% in the protein and fat content, respectively.

Keywords: Almonds; Food Processing Aspects; Lipid Oxidation.

1. Introduction

In the past, the development of industrial food processing has sometimes privileged productivity rather than nutritional properties of the products, even arising some concern for consumer health and safety. With the demographic imperative of an aging population worldwide, there is an understandable emphasis today in the food industry to manufacture products that can be labelled with claims for health promotion, quality and safety (Chen *et al.*, 2006). The establishment of production processes preserving the nutrient content of foods is hence the new frontier of process innovation in the food industry. This paper refers to the grinding and homogenization of almonds which is commonly employed in several production processes. These processes severely damage the raw material resulting to significant loss of nutritional content, as for example in production of almond milk, which is an aqueous dispersion of almond powder. The evidence of beneficial influences of almond consumption on human health has been confirmed by several researches (Lapsley, 2003; Chen *et al.*, 2006), however industrial production processes generally fail in delivering the nutritional content to the finished products. The traditional (“homemade”) production cycle in fact originates an aqueous dispersion which is unstable at room temperature, unless extremely small particle size distribution is achieved. In addition the presence of water originates favourable conditions for micro-biological growth which drastically reduces the shelf-life of the product. Another critical issue is that almonds are rich in omega 6 fatty acids, which are significantly affected by the lipid oxidation phenomenon during grinding and homogenization processes. These are the main reasons why industrial almond milk production is difficult.

In this paper a production cycle is proposed which preserves the nutritional content in the raw material to the final product. The study involves a preliminary investigation of the raw material and a subsequent analysis of the process conditions that affect the quality and nutritional content of the product. Once the raw material with the highest nutritional content has been selected, an innovative refrigerated and oxygen-free homogenization process is established. An experimental analysis has been finally carried

out to determine the nutritional value of the product thus obtained, and a comparison with the traditional products taken as reference has shown the effectiveness of the proposed approach.

2. Materials and Methods

2.1 Raw materials analysis

The sweet almond, (*Prunus Dulcis* L.) is a stone fruit commercially cultivated in Mediterranean countries, Armenia, Iran, California (U.S.A.), and Australia whose beneficial properties are nowadays recognized (Lapsley, 2003; Chen *et al.*, 2006; Mandalari *et al.*, 2008). Such properties originate mainly from the content and composition of fatty acids, proteins, and vitamins. The antioxidant activities of almonds have emerged in various studies (Wu *et al.*, 2004; Amarowicz *et al.*, 2005) and their consumption has been associated with several benefits, as for example in reducing risk of coronary heart disease. Nutritional values however slightly vary according to the genotype and fatty acid composition and they can be influenced by ecological conditions, variety, location, and technical-cultural practices. In the present research, in order to obtain a high nutritional almond paste, the selection of the raw material with highest nutritional value is required. For such purpose 6 different cultivars (Tuono, Ferragnès, Fascionello, Romana, Genco and Pizzuta d'Avola) have been analyzed and their content of proteins, fatty acids and vitamins has been measured. The beneficial properties related to these elements are briefly described below.

Vitamin E. Among dry seeds and fruits, almonds are the best source of Vitamin E in the form of alpha-tocopherol, with a percentage of approx. 250 mg/kg. Alpha-tocopherol is the most active component of the Vitamin E and the most powerful antioxidant in the lipid (fat) phase of the human body (Burton, 1989; Niki *et al.*, 1989). Vitamin E cannot be synthesized by the body and must therefore be supplied in the diet or through supplementation. The extremely critical role of alpha-tocopherol in protecting against free-radical reactions becomes apparent when considering the vast number of diseases (e.g. Senile dementia, Alzheimer, Atherosclerosis and other circulatory diseases) thought to be caused by these reactions (Ames, 1983; Cross *et al.*, 1987). Recent studies have also shown that a low vitamin E concentration in human blood is associated with an overall increased risk for many cancers, including breast and lung cancer (Wang *et al.*, 1989; Stahelin *et al.*, 1989; Menkes *et al.*, 1986).

Proteins. Almonds are a good source of proteins, with a content of approx. 25%. Almond protein profile is mainly constituted by AMP or amandin (Sathe Shridhar *et al.*, 2002). Despite the long history of global cultivation and ready consumer acceptance of almonds, data on almond protein quality are still researched. Amandin is considered as an allergen, probably due to its high content of nitrogen (approx 19%), however although allergy to nuts has been frequently reported, there is no reliable data on the identification of amandin as an almond allergen. To date, evidence suggests that amandin is not as highly allergenic as the proteins found in peanuts or walnuts (Roux *et al.*, 2001). Finally amandin is reported by some authors as a highly digestible protein and antigenically stable toward various food processing methods although it has poor nutritional value (Venkatachalam *et al.*, 2002).

Lipids and Fatty acids. Fatty acids are categorized by the number of double bonds present between the carbon atoms in their carbon chain in "saturated", "monounsaturated", and "polyunsaturated". Polyunsaturated fatty acids (PUFA) can be further divided into omega-3 and omega-6 fatty acids, based on the location of the first double-bond in the carbon chain. Certain omega-3 and omega-6 PUFA are considered to be Essential Fatty Acids (EFAs) because they are necessary for health, but cannot be synthesized by the body, it is therefore important to supply them through daily dietary intake. Alpha-Linolenic Acid (ALA), an omega-3 fatty acid, and Linoleic Acid (LA), an omega-6 fatty acid, are the predominant essential fatty acids in humans. Omega-3 fatty acids have a balancing effect on omega-6 fatty acids. Both are essential nutrients, but they should be consumed in equal proportions. Lipids are the main component in all nuts reaching approx. 50% of weight in almonds, with oleic and linoleic acids representing more than 80% of the total fatty acids while linolenic acid is present in extremely small percentage. There are many health benefits attributable to essential fatty acids, for example it is generally accepted that omega-3 fatty acids help to reduce the levels of triglycerides in the body, thus decreasing the risk of heart disease. Omega-6 fatty acids have been shown to be beneficial in the reduction of cholesterol levels when they are substituted for saturated fats in the human diet. The benefit in consuming omega-6 fatty acids therefore lies in the fact that they reduce the incidence of coronary artery disease.

