Graduate School in Molecular Sciences and Plant, Food and Environmental Biotechnology

UNIVERSITÀ DEGLI STUDI DI MILANO

FACOLTÀ DI SCIENZE AGRARIE E ALIMENTARI

PROCESS INNOVATIONS FOR QUALITY FOOD PRODUCTION IN A SHORT SUPPLY CHAIN CONTEXT USING CONVENTIONAL AND ALTERNATIVE ENERGY SOURCES

Marcello Italo della Campa

XXVI Ciclo

Tutor: Prof. S. Iametti
Co tutor: Dr. T.M.P. Cattaneo
Coordiantor: Prof. M.G. Fortina

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Riassunto

La sopravvivenza delle numerose imprese piccole e molto piccole che caratterizzano il contesto agricolo italiano, dipende dalla loro capacità di differenziare la loro produzione e dalla propensione al rivolgersi verso nuove forme di reddito, come i mercati contadini e il commercio in rete. Certamente la Legge Finanziaria del 2007 ha dato un vigoroso impulso a tutto ciò che gravita intorno alla filiera corta in ambito agroalimentare. Questo tipo di orientamento tuttavia presuppone dei cambiamenti strutturali nelle aziende. Una tale metamorfosi riguarda in primo piano anche la dotazione impiantistica e la capacità di utilizzarla. Da uno studio condotto dal progetto MIERI, il mercato di impianti per la produzione industriale di cibo presenta una scarsissima offerta di apparecchiature di piccole dimensioni. Esiste quindi una profonda mancanza di soluzioni tecnologiche compatibili con le esigenze delle aziende che vorrebbero entrare nei promettenti circuiti commerciali legati alla circolazione di alimenti trasformati in un contesto di filiera corta.

Inoltre la moderna industria è costantemente alla ricerca di nuovi percorsi finalizzati alla nascita di prodotti innovativi. Quindi, sempre più spesso, l'attenzione degli sviluppatori di nuovi prodotti è rivolta alla loro naturalità e salubrità. In un tale ambito i piccoli produttori sono svantaggiati per molte ragioni, in special modo per problemi di sicurezza alimentare e da mancanza di tecnologia

Recentemente la ricerca alimentare relativa agli impianti sta lavorando nella direzione dei piccoli produttori artigianali. È infatti ora possibile avere accesso a soluzioni impiantistiche capaci di combinare: la qualità e la sicurezza alimentare, tipici della grande industria con l'altissima qualità delle materie prime che caratterizza molti produttori artigianali, inoltre risolvendo molti dei problemi legati a sicurezza, tecnologia, logistica e, accessibilità tipici di molti piccoli produttori.

Negli ultimi anni l'attenzione all'uso di energie alternative e alla riduzione di scarti e sprechi, volti nella direzione di una produzione più sostenibile, è diventato un tema globale. Le piccole e piccolissime produzioni industriali hanno le caratteristiche, diversamente dalla grande industria, per poter inserire nei loro cicli produttivi l'impiego di energie rinnovabili e di operare un'attenta politica di riduzione di scarti e sprechi.

Questo studio si è occupato in primo luogo di sviluppare una serie di prodotti alimentari tenendo conto di quanto detto finora e cioè: legame col territorio, tradizioni locali, qualità e sicurezza alimentare, impiego di energie alternative. In secondo luogo lo studio tratta la verifica da un punto di vista biochimico e sensoriale della qualità degli alimenti sviluppati. In ultima analisi viene fatto un bilancio energetico relativo alle produzioni che consentono l'uso di energie alternative.

Durante il presente lavoro di dottorato sono stati sviluppati 14 prodotti: 4 tipi di marmellata, 1 dolcificante multifunzionale, 3 prodotti essiccati, 5 tipi di yogurt, 1 tipo di caramella di frutta. Per il loro sviluppo sono stati impiegati due impianti prototipo: una linea di trasformazione polifunzionale miniaturizzata ed un essiccatore ad energia solare. Per ogni prodotto sviluppato è stato seguito il comportamento di uno o più marker di processo (molecole termicamente instabili considerate importanti da un punto di vista nutrizionale e che sono naturalmente presenti nelle materie prime).

Nella maggior parte dei prodotti sono stati ottenuti buoni risultati con i test sensoriali ed è stata osservata una considerevole ritenzione dei marker di processo, confermando quindi la buona qualità dei prodotti sviluppati. Il livello di ritenzione dei marker varia in funzione del prodotto specifico e dei trattamenti tecnologici utilizzati. Anche l'analisi sensoriale, dove eseguita, ha dato risultati che rispecchiano un alto gradimento dei prodotti testati.

Le prove realizzate col fine di valutare l'uso di energie alternative per la produzione di alimenti o semilavorati hanno dato risultati nettamente positivi, nonostante, in alcuni casi, le condizioni sperimentali e impiantistiche si siano rilevate limitanti.

Abstract

The survival of many small and very small businesses that characterize the Italian agricultural context, depends on their ability to differentiate their products and the propensity to turn toward new forms of income, such as farmers' markets and network trade. Certainly the Italy's Finance Act of 2007 gave a powerful boost to everything that revolves around the short supply chain in agro-food sector. Such a change, however, requires structural changes in companies indeed. The consequent metamorphosis also relates with the company technological facilities and the ability to use it. A study conducted by the project MIERI, shows that the equipment's market for food industrial production offers a very narrow range of small size equipments. Enterprises who would like to enter the promising markets connected to the processed food trade in the context of a short chain cannot easily find, on the facilities market, technological solutions consistent with their needs.

Modern food industry is constantly looking for new paths in order to obtain original products. More and more often the attention during their development is focused on their healthiness and naturalness. In this context small producers are penalized due to several reasons, mostly depending on food safety and a lack of technology.

Recently, research on small food processing plants is giving new tools to small and craft producers. It is now possible to combine food safety and quality, typical of big factory, with high quality raw materials, typical at many craft producer, thus solving many typical problems of craft producers, related to food security, technology, logistics and accessibility.

In recent years the focus on the implementation of alternative energy sources use and the reduction of scrap and waste, aimed in the direction of a more sustainable production, has become a global issue. Unlike big industry, small and very small producers own the characteristics to include in their production cycles both the use of renewable energy and the option to operate careful policies aimed to a real reduction of scrap and waste.

This study focused firstly on developing a number of food products, taking into account the above, namely: link with the territory, local traditions, food quality and safety, use of alternative energy. Secondly, the study focused on the verification both by a biochemical and a sensory point of view of the developed foods quality. As final analysis is carried out an energy balance concerning the productions that allow the use of alternative energies.

During this study were developed 14 products: 4 types of marmalade, 1 multifunctional sugar substitute, 3 dried products, 5 types of yogurt, 1 type of fruit candy. Their study and production took place by means of two prototype systems: a miniaturized processing line and a solar drier system. For each product type was followed the behavior of one or more process biochemical markers (thermally unstable molecules considered important from the nutritional point of view).

In most of the products developed were obtained good results in sensory tests and was observed a considerable retention of the quality processing markers thus both confirming the good quality of the products developed. The markers retention varies according to the specific product and the technological treatments used. Moreover, sensory analysis, gave results that reflect a high overall liking of the products tested (where performed).

The trials performed with the aim to evaluate the use of alternative energy sources for the production of foods or semi-finished products gave clearly positive results, despite, in some cases, the experimental and plant conditions have been observed as limiting.

0 PREFACE

The interaction among human, nutrition, food production and the environment is a strongly recurring theme at the global level. This is evidenced by the significant actions taken by the European Union regarding the funding of research and information in health, agriculture and food production. In facts, three out of nine topics of the "Seventh Framework Program on Scientific Research" are concerning the issues mentioned above; in addition, the Regulation (EC) no. 814/2000 and its subsequent amendments are related to information measures relating to the common agricultural policies, and many others actions in the same field. At the national level, where the survival of many small and very small businesses is recently exposed to a risk, there is still much work to be done. In this direction, the Ministerial Decree published in the Official Gazette on 29-12-2007 (Italian law, 2007), in force from 01-01-2008, *de facto*, has instituted in Italy the discipline regarding the farmers' markets. It defines: the market boundaries, the entities admitted to the sale, the administrative discipline, the product' sale rules.

Even though Italy arrives to the farmer's market legitimateness much later than other European countries, this circumstance opens the doors to the agricultural short supply chain market, a very important economic space in which co-exist important themes such as food quality, sustainability (applied to production, logistics and sale), organic production, use of renewable energy, typicity, PGI products, reduction of waste and scraps, etc. This market opportunity regards both fresh and processed foods. Managing these two macro-groups involves a law regulation and a set of facilities that can be significantly different. This study regards only the processed foods macro-group.

If, in general, educational or communication initiatives oriented to consumer follow a path free from technological or economical barriers, this is not always true in product innovation, where there are constraints (especially economical and cultural) limiting the small businesses. The big food industry has the potential to obtain the necessary human resources and key information in the food quality field, while it is not the same for small and very small producers of processed foods. In fact, the latter often do not have (and often can not afford it) the necessary technical and scientific knowledge.

On the one hand, the large food industry has the knowledge and the equipments that allow to obtain high quality products, in spite of the raw materials used that, in most cases, do not meet specific requirements of excellence (for reasons mainly due to logistics and supplying). This high quality level can be achieved using technologies that are able to protect, during the processing, peculiar compounds (constituents with high nutritional value but often heat-labile) that are naturally contained in some kinds of raw materials.

On the other hand, the small and very small producers often process excellent raw materials (for genetic trait, cultivation technique, geographic conditions, etc.), through too drastic technologies, obtaining highly degraded products. In many cases the degradation level is so high as to run the risk of losing part or entirely the recognizability of the raw material used. Ironically, often consumers identify the typical sensory attributes caused by a strong chemical and physical degradation as positive factors. For many types of products (especially fruit preserves) the common association "homemade = nutritionally rich = healthy" has no parallel in reality. Unfortunately, this belief is widespread and deeply rooted in the average consumer.

Recently, research on small food processing plants is giving new tools to small and craft producers (Maestrelli A. and Della Campa M., 2011). It is now possible to combine food safety and quality, typical of big factory, with high quality raw materials, typical at many craft producer, thus solving many typical problems of craft producers, related to food security, technology, logistics and accessibility.

The present work is aimed to give a scientific but also practical answer to some of the many questions regarding this very complex technical, social, economic, environmental context.

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1 STATE OF THE ART

1.1 Introduction

According to the latest ISTAT surveys (ISTAT, 2013), the situation and the outlook for many of the small and medium-sized Italian farms, are not the best and a high number of them will probably close in the short term, in line with the situation in other European countries. Their survival chance will depend on their ability to access, but also to create alternative markets, adopting criteria of multifunctionality: in particular through the various forms of "short chain" such as direct sales in local markets and network trade (Boschetti M., 2009).

Small Italian agricultural enterprises who decided to catch the wave related to short supply chain after 2008, had to face many obstacles to overcome, two major of which are: the lack of technical and scientific knowledge; the lack of a market of small scale professional processing plants (MIERI project, 2009). The latter has assumed major importance since processing is the key feature in this field, especially when the intention is to produce quality foods.

1.1.1 Thoughts about the definition of quality

The meaning of the word "quality" is often unclear and poorly defined. In general quality is the ability of a product to meet certain specifications required or expected. It may be related to different areas: for instance, one of the most general concept of quality represents, for a consumer, the satisfaction degree that a specific product achieves, with respect to expectations. In this case the concept of quality appears to be entirely subjective. One possible way (among many others) to improve the representation of quality, can be splitting its significance in different concepts. In a food technology context, quality could be usefully referred to three specific types of ideas:

1) sensory quality
2) nutritional quality
3) product regulation quality.