Amygdalin. Amygdalin is a cyanogenic glycosides which determines the difference between bitter almonds (*Prunus Amygdalus*), containing 3 to 5% of amygdalin and sweet almonds containing only traces of amygdalin. Amygdalin is thought to have beneficial effect in the cure of cancer although it is considered highly poisonous because it can be hydrolyzed to yield deadly hydrocyanic acid (HCN). Bitter almonds hence are not used for food preparation. In the present research Amygdalin content has been evaluated to detect and avoid cultivars which might be unsafe for food processing.

Almond samples were collected from six different cultivars: Tuono, Ferragnès, Fascionello, Romana, Genco and Pizzuta d'Avola. 'Ferragnès' is the result of the European almond cultivar breeding programmes, it was obtained in France in 1960 by crossing the local 'Al' with the Apulian 'Cristomorto' (Grasselly and Crossa-Raynaud, 1980). The positive traits of 'Ferragnès' are its late blooming, satisfactory shelling percentage, absence of doubles and good kernel features. On the other hand, the negative characteristics are its tree weeping habit, and especially self-incompatibility, meaning that without cross-pollination a viable crop is highly unlikely. 'Genco' is another recent Apulian cultivar while 'Tuono' (Grasselly *et al.*, 1992) is an ancient Apulian variety which has the defect of producing medium to high percentage of double kernels. Romana, Pizzuta d'Avola and Fascionello are Sicilian cultivars: the first one is considered to have the best sensorial quality, the second and the third have low market value due to the irregular shape of the kernels. An experimental campaign and a statistical analysis of the results was performed in order to

select the cultivar with the best nutritional profile to be employed for subsequent processing phase. For experiments twenty samples of approx 50 g from each cultivar were acquired and analyzed accounting a total of 120 samples. Samples were extracted from 10 different batches (2 replicates for each batch) of the same cultivar grown in the same crop year but gathered in different days. All batches came from experimental fields in the same geographic area (central Sicily) cultivated with the same methods. Samples were powdered at room temperature using a mortar and pestle and stored in an airtight container at -20°C . Statistical analysis was conducted taking the average protein, lipids, amygdalin and vitamin E content of the 2 replicates of each sample thus obtaining 10 values for each cultivar. For each set of 10 values thus obtained the average and the standard deviation of the samples were determined. Also the error bars have been evaluated as the differences of the maximum and minimum values achieved and the average previously calculated. The same samples were also used to determine the fatty acids profile. Also in this case the results in each replicate were averaged thus obtaining 10 values for each cultivar. The average and the standard deviation of the 10 values thus obtained were calculated and the error bars were evaluated considering the maximum and minimum values achieved.

2.2 Particle size analysis

A particle size analysis is required to investigate the problem of emulsion stability. The methods here considered for particle size measurement are sieves, sedimentation, electrozone sensing and laser diffraction. Sieves can be used for large particles and are not suitable for fatty acids emulsions. Sedimentation has an applicable range of 2-50 μm but it is affected by significant measurement errors. Electrozone requires expensive calibration and the measurement of small particles is quite difficult. Laser diffraction (LD) is a method finally employed for particle size measurement, and it is based on the properties of particles to scatter light. This method has become the preferred standard in many industries for characterization and quality control. In this study particle size analysis was carried out by means of Malvern Particle Size Analyzer - Mastersizer 2000, which uses a He/Ne Laser 633 nm (red) for materials in the range 0.02 μm to 2000 μm .

For experimental analysis the process was fed with pure almonds of the same cultivar *tuono* and two sampling points have been established at two different stages of the production (namely after the cutter mill operation and after the ball mill operation) process to monitor the particle size distribution during the two steps of grinding/homogenization process. The experimental procedure involved the extraction of 4 set of samples with 4 replicates each in both the sampling points, resulting in 32 samples of 20 g each. Sample replicates were taken at time intervals of 15 mins, with the same processing parameters (milling chamber temperature, cutter rpm, duration). All the samples were produced in the same processing conditions and all the replicates were obtained with the same batch of raw material, however different lots have been employed under different sets of experiments. Results were analyzed comparing the shapes of the particle distributions obtained.

2.3 Nutritional content analysis

The assessment of nutritional content is based upon the evaluation and the comparison of proteins and lipids percentage in the raw material and in the finished product. The nutritional content of the product thus obtained was evaluated. Determination of the protein content have been conducted by the Kjeldhal method (UNI ISO 8968-1:2002). Protein content denaturation is generally the consequence of high temperature or pressures during processing and, depending on the denaturation effect can be measured by standard tests as Protein Dispersibility Index (PDI), Nitrogen Solubility Index (NSI) and indirectly by Water Absorption Index (WAI). In this research, however, only the protein content has been evaluated analogously to similar researches (Ignário *et al.*, 2007) by means of the Kjeldahl method. This methodology leads to a rough evaluation of the protein denaturation effect, and the results here presented, consequently, must be considered preliminary. The employment of more accurate techniques requires a more detailed analysis of the typology of denaturation effects.

Total fat content has been determined by releasing lipids using acid hydrolysis (UNI 22605-1992). The Fatty Acids analysis was then carried out by converting them into their methyl esters which were finally analyzed by gas chromatography according to ISO 5508:1990 method.

Concerning the lipids and protein content, the protocol was carried out using 5 samples of the previously analyzed raw material of cultivar *tuono*, which emerged as the local cultivar with highest protein and fat content. Also an homogeneous process setup was established by fixing a constant set of process parameters. Production of almond paste was hence started, according to traditional recipe with sugar addition after homogenization (approx. 30% in weight), until steady state was reached. Four replicates for each sample point were carried out resulting in a total of twenty samples (20 g each) of finished product. The replicates were extracted each 15 mins. after the achievement of the steady state condition, with the same batch of raw material. Experimental tests for the different set of samples were carried out in different days but with the same process setup after complete cleanup of the machines. The samples thus obtained were analyzed and the total protein and fat content was determined.

3. Results of the raw material analysis

Average values of the above indicators (Vitamin E, fats, proteins, and amygdalin) for the 20 samples examined are given in Table 1.