1) This represents how much the individual attributes perceived from a given product deviate from its typical properties and/or expectations (such as ripeness, freshness, appearance, texture, aroma, flavor, and others). This attitude characterizes the specific product, be it fresh or processed. The greater the similarity of a given product's sensory attributes with those of the reference product and the greater its sensory quality perceived.
2) It takes a different meaning if it refers to raw materials (fresh) or processed products. Depending on this, it may indicate nutritional aspects in general or at specific level. In general, the higher the nutritional quality of a given fresh product, the higher the amount of certain chemical compounds considered of high nutritional value that are naturally present in that type of product. At specific level, it is related to the presence of a single compound or to a class of chemical compounds considered of particular importance or value.
   The nutritional quality of a processed product provides information to a specific level and it refers also to:
   - The amount of a given compound or a compound class that is already present in the raw materials; in this case, indicates how much of that specific compound is still present after processing and thus is still measurable in the processed material
   - The amount of a given compound or chemical compounds class, also not necessarily present in the raw materials (or present in a minor amount), whose formation is induced by certain treatments or spontaneous reactions; in this case it indicates the amount of that compound that is present in the processed material.

   Usually these information are used in science or, where appropriate, by industry insiders. In practice it is rare to find commercial products showing on the label what is the quality reference compound. More commonly the expression "Product of high nutritional quality" informs that the product contains substances considered valuable for their high nutritional

value, or other reasons. This give no information about whether they derive from the use of technical measures able to protect the raw materials, or if the "worthy" compounds presence derives from treatments capable of inducing their formation.
The research regarding the interaction between diet and health has led in recent years to focus on the nutritional aspects, especially for fruit and vegetables, as it is well established that their widespread use has a positive impact on human health because of the presence of phytonutrients (Bazzano et al., 2002).

3) It is one or more quantitative parameters that allow to classify the products in "categories" referable to clearly defined attributes (usually easy to measure) such as Brix, size, weight, colour, etc. These attributes are often law enforcement linked to the marketing of those products.

Within this thesis the quality of a product is referred to the similarity degree of the finished product compared with the raw materials used to obtain it. This similarity involves both sensory (colour, odour, taste, etc.) and biochemical characteristics. For the first, rigorous and/or informal sensory tests were performed. For the second, in this dissertation, is usually taken into account the amount of certain molecules naturally present in the raw materials which final content in the finished product vary depending on the production technique used. Examples of such molecules (which is becoming a common topic among consumers), are phytochemicals, compounds considered important for human health.
Usually a product can be defined as of "high quality" if shows a high content of one ore more biochemical compounds considered as quality markers. When the quality attributes are imbedded in a product's commercial denomination, the regulation often defines specifically the minimum concentration of such compounds used as quality markers, for each single product. For instance, in Italy a cow milk can be sold under the denomination "high quality milk" only if (in addition to other restrictions) the content of undenatured soluble seroproteins is greater than 15.50% of the total protein (Italian law, 1989).
However, the interpretation of the quality of a food product from a biochemistry - analytical point of view is far from simple and the debate related to this topic is very controversial within the scientific community. In fact, the quality markers analysis is normally performed in vitro rather than in vivo, due to obvious reasons of cost and research complexity. So most of the available data are the result of a simplified simulation of mechanisms that are actually much more complexes. Moreover, the scientific community continues to debate the subjects about real bioavailability, actual action mechanism and the action synergies role of the substances considered to be bioactive.

1.1.2 Biochemical justification of short supply chain in agro-food

Many fresh fruits and vegetables have been found to contain natural antioxidants, mainly phenolic compounds such as ferulic acid, catechins, as well as ascorbic acid and many others (Long L. H. et al, 1999).
An important class of such compounds are phenolic antioxidant compounds: their nutritional importance is due to their ability to act as free radical scavenger (Burns et al., 2000; Sanchez - Moreno et al., 1999).
The time interval between harvesting and processing is a critical point for several products. If for some species the chemical/physical consequences of the elapsed time are obvious, this may not be true for others. Moreover, in many cases, the changes are subtle and may affect only the nutritional value of that given product.
In this respect, it has been shown that many important compounds (from a nutritional point of view) decrease quickly after the harvesting. In the following examples is reported the relationship existing between the amount of some antioxidant compounds naturally contained in different common products and the time elapsed after harvesting and analyzing.

Value from INRAN	Average value from CRA_IAA 2005-2007	5 hours after harvesting
59	85	137

Table 1. Ascorbic acid content in pigmented cauliflower *(Brassica oleracea* L., var Botrytis cv Romanesco), mg/100g fp.

Value from INRAN	Average value from CRA_IAA 2007-2008	6 hours after harvesting
166	186	210

Table 2. Ascorbic acid content in sweet pepper (*Capsicum annuum* L., several cv), mg/100g fp.

Minimum amount requie by processing factories	24 hours after harvesting
100	160

Table 3. Total anthocyanins in red orange juice (*Citrus aurantium* L., cv Moro), mg/l.

Average value in literature (Hanson et al., JFCA 2006)	Inmediatelly after harvest (Mennella et al., JAFC 2010)
1000	1930

Table 4. Total polyphenol index of eggplant (*Solanum melongena* L., several cv), mg/100g dp.

The correlation between a diet rich in phenolic compounds and a low incidence of degenerative disorders which are probably caused by an excess of free radicals (Bazzano et al., 2002; Flood et al., 2002) remarks the importance of a high retention of such molecules in marketed fresh or processed foods. In particular for those obtained by raw material that naturally show a high content of phenolic compounds and other molecules considered nutritionally important.

1.1.3 Prototype plants

Two prototype plants have been used for the product development: a miniaturized, polyvalent processing line and a solar drying system.

1.1.3.1 miniaturized, polyvalent processing line

The processing line is a pilot plant consisting of a sequence of miniaturized equipment, able to process small quantities of product. The peculiar features of this equipment allows to obtain many kind of products: F&V preserves (acid and non acid), sauces, "paté" and even dairy products. The steps are: a) the washing container; b) pulp /refiner (a vertical cylinder lined with a sieve of different hole diameter: 0.5 ÷ 5 mm) that separates the pulp from seed, skin, stalk; c) concentration "boule", the equipment core, in which the product is concentrated and/or cooked in different, adjustable conditions.

Fig. 1. The multi functional processing line and its components.

It can be used as open container (Fig. 2), closed container at ambient pressure, closed container under vacuum. The boule can contain a maximum volume of 26 l of finished product. A set of electric resistors heats the process water, stored in a tank. The heat is carried by a process fluid (softened water), which circulates through the gaps present in the heating surfaces of the plant; d) pasteurization of product is carried out in the same equipment as for washing, by an electric resistor integrated in the washing cylinder; e) sterilizer, for non acid preserves (Della Campa M., 2011).

Fig. 2. The concentration boule in "open container" configuration.

1.1.3.2 Solar drying system

The drier prototype is a very simple but efficient machine (fig. 4, 5). It consists in an alveolar polycarbonate box. At its top is located the air heating chamber. Directly under the transparent roof there is a steel wool layer which is heated by sun radiation. In addition to heating, it slows the air speed passing through it, increasing the heat transfer. The air flow enters the chamber through fissures on one side, passes through the heating chamber, laps the product on the trays and goes out through the floor, pushed by 2 fans (Fig. 3). The power supply is generated by a 12 V 50 Ah battery, charged by a photovoltaic solar panel located nearby the drier (Della Campa et al, 2010).
A metallic net is placed At the air inlet to prevent the entrance of insects or animals.

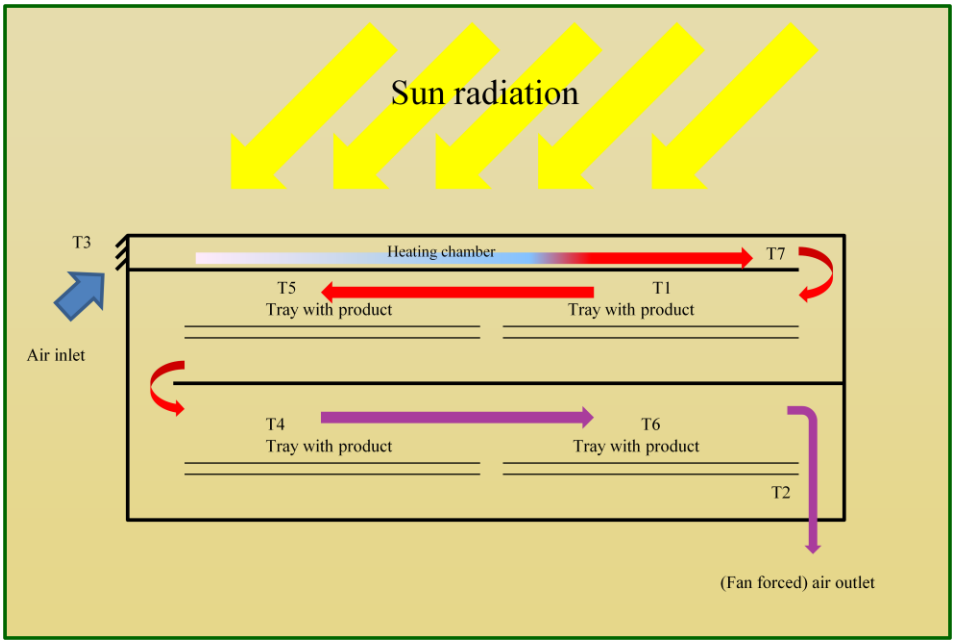

Fig. 3. Scheme of the air flows inside the solar drier and positions of the thermal probes which temperatures values are shown in fig. 4.

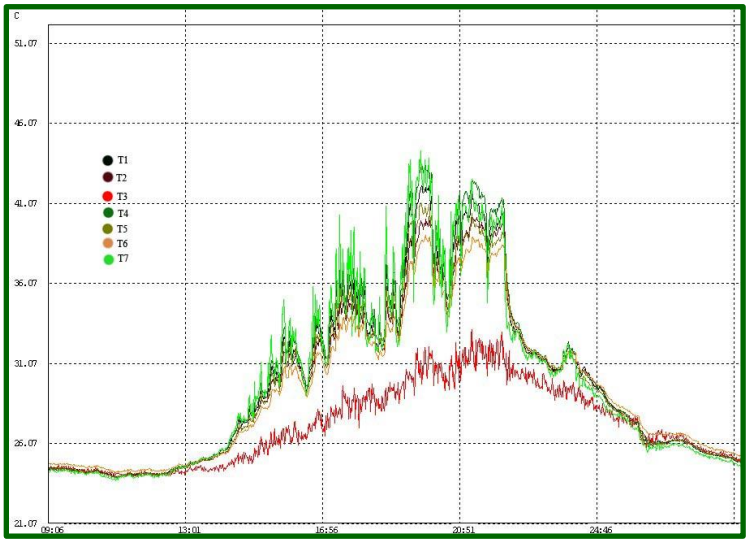

Fig. 4. Example of solar drier performance during a sunny/cloudy summer day at Milan's latitude. Numbers refer to the probes located as shown in fig. 3

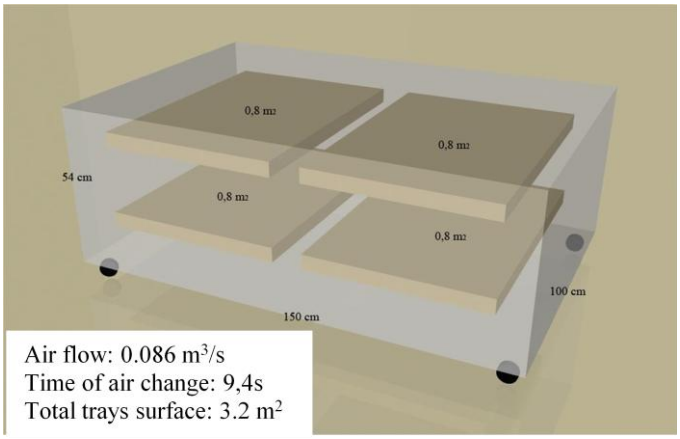

Fig. 5. Solar drier technical characteristics.

Fig. 6. A view of the solar drier system working at CRA-ACM in Acireale (CT).