Table 1 – Comparison of the cultivars according to their nutritional content indicators

Nutritional content				
	Vitamin E (mg/kg)	Amygdalin (mg/kg)	Proteins (%)	Total lipids (%)
fascionello	203.33 (\pm 33.8)	78.09(\pm 11.4)	20.2(\pm 1.59)	48.52(\pm 4.9)
romana	196.34 (\pm 36.6)	78.38(\pm 10.9)	22.2(\pm 1.50)	47.44(\pm 5.0)
tuono	227.22(\pm 33.3)	79.99(\pm 11.9)	25.5(\pm 1.56)	50.01(\pm 4.9)
genco	189.52(\pm 39.0)	76.7(\pm 11.6)	24.1(\pm 1.53)	46.2(\pm 5.0)
ferragnès	202.08(\pm 37.9)	80.03(\pm 11.5)	23.6(\pm 1.54)	46.62(\pm 6.0)
pizzuta	213.07(\pm 32.5)	78.48(\pm 11.8)	22.6(\pm 1.65)	48.99(\pm 5.0)
<i>average</i>	<i>205.26</i>	<i>78.61</i>	<i>23.03</i>	<i>47.96</i>

For the analysis and selection of the raw material, however, the average value is not sufficient since it gives no information about the variability of the nutritional properties. In order to obtain a robust production process, hence, the standard deviation of the samples has been evaluated and reported in Table 1. In addition a graphical representation of the values of the aforementioned indicators is given in Figure 1 for all the cultivars considered. Such figure shows in a radar graph the deviations from the average value of each indicator for all the cultivars considered.

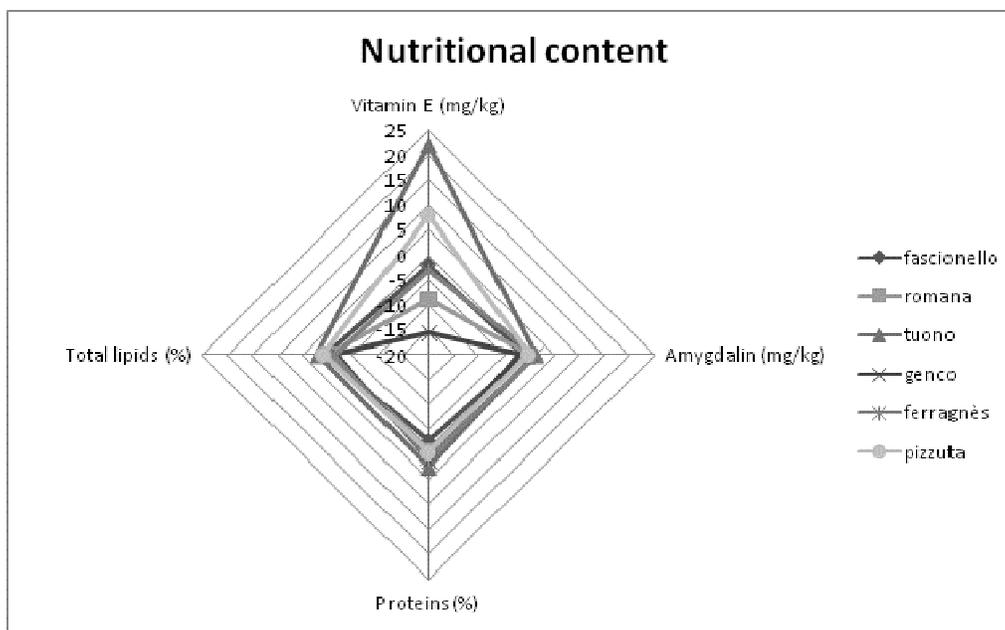


Figure 1 - Nutritional profile

This representation gives a clear information of the nutritional profile of the different cultivars and helps in selecting the most suitable for the purpose of this research. A detailed analysis of the fatty acids profile has been carried out with the same methodology. According to the profile of fatty acids (Table 2 and Fig. 2) the kernels examined showed a high amount of monounsaturated fatty acids, mainly oleic acid, and low amounts of saturated (palmitic and stearic) and polyunsaturated (linoleic) fatty acids. Among selections, differences in fatty acid composition were highly significant for oleic and linoleic acids, and less significant for palmitic, palmitoleic and stearic acids. The proportion of oleic acid was the highest, ranging from 68.26 to 70.22%. The percentage of linoleic acid was lower, ranging from 19.72 to 21.25%. Experimental results showed that the cultivars

considered are quite similar according to their nutritional values, thus leading to the conclusion that the choice of a particular cultivar within those analyzed does not have a crucial influence on the quality of the final product. This conclusion does not affect the correctness of the methodological approach as in fact when the development of a food product is undertaken raw material must always be characterized preliminarily. In the case presented, the cultivar “tuono” dominates all others according to the characteristics considered and for this reason this cultivar was chosen for further processing.

Table 2– Comparison of the cultivars according to their fatty acids

Fatty acids profile					
	palmitic C16:0 %	palmitoleic C16:1 %	stearic C18:0 %	oleic C18:1 %	linoleic C18:2 %
fascionello	5.89(±0.44)	0.58(±0.10)	2.07(±0.45)	69.54(±1.43)	20.14(±1.64)
romana	5.93(±0.37)	0.53(±0.11)	2.10(±0.42)	68.26(±1.98)	21.02(±1.92)
tuono	6.17(±0.34)	0.63(±0.09)	2.19(±0.52)	70.22(±1.17)	21.55(±1.67)
genco	5.78(±0.38)	0.32(±0.11)	1.93(±0.43)	69.27(±1.42)	19.72(±1.51)
ferragnès	5.92(±0.68)	0.56(±0.14)	1.53(±0.63)	70.11(±1.50)	20.40(±2.30)
pizzuta	5.87(±0.45)	0.58(±0.11)	2.07(±0.47)	69.18(±1.30)	20.41(±1.53)
average	5.93	0.53	1.98	69.43	20.54