1.1.4 Use of renewable energy sources

Regarding a general approach to the use of alternative energy in food production, it is possible to identify two main situations: on the one hand, the big industry can not implement its use -even partial- for reasons generally related to the large product volume handled and the processing timing; on the other hand, the small-scale production, for the opposite reasons, can, or rather they could use it.

Within this work three different equipments capable to catch the energy from sun radiation and provide it to other devices were used: a sun dryer system, able to heat an air flow; photovoltaic panels, able to produce an air flow (by means of a an electric system and a fan); sun thermal panels, able to heat the process water used by the miniaturized multi function processing line.

1.1.5 Products developed

One of the project's milestone has been the development of food products obtained in accordance with certain conditions:

- the product is of "high quality" from a nutritional and sensory point of view
- the process is a part or entirely represent an agro-food short supply chain
- the process can be adopted (by means of particular equipments) in an artisanal dimension
- the raw materials have a strong link with the territory (from an agricultural and traditional point of view)
- the process can be partially (or even totally) powered by the use of renewable energy sources.

The products which have been developed are 14 and they can be grouped into three different areas, according to the characteristics of the production plant and methods employed to produce them:

- processing line: Bitter orange marmalade, Sanguinello orange marmalade type 1, Sanguinello orange marmalade type 2, Tarocco dal muso orange marmalade, Multi-Purpose Industrial Sugar Substitute, compact and creamy plane Yogurt
- Solar drying system: Tarocco orange and Femminello Zagara Bianca lemon dried slices, Dried Peperone di Senise
- combined techniques: Apple candies, Flavoured yogurts (3 flavours).

1.1.6 Analytical approach overview

Both the choice of which products were suitable to carry on developing, and their analytical approach have been considered intertwined. During this decisional process have been taken into account many aspects. In addition to the conditions exposed in § 1.1.5, have been considered the following aspects: the equipment's features, the product's availability (from an agricultural point of view and its compatibility with the project timetable), the amount of some bioactive compounds typically present in the specific product. The latter condition has a special relevance in the hypothesis that a high amount of bioactive compound in the raw materials can bring several advantages. The higher their concentration: 1) the easier is their evaluation; 2) the wider is the degradation range monitored; 3) (using protective processing techniques) the higher is the probability to obtain products with high bioactive compounds concentration, thus characterized by a high nutritional value.

During processing often occur tissue decompartimentalisation causing: blending of cellular fluids (rich in enzymes and substrates) and exposure to atmospheric oxygen, at which is added a high temperature and a natural low pH value. In this complex reaction environment, many enzymatic and non enzymatic oxidation reaction can occur.

Many of the (non enzymatic) oxidation reactions (related to vegetal products processing or senescence) occurring in fresh products, are carried out by free radicals. Their activity may be slowed by the action of unstable compounds which are characterized by a strong tendency to oxidation.

Some phytochemicals are very unstable and can act as antioxidants. In literature is present a series of studies (Rossi et al., 2003; Lo Scalzo et al., 2004) in which is studied the phytochemicals content behavior using controlled temperature from the beginning of fruit and vegetables processing.

The key to maintaining product a high retention of these compounds is temperature control: during processing, a compromise usually must be made between food safety (by pasteurization or sterilization) and the intrinsic quality of the product.

These are some of the most important reasons why 7 out of 15 methods (see table 5) are related to antioxidant activity. Their joint use has been evaluated as the right approach in order to discriminate among different situations otherwise difficult to be detected. In facts, degradation reactions which take place in vegetal or animal tissue (a very complex biological matrix) can lead to the neo-

formation of substances characterized by new additional antioxidant activity. Therefore, in addition to the conventional analytical quantification of bioactive compounds (ascorbic acid, carotenoids, hydroxycinnamates, quercitins, anthocyanins, total phenols content), has been evaluated the *in-vitro* antioxidant activity through different methods.
The electronic paramagnetic resonance (EPR) is a very effective tool able to measure the activity of stable synthetic free radicals. Depending on the radical used, it's possible to quantify different groups of compounds acting as antioxidant.
It is also important to stress that in this work no research has been carried out on the analytical methods used. Analysis has been used as a tool for the comparison among samples. Nevertheless, the choice made among the analytical methods has been a relevant topic in this research, according to the reasons mentioned above.

	Analysis \ ***Product***	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**	**I**	**J**
1	**Ascorbic acid**	■	■					■	■		
2	**Carotenoids content**								■		
3	**Class phenols content**	■	■			■		■	■		
4	**Colour analysis**									■	
5	**EPR probe Fremy' salt**		■	■				■	■		
6	**EPR probe Tempo**		■	■				■	■		
7	**Folin Ciocalteu index**	■	■	■		■		■	■		
8	**Karl Fisher analysis**							■			
9	**Antioxidant activity by Photochem**							■	■		
10	**RSR**		■	■							
11	**Sensory analysis**		■	■	■		■	■	■	■	■
12	**Sugar composition**					■					
13	**Texture analysis**									■	
14	**Titrable acidity**		■	■							
15	**Water activity**					■		■	■		

Table 5. The analytical methods used in this thesis and which of them has been used with each product. Legenda: (A) Bitter orange marmalade, (B) Sanguinello orange marmalade type 1, (C) Sanguinello orange marmalade type 2, (D) Tarocco dal muso orange marmalade, (E) Multi-Purpose Industrial Sugar Substitute, (F) trials of Yogurt production, (G) Tarocco orange and Femminello Zagara Bianca lemon dried slices, (H) Dried Peperone di Senise, (I) Apple candies, (J) Flavoured yogurts

Product	**Analytical method used**
1	HPLC, inverse phase, UV detector
2	Spectrophotometric method
3	UV VIS scan
4	By a D65 illuminant/10° observer reflaction colorimeter
5	Fremy' Salt 2 mM in PBS 0,1M
6	radical Tempo 0,1 mM in methanol calibration with Amadori reagent
7	Folin Ciocalteu official method
8	Karl Fisher official method
9	Photochem® antioxidant analyzer, by Analytik Jena
10	Official AOAC method, 1980

11	Napping ® test / triangle test / questionnaire / informal session
12	HPLC and refractometry
13	Texture analyzer fitted with a 5 kg cell and a Warner - Blatzer blade
14	Official AOAC method, 1980
15	By a dew point water activity meter

For any details and references, see Materials and Methods paragraphs.
Statistical elaboration were performed by ANOVA, using Statgraphics Plus 5.0 (Manugistics Inc, Rockville, USA).

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2 AIMS OF THE STUDY

The aims of this doctoral work were to develop a set of foods (and semifinished products) in order to investigate the possibility to obtain quality production at artisanal dimension in an agro-food short supply chain context and verify and quantify the possibility to use renewable energy sources during their production.
The targets have been reached through the development of the following topics:

- Identification of the most suitable raw materials and the "kinds" of products to be developed
- Develop proper production processes
- Verification of the product's final quality level
- Set up of trials using renewable sources
- Evaluation of the amount of renewable energy used in some processing cycles used as reference models.

3 RESULTS AND DISCUSSION

3.1 Group 1: Products obtained using a miniaturized, polyvalent processing line

The products obtained by means of the multifunctional processing line belong to two very different groups: fruit derivatives and milk derivatives. The differences are both in raw materials and in production processes. They were chosen specifically for their diversity.
The firsts products belonging to this group are acid preserves of fruit origin and have all been obtained through evaporation, under different conditions and reaching different product concentrations, depending on the specific product. Were also adopted some pretreatments for the products that required it. The majority of the raw materials (four out on five) are PGI products, to be consistent with the product's geographical link that was set in § 1.1.5. In addition, particular attention was used with the aim to minimize the production waste amount: in particular, all citrus derivatives here studied are obtained by processing the whole organic fruits.
Yogurt is a good example of a dairy product for which is possible to realize the entire production cycle in an artisanal context.

3.1.1 Bitter orange marmalade

3.1.1.1 Raw materials description and peculiarity

Although *Citrus aurantium*, L. is the most common rootstock used in citriculture, its fruit is rare in the market because of its low and local production. It's important to note that the fruit production is almost totally absorbed by the pharmaceutical and food industry. It is important to stress that this orange is not edible in the fresh state. This fruit, known as bitter orange, Seville orange, sour orange, etc. is used in food industry to produce "bitter orange marmalade", or simply "marmalade", a wide world spread preserve. Moreover no commercial cv were ever developed (early, late, seedless, etc.), hence it is present on the market only during January, in a very narrow ripening period.
Citrus aurantium, L.shows a natural high content in bioactive compounds (vitamin C, polyphenols, carotenoids, etc. (Cutuli and al., 1985 b) thus it can be potentially used in order to obtain an high quality product (according to § 1.1.1).
In addition to industrial product, it is possible to find on the market handicraft bitter orange marmalade, but its quality is, in most cases, very low due to the lack of technology that commonly characterize small and craft producers.

3.1.1.2 Blanching and non enzymatic browning

Since a temperature of 43°C can be considered as optimal for oxidative enzyme action (Zhou et al., 1993; Valero et al., 1988), during the bitter orange marmalade development was hypothesized that for the samples concentrated under vacuum (evaporation temperature ≈ 43°C), the time between pulp separation and thermal stabilization is a quality critical point
Blanching, as a pretreatment, can be an effective tool when protection from enzyme's degradative activity is needed during the first processing steps. In this case the tissue decompartimentalisation due to the pulp refiner action used to separate pulp from solids (skins and pips) causes undesirable reactions, responsable of a sensory and biochemical product depletion. One of the most important reaction takes place by the action of polyphenoloxidase (PPO). In vegetal cells the enzyme is localized in the thylakoid membrane of chloroplasts (Nicolas et al., 1994), as well as in mitochondria and exceptionally at the level of peroxisomes. When the cell structure is broken, enzymes and phenol compounds (normally segregated in vacuoles), interact together and with oxygen as well. The enzyme catalyzes two distinct reactions involved in the oxidation of phenolic compounds; in both reactions the molecular oxygen is used as a co-substrate:

– hydroxylation of o-monophenols to diphenols

– oxidation of diphenols to o-quinones

The quinone compounds are unstable and susceptible to new condensation reactions with phenolic compounds, flavonoids, amino acids and proteins, able to generate pigments whose color varies from yellow to brown (Rapeanu et al., 2006).
The catalytic activity of the PPO is influenced by environmental parameters such as temperature and pH (Yoruk & Marshall, 2003). It is known as high temperature denatures and destroys the delicate enzyme structure (Segel, 1976).

3.1.1.3 Research goals

The purpose of this work is to study an artisan production process for the preparation of bitter orange marmalade, possibly preserving as much as possible the raw material nutritional value. The product had to be prepared in a craft dimension embedded in a context of a short chain and using a miniaturized system. It was also rated the behaviour of bitter orange after blanching and vacuum concentration (and cross conditions) during marmalade processing.

3.1.1.4 Materials and methods

3.1.1.4.1 Production method

One hundred kg of organic *Citrus aurantium*, L. fruits were collected by a Sicilian producer. The fruits (obtained by organic cultivation), after the random splitting into five groups (corresponding to the five different processing), were immediately processed according to the production diagram (Fig. 1), using a prototype miniaturized plant (Della Campa, 2011).
After cutting, SCPA and SCSV orange segments have been blanched by immersion in boiling water for 3 min and then immerged in a water-ice mixture for 10 min, (Lo Scalzo et al., 2004). Later, all oranges segments were subjected to a debittering treatment by immersion in cold water for 24 hours. The next step have been the concentration. During the concentration step, the boiling temperature of the mass (under vacuum conditions), was 43°C±2°C. On the contrary, during evaporation at ambient pressure, the boiling temperature of the mass was 102±1°C. The first 300 ml of rich in fragrance condensed vapour, have been collected at the beginning of vacuum concentration.
Once reached 66±2° Brix, the collected fragrance condensed vapour has been added to the product mass and then, the product has been bottled in glass jars (volume: 390 ml), sealed with a proper cup and thermally stabilized by immersion in boiling water. The thermal treatment chart is reported in fig. 8 and production scheme in diagram 1.