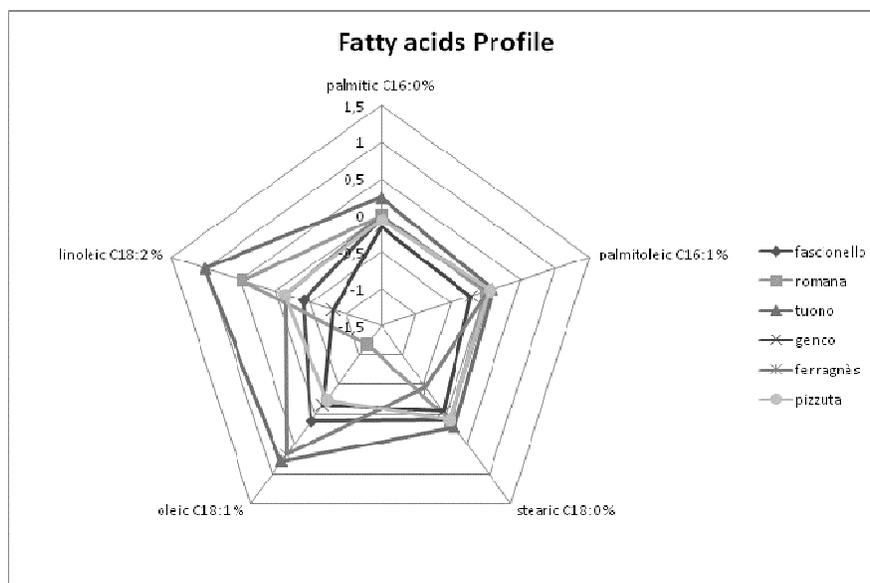


Figure 2- Fatty acids profile

4. Almond Paste Production Process

The traditional manufacture of almond milk involves the preparation of a mother almond paste as a product of the crushing of blanched sweet almonds mixed with saccharose and a certain percentage of water or milk. The production process here described in particular focuses on the production of a dehydrated almond paste with a water content of about 10% by weight, and various additional elements in order to improve the texture, taste, appearance, or to extend the shelf life. Traditionally there are two

manufacturing processes which may be distinguished, one being a combined process of cooking and crushing, and the other an evaporation-crushing process. According to the first process, named the “French” process, dry blanched almonds are grated and then subjected to pre-crushing, for the purpose of tearing a large number of cells which enclose the almond oil, and thereby obtain pure almond paste. The various sugars, saccharose, syrup are then mixed with a certain quantity of water to produce a direct solution, while a cooking step enables the quantity of water to be reduced and the consistency of the paste required for the manufacture to be obtained. The products thus issuing from the two preceding steps are introduced into a combined cooker and malaxator, followed by cooling and crushing. It is in the course of this step that the various perfumes, alcohols and other additives, are added to the mixture. According to the second evaporation-grilling process, also termed the “German” process, the blanched white almonds are mixed with crystalline sugar, and the mixture is then subjected to crushing. Thereafter, water is added to facilitate, during the grilling, Maillard reaction which thus develops the formation of the aromatic substances, and the evaporation of a certain quantity of water. Cooling is then necessary, and is generally achieved by a current of cold air, and the product thus obtained is termed the mother almond paste. Added to this mother paste are confectioner's sugar, glucose syrup and other additives which, when mixed, result in the final almond paste. The two processes clearly generate differences in the rheological and organoleptic properties of the finished products since the Maillard reaction is developed in different conditions.

Almond milk is finally obtained by mixing the almond paste, produced according to the processes above described, with water, thus resulting in an aqueous emulsion of an organic liquid (an oil). Organoleptic characteristics of almond paste depend on its formula and method of manufacturing, however the most important factor, be it from flavour, appearance and texture, is oil separation in the product, which is a consequence of the leakage of oil from almond paste. Emulsions made by mixing of pure immiscible liquid phases are in fact very unstable and separate rapidly (Meunier and Mengual, 1996). Only micro-emulsions are thermodynamically stable dispersions, which means that they form spontaneously and are stable indefinitely. Most macro-emulsions require the input of considerable amounts of energy for their production and can only be stable in a kinetic sense. The kinetics of the emulsion breaking process are governed by three different mechanisms: brownian flocculation, sedimentation, and creaming. In order to improve their stability, it is therefore crucial to identify the major instability mechanism for the specific food emulsion of interest. In the case here considered, brownian flocculation can be neglected since it affects extremely small particles (nanometer size). On the contrary, sedimentation and creaming, which result from the action of gravitational force on phases that differ in density, are responsible for the separation of fatty acids (oil) from the aqueous phase of the composition. Sedimentation and creaming have been extensively analyzed using Stokes law which describes the velocity of the upward or downward motion of a droplet as a function of droplet radius (Dickinson, 1992):

$$V = \frac{2 \cdot g \cdot r^2 \cdot (\rho_1 - \rho_2)}{9 \cdot \mu_2}$$

Where V= velocity of separation rate of creaming (cm/sec), g= gravity acceleration, r= droplet radius (cm), ρ_1 =density of the dispersed phase (g/cm^3), ρ_2 =density of the continuous phase (g/cm^3), μ_2 =viscosity of the continuous phase (Pa sec).

From Stokes law it is shown that the rate of a droplet to move to the top (V) is directly proportional to the density difference of the oil phase from water phase and to the square radius of the droplet. It is also inversely proportional to the viscosity of the water phase. Of these factors, only ρ_1 and r can be manipulated in order to achieve emulsion stability. A variety of methods have been developed in order to stabilize oils by preventing separation. Typically, current stabilization of oils involves the use small droplet size, and / or weighting agents to increase the density of the oil phase. As a result, current stabilization technologies require complex homogenization equipments and stable surfactants. Recently, methodologies have been developed to stabilize fatty acid oil droplets having a wide range of particle sizes (about 5 microns to about 20 microns, rather than only around 0.1 microns as is typically used in emulsified oils) without surfactants using for example pectin and alginate compounds (WIPO Patent No. 03/003849 A2). For fatty acids emulsion stability, hence a homogenization process has been setup to achieve a 5 microns average particle size. It is generally recognized, however, that during the homogenization, the disruption of cells and resulting increase in surface area promotes oxidative deterioration and higher rates of microbiological and enzymatic activity (Lethuaut et al., 2002), although this effect has not been confirmed by other researches (Charikleia et al., 2007).