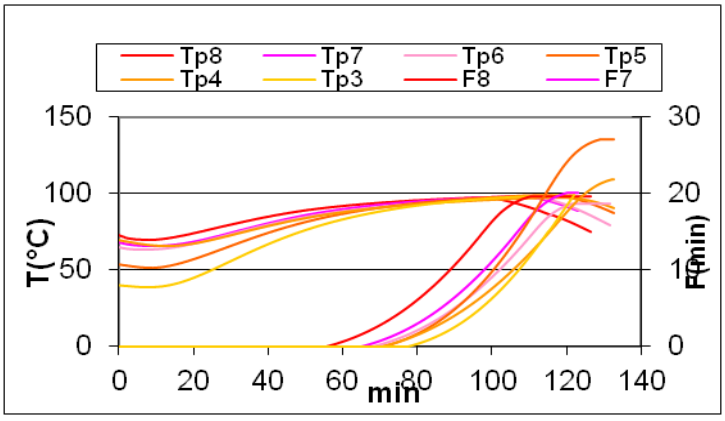

Fig. 8. Bitter orange thermal treatment chart. Different lines correspond to different probes locate in the core product (F3, Tp3) and in different position in the pasteurizing container.

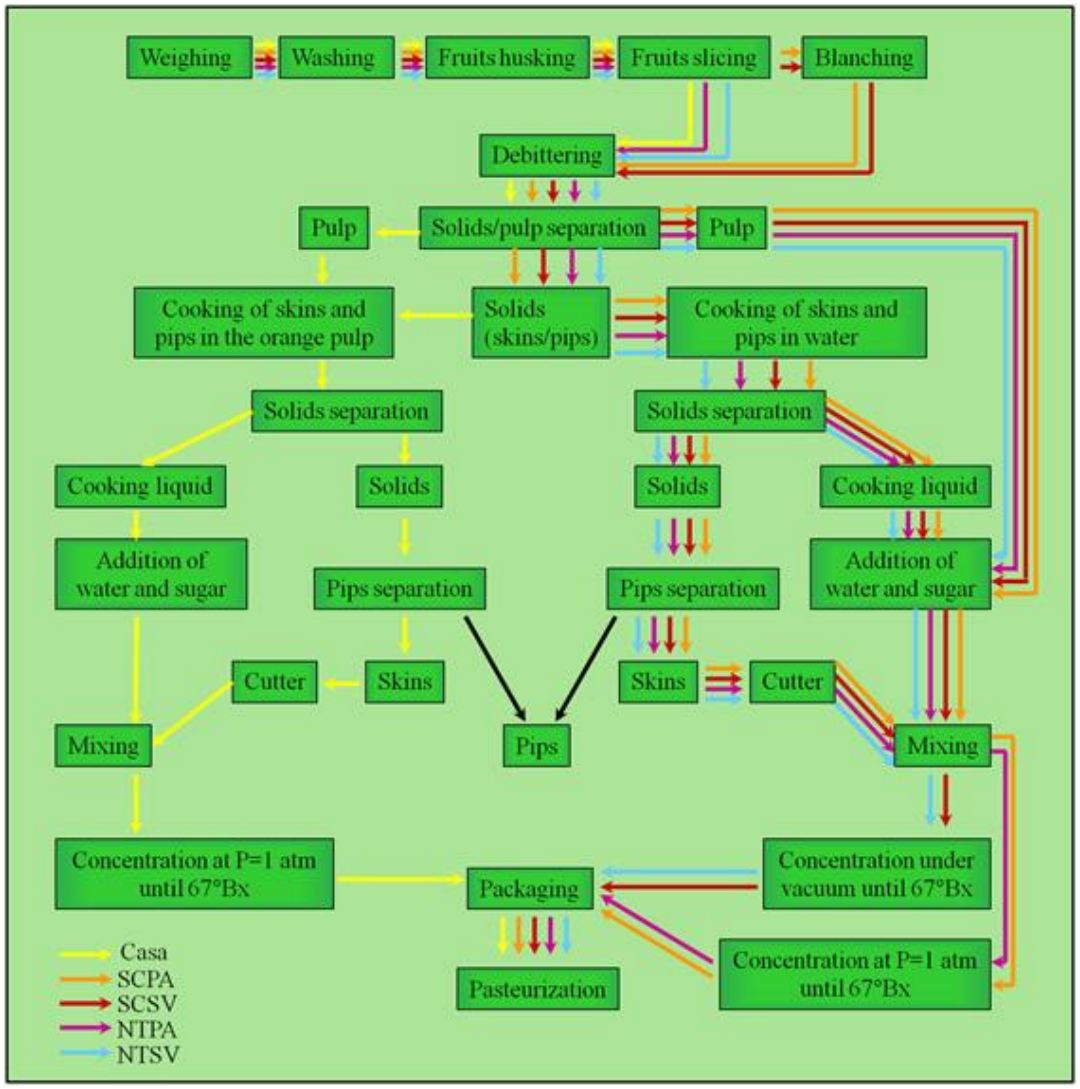

Diagram 1. Bitter orange marmalade production scheme. The different colours of the arrows indicates the technological path of every thesis, subjected to different treatments or conditions.

An explicative video of the process (sample CASA) is visible on the world wide web at the address: http://www.youtube.com/watch?v=IY16MoKAjyI.

3.1.1.4.2 Product description

The same ingredients (in the same proportions) were processed within five different production cycles obtaining the following thesis:

Fig. 6. A view of bitter orange marmalade samples.

- Casa: a home-similar product; only for this thesis the skins have been cooked in the orange pulp, for all the others it occurred separately, in boiling water; concentrated at ambient pressure
- NTPA: concentrated at ambient pressure
- NTSV: concentrated under vacuum
- SCPA: orange segments with skin have been blanched; concentrated at ambient pressure
- SCSV: orange segments with skin have been blanched; concentrated under vacuum

	%	Sd
Orange pulp	17,95	1,15
Orange skin	18,02	1,94
Lemon juice	3,55	0,16
Sucrose	60,47	2,64

Tab. 6. bitter orange marmalade average initial composition.