Since traditional almond paste processing involves the addition of water at some phase, resulting moist causes the paste to deteriorate rapidly if other preservative measures (for example chilling, freezing and heat processing) are not taken. Oxidative deterioration is typically initiated by Lipoxygenases (LOX) that are dioxygenase enzymes containing nonheme iron protein. Lipoxygenase is distributed throughout many seeds, but the enzyme is inactive because of its limited contact with oxygen. Breaking of cell structure during the size reduction operation causes the Lipoxygenase to catalyze reactions of polyunsaturated fatty acids with oxygen (Hamberg and Samuelsson, 1967; Hamberg and Hamberg, 1980). Deactivation of almond lipoxygenase has not only theoretic but also practical importance because they are significant quality deteriorating agents. Due to Lipoxygenase activity in almonds there are changes in the colour, flavour during size reduction. Additionally the release of cellular materials provides a suitable substrate for microbiological growth and this can also result in the development of off-flavours and aromas and safety related issues. The duration of size reduction process and the delay before subsequent preservation must be accurately controlled to achieve the desired texture. The relationship between the size of food particles and perceived texture is discussed by

Stanley and Tung (1976); and by Sherman (1976). The control of off-flavors, therefore, requires inactivation of lipoxygenase enzyme. Since lipoxygenase is heat sensitive, its in-activation is most commonly accomplished by thermal processing. At temperatures above 60°C, the half-lives of the various lipoxygenase enzymes rapidly decrease with increasing temperature. Recent researches (Buranasompoba *et al.*, 2007) report that even 2 minutes at 55°C may suffice to inhibit lipoxygenase. However, heat treatment also reduces the nitrogen solubility index and protein dispersibility index. Such approach, hence, tends to degrade the end product nutritionally or functionally. Protein denaturation is commonly defined as any non-covalent change in the structure of a protein. This change may alter the secondary, tertiary or quaternary structure of the molecules. One of the most common effects of denaturation is the loss of solubility which can be related to the loss of a great number of desirable characteristics of the protein. The role of many process designs and food additives is hence to maintain protein solubility.

5. New Process Setup and Results

On the basis of the above considerations, a new production process is here proposed which aims at obtaining a stable emulsion of almond fatty acids. Emulsion stability is obtained by reducing the average particle size up to 5 µm, and the production process presented is designed to preserve the nutritional content, the flavour of raw material, in an industrial product with suitable shelf life. As discussed before the most critical aspects in almond processing are:

- emulsion stability;
- protein denaturation;
- lipid oxidation.

This study proposes a low temperature almond paste processing process and is focused on the grinding process, which is the main cause of nutritional loss in the finished product. Traditional grinding processes can be carried in wet or dry conditions. In general wet grinding process is faster and more energy efficient, as in fact wetting agents break down surface tensions of aggregated particles and absorb excess heat produced. However, as stated before, the presence of water typically increases microbiological growth and lipid oxidation. For such reasons, a “dry” grinding process is here adopted which involves two subsequent phases of cutting and homogenization. According to such procedure, raw material is grinded without the addition of water. The humidity and the temperature of processing are in fact the parameters which most directly influence the quality of the resulting product. Previous studies on the effects of the water activity on lipoxidation, using specific methods of detection, have mostly supported the commonly accepted scheme described by Labuza (1971), according to which the rate constants decrease with increasing a_w values, up to about 0.3, when the tendency is reversed. However, some authors have reported that this is not the case in all situations; and recent studies (Tazi *et al.*, 2009) describe the effects of a_w in almond paste at various heating temperatures, according to the recently developed integrative analytical method of lipoxidation based on the detection of the first stage peroxides (CL) and advanced stage carbonyls (TBARS). This study demonstrates that the conjoint effect of temperature and a_w on lipoxidation is much more complex than the classical theory describes, and at low temperatures (60 to 80°C) the Kinetics of the reaction increases with a_w . Nevertheless, a detailed analysis of such phenomena should involve a better knowledge of how temperature affects the development of lipid oxidation oil-water emulsions, and should take into account additional process parameters in a specific optimization context, as reported for example in De Pilli *et al* (2008) for a similar extrusion-cooking process.

The cutting process is carried out in a cutter mill where the milling action is produced by a rotating assembly that uses sharp knives or blades to cut the particles. A subsequent homogenization process, through a ball mill, has been considered to obtain a uniform particle distribution. In addition, in order to reduce the effect of protein denaturation caused by temperature rise during grinding, water-cooled milling chambers have been employed.

A final issue concerns the inhibition of off-flavours related to the lipid oxidation phenomenon during grinding. Since this problem is well-known to food manufacturers, some technologies such as grinding vacuum, inert gases (nitrogen) or deoxygenating agent have been developed. In this research, in order to inhibit the effect of lipid oxidation a vacuum milling process has been setup for experiments. Experimental test configuration is given in figure 3 and 4. The process involves an initial blanching phase (1) and the subsequent milling phase subdivided in two steps carried out in the cutter mill (2) and in the ball mill (3) respectively. The product obtained is then filtered into a sieve (4) and stored into a silo (5).



Figure- 3 Refrigerated vacuum milling chamber

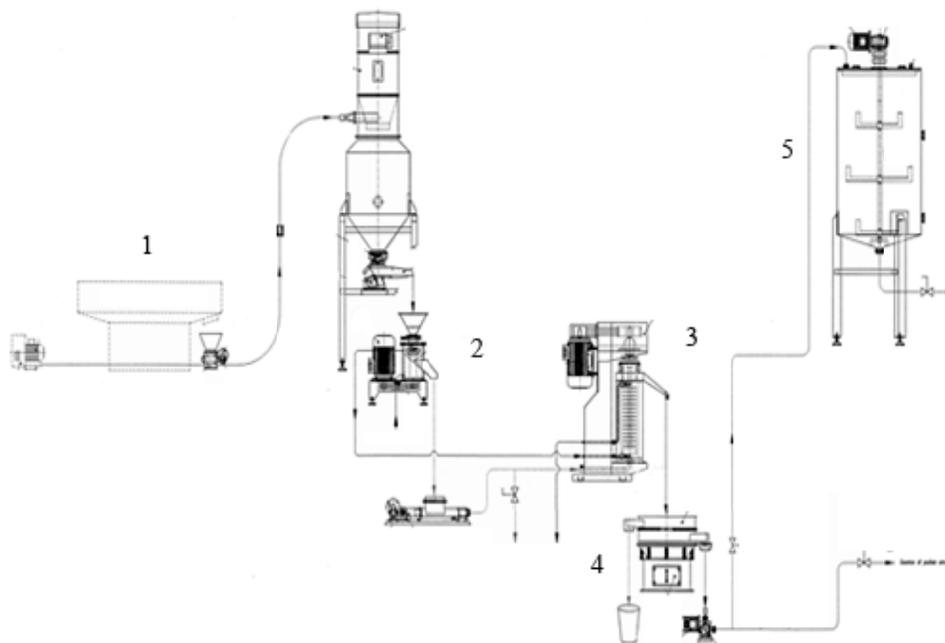
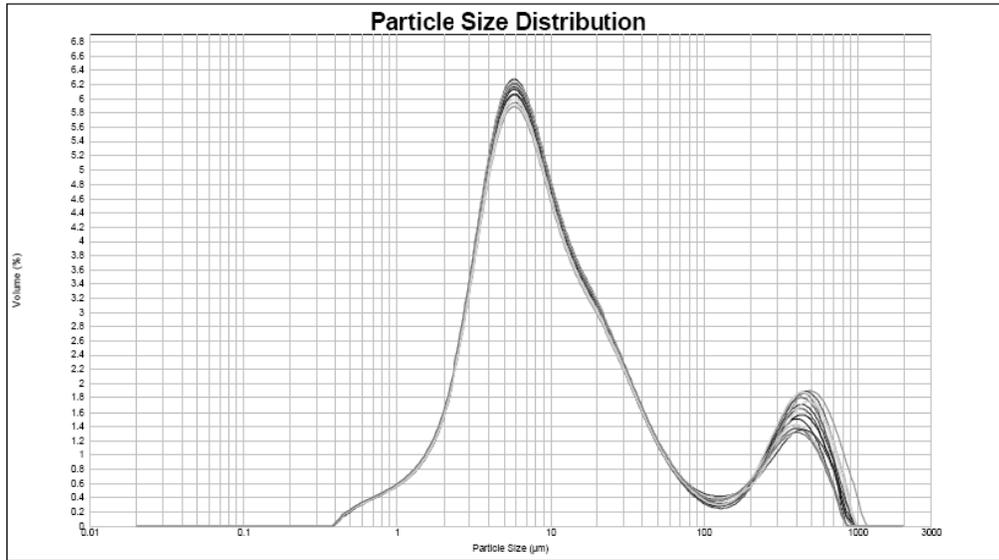


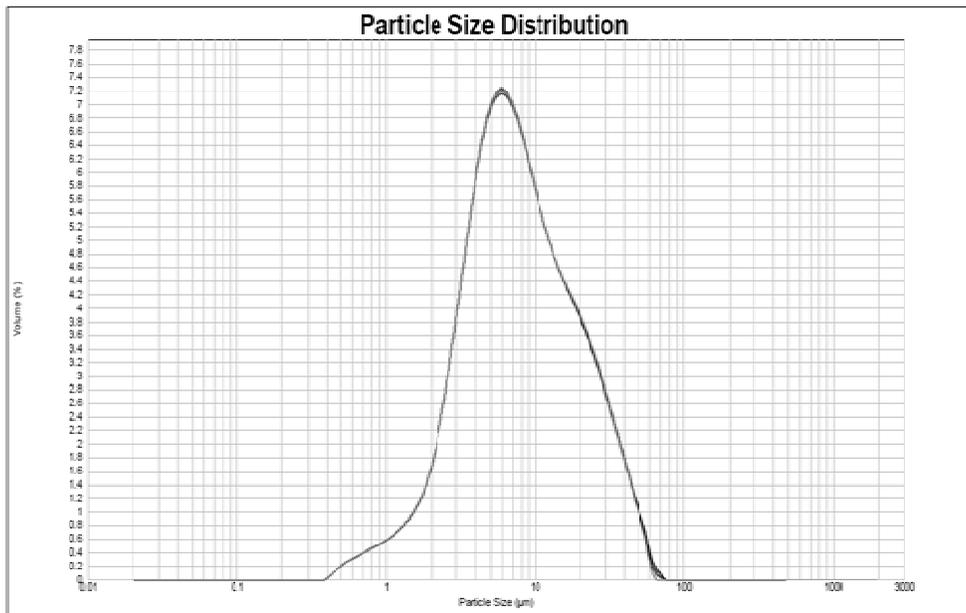
Figure 4- the proposed production cycle: (1) Blanching (2) cutter mill (3) Ball Mill (4) sieve (5) silo

An experimental analysis has been finally performed in order to evaluate the quality of the product obtained by means of the experimental production process. The experimental analysis has been performed by measuring the nutritional value (protein and fat content) of the raw material and the final particle size distribution of processed almonds. The process has been carried out in an experimental rotary cutter mill and ball mill homogenizer both equipped with a vacuum pump and a refrigeration system, as discussed in the previous paragraph. A thermocouple for temperature monitoring was also mounted in the milling chamber.

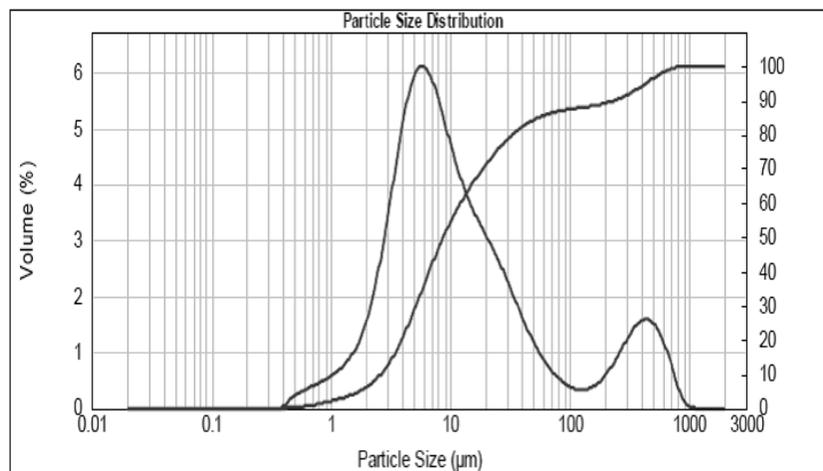
The experiment design involved the evaluation of the particle size distribution for all the samples, and the comparison of their average values and shape factors. The indicators thus obtained have been averaged among the replicates, in order to reduce the intrinsic effect of random factors. The results thus obtained for the complete protocol were extremely similar, thus demonstrating the homogeneity of the complete set of samples, and the negligible effect of the different raw material lots. Due to the substantial invariability of the indicators, the complete distributions of the full set of experiments (16 samples extracted after the cutter mill) is reported in figure 5a for better comprehension.



a- Knife mill



b-Ball mill



c-Cumulative knife mill

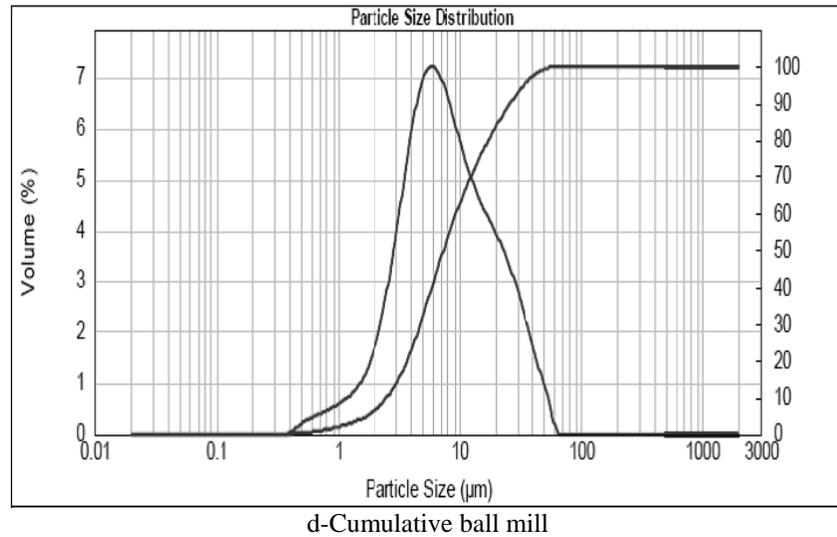


Figure 5- Particle size distribution

The particle size distributions range between 1 µm and 1000 µm and have a first peak at 6 µm and a secondary peak between 400 and 500 µm. Finally, the temperature measured during the refrigerated cutting process was approximately 43°C with little variations and did not exceed 45°C confirming the achievement of a steady state condition. The average percent distribution curve was also extracted and the cumulative function was calculated. These curves are shown in fig. 5c.

Experiments confirm that the final processing phase in the ball mill allows to achieve an homogenized product where the tail of the distribution is completely removed, with an overall particle size below 100 µm and a single peak at 5 µm and 65% of the distribution below 10 µm. In this case also, the milling chamber temperature was below 40°C. Again the average particle distribution was obtained and the cumulative distribution was calculated. These results, given in fig 5b and 5d, again show a stable distribution

The comparison of the protein content of raw almonds and almond paste on the basis of referenced values, given in Table 3, shows that the traditional almond paste manufacturing process delivers the protein content of the raw material to the final product to an extent of approximately 35% only.

Table 3 – Comparison of selected indicators with reference values

	reference	Reference	Percent
	raw	almond	difference
	almond(*)	paste(**)	
Protein %	25.3	8.81	65.18%
Tot Lipids	49.5	27.75	43.93%

(*)Almond Board of California

(**)USDA National Nutrient Database

The protein content in fact turns from 25% of raw material to 8% in the almond paste. The remaining difference of 65% is due to the formulation of the almond paste and to the denaturation effects. Roughly speaking we can consider that traditional almond paste recipe involves the addition of 30-35% of sugar and aromatic compounds to the pure almond paste, the loss of proteins due to denaturation can hence be estimated to be about 30%. Analogously, approx 56% of the fat content in the raw material can be found in the finished paste, as in fact the content of lipids of raw almonds is 50% and becomes 27%. Based on the comparison of

referenced nutritional value, hence, almond paste results as a low nutritional content product, although the raw material has good initial nutritional properties.

The fat and protein content of the product obtained according to the process here proposed was evaluated by means of a suitable experimental protocol carried out according to the procedure stated before in paragraph 2.3. The average protein content of the four replicates for the five sampling point are depicted in Figure 6 a, which also shows the error bars for each set of samples and the total average value. The same results are also given for the total fat content in Fig. 6 b.

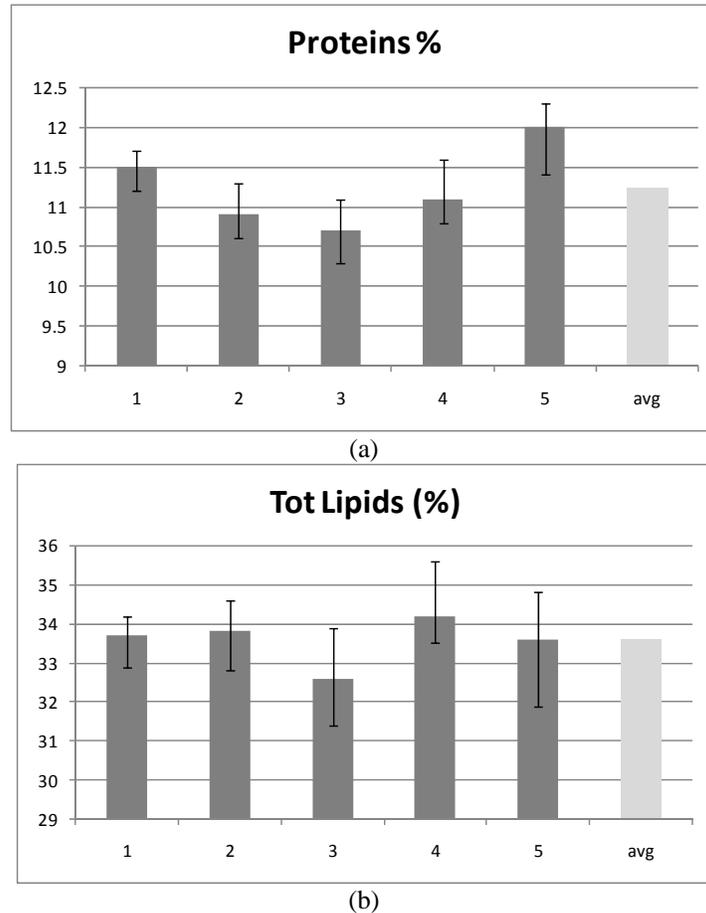


Figure 6- Error bars for each set of samples and the total average value

Obtained results show that the process described in this study is effective in preserving the nutritional content of the raw material in the finished product, as in fact the protein content measured in the almond paste ranged from 10.7 % and 12 %, with an average value of 11.2% and a standard deviation of 0.59. The corresponding gain, compared with the reference values, ranges from 25.8% to 28.9% with an average value of approx 27%. Similarly, the lipids content measured in the 5 samples ranged from 34.2% to 32.6% with an average value of $33.6 \pm 0.5\%$. The corresponding gain is 21.07%. The comparison of protein and lipid content obtained by the experimental process and reference data is shown in Fig. 7 a and 7 b.

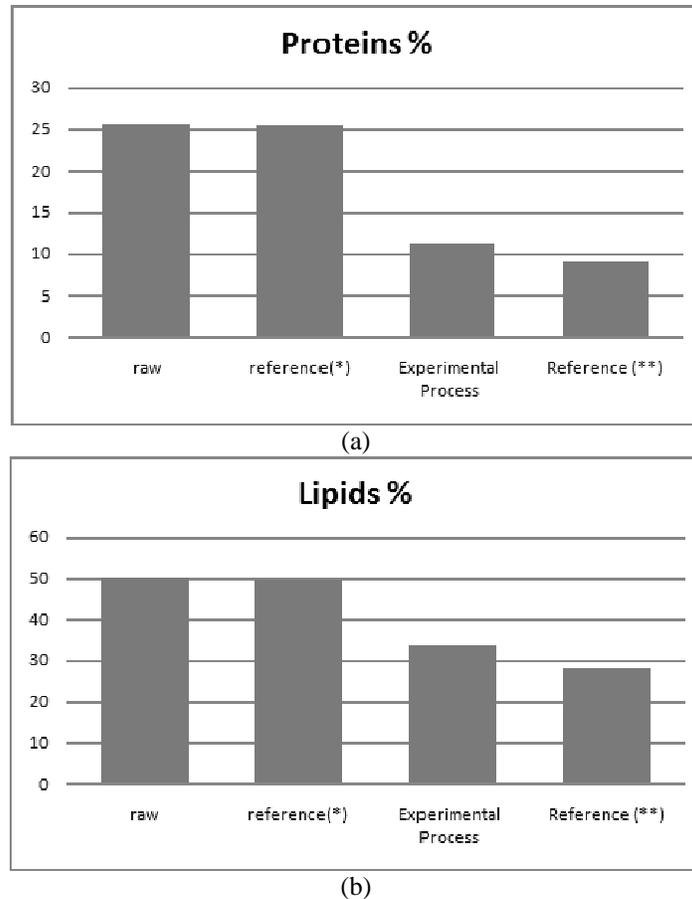


Figure 7-Comparison of protein and lipid content with reference values

6. Conclusions

The consumers' concern about the quality of the products nowadays requires the industrial products not only to be attractive in colour, aroma, taste and texture but also nutritious, and safe. As a result, food industry is researching new production processes which allow to deliver higher quality products. The purpose of this research is to demonstrate that the employment of new technologies in food processing can lead to higher quality products. In particular the milling process for the production of almond fatty oils emulsions has been investigated. Such production process well fits to the purpose of the research since it is carried out on crude raw almonds with a high content of proteins and fatty acids which however are not conserved in the final product. The traditional production process is generally carried out at high temperature (80-90°C) in order to inhibit microbiological growth. Currently available methods for the effective elimination or reduction of off-flavours are not compatible with the preparation of highly nutritional foods because they require conditions that cause denaturation of proteins. This research demonstrates that by selecting a suitable raw material with high nutritional content and by applying proper processing technologies, a significant part of the nutritional content of raw materials can be effectively conserved in the final product. Such result is obtained by maintaining the temperature below 50°C throughout the entire production process. Off-flavours generated by lipid oxidation have been inhibited by oxygen-free processing. Experimental results show that it is possible to achieve small particles distribution (5 micron average) by means of a two step cutting and homogenization process. The establishment of an experimental process involving temperature control and oxygen-free conditions allowed to reduce the effects of denaturation and oxidation, recovering 27% of the protein loss and 21% of total lipids. There is also nowadays the trend of ensuring food safety by means of high temperature or high pressure processes, as for example the mandatory pasteurization of raw almonds enforced by the California Almond Board (Federal Register, 2007). The present research relies on preserving the nutritional value during food processing, demanding the assurance of food safety to the employment of selected raw materials and to the implementation of safety monitoring systems throughout the entire food chain. Additional research towards the statistical optimization of process parameters and a more detailed analysis of the denaturation phenomena might improve the results obtained. Also nutritional values should be balanced by adding proper additional substances. For example, in the case considered omega 3 fatty acids should be added to balance the significant content of omega 6 fatty acids in the raw material, thus obtaining a better product. Finally, the improvement of organoleptic properties of the product obtained should be assessed in order to depict a complete picture of the problem here analyzed. Organoleptic quality

assessment of processed foods involves the preliminary definition of a sensorial profile described by specific criteria such as taste, aroma, texture, and the selection of pertinent indicators and testing procedures for each criteria. Such indicators are generally qualitative, requiring sensory analysis carried out by panel-tests for their evaluation, which is out of the scope of this paper. The development of a new process is in fact the result of an optimization approach based on objective indicators, such as those proposed in the present study, and a subjective parameters which require qualitative evaluation criteria and methods. It is premature to address the latter topic until a reference sensory profile is individuated for the product considered.

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