3.1.1.4.3 Analytical methods

In this work, home-similar samples (CASA) and samples obtained by the same raw material and composition (varying the technology) were compared. NTSV and SCSV samples were exposed to high temperature only during the thermal stabilization treatment and the blanching pre-treatment (samples SCSV).

Ascorbic acid content was measured in according to Picchi et al. (2012) as a first heat treatment marker. The following modifications were introduced in the sample preparation step: 2g of marmalade were extracted with 4 ml of 6% metaphosphoric acid (at 4°C) and 4 ml of water (at 4°C), homogenized and centrifuged at 9,000 rpm for 15 min at 4°C, and immediately analyzed.

1 g for each sample were extracted in 9 ml of ethanol, HCL0,02N 1:1 solution, mixed with a Vortex equipment for 2 min, than centrifuged al 10000 rpm for 10 min. The supernatant were stored at -80°C for further analysis. Total polyphenols index has been evaluated by the Folin-Ciocalteu reaction, as described in Singleton and Rossi (1965) on samples diluted 5 folds v/v.

Class Polyphenols content have been evaluated by spectrophotometric scan in the UV-VIS from 275 nm to 600 nm, as described by Di Stefano and Cravero (1991). An extract solution diluted 10-fold

v/v , has been analyzed as follows: total phenolics at 280 nm, total cinnamates at 325 nm, flavonols at 360 nm. The system was calibrated with (+)catechin at 280 nm, caffeic acid at 325 nm, quercetin at 360 nm.

3.1.1.5 Results and discussion

As expected, according to the different processes applied to the same formulation, five different products were obtained. They showed noticeably differences in colour, consistence (viscosity), taste and smell. Since all comparisons using as reference the fresh product, it is important to take into account that all orange segments were debittered by immersion in cold water for 24h.

Ascorbic acid content showed that the blanched sample had a lower retention than the untreated samples, while the vacuum concentration has always had a positive effect on ascorbic acid retention (Tab. 7). Probably a first loss of ascorbic acid was caused by the primary operations (debittering, separation solids/liquids) and, moreover, leaching may have an important role to explain the ascorbic acid decrease in blanched samples.

	AsA (mg/100g fp)	Sd	% loss
casa	11,97 b	0,69	-78,37
tq pa	15,43 f	0,62	-72,13
tq sv	28,57 d	1,03	-48,39
sc pa	13,09 ab	0,89	-76,35
sc sv	17,57 e	0,62	-68,26
Initial material	55,36 g	14,01	

Tab. 7. Bitter orange marmalade: effect on ascorbic acid retention before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

In this matrix, the Folin Ciocalteu test is sensitive to a double contribution: that of ascorbic acid and that of the other endogenous antioxidant substances, to which are added those derived by processing. The table 8 indicates that the sample with higher index is TQPA. In index's descending order, are the samples: TQSV, SCPA, SCSV. This trend would suggest that during the concentration process, occurs the formation of compounds with antioxidant action, presumably derived from the Maillard reactions. In this case, both a temperature rise and an availability rise of oxygen, should determine the better conditions for the Maillard reactions. At the same time, however, it seems that the blanching process, manifests an inhibitory effect towards the same reaction, given that the samples with the lowest index are the two blanched and the lowest is the SCSV, obtained after blanching and with low oxygen concentration. By tab. 8 one might assume that the blanching inhibiting effect has a greater weight than the stimulating effect due to oxygen, certainly available in high concentration to PA samples, in this case. The sample CASA shows, as expected, a high index value.

The total phenol content (Tab. 9) shows a similar trend, but characterized by higher levels of loss. Cinnammates and quercitines (Tab. 9) show a consistent loss related to all treatments, in particular for the samples concentrated under vacuum.

	Total polyphenols mg/100g fp	sd	loss %	Total phenols mg /100g fp catechin eq	sd	% loss
Casa	428,57 c	12,37	-16,74	200,48 a	2,03	-52,80
Tqpa	500,00 a	38,18	-2,87	228,11 e	4,23	-46,30
Tqsv	391,64 c	3,65	-23,92	101,20 c	16,05	-76,18
Scpa	348,52 b	8,82	-32,29	129,78 ce	17,09	-69,45
Scsv	300,28 e	13,76	-41,67	87,92 bc	4,91	-79,30
Initial material	514,75 a	5,70		424,76 f	34,34	

Tab. 8. Bitter orange marmalade: total polyphenols and total phenols before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

	Cinnamates mg/100g fp caffeic acid eq	sd	% loss	Quercitines (mg/100g fp)	sd	% loss
casa	32,61 e	0,69	-69,68	16,22 c	1,07	-63,85
tqpa	31,57 e	0,59	-70,65	14,49 c	0,39	-67,69
tqsv	24,62 b	1,88	-77,12	11,94 a	1,22	-73,38
scpa	23,99 b	0,89	-77,70	11,59 a	1,17	-74,15
scsv	21,97 b	0,98	-79,57	10,42 a	0,29	-76,77
Initial material	107,58 d	5,80		44,86 b	1,56	

Tab. 9. Bitter orange marmalade total cinnamates and total quercitines before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.1.1.6 Conclusions

The purpose of the research has been achieved since the product obtained has the desired characteristics. The product's different variants obtained show different biochemical and sensory characteristics. In any case, all types obtained possess the typical characteristics of the bitter orange marmalade (a domestic and internationally popular product). The samples concentrated under vacuum present sensory characteristics (colour and odour) much more similar to the starting material They are more associable to industrial products available on the market. Instead, samples obtained at ambient pressure are much more brown coloured (as evidenced also by the biochemistry) and are more associable to artisanal products available on the market. The samples that have the greater retention of ascorbic acid are those obtained under vacuum. The blanching was not useful, probably due to an effect of leaching, accentuated by the debittering process. Informal sensory tests showed a clear preference for the samples obtained under vacuum, due to their bright colour and their high intensity of orange flavour.

3.1.2 Sanguinello orange marmalade type 1

3.1.2.1 Raw materials description and peculiarity

Citrus sinensis, L.var Sanguinello is one of the three PGI citruses named "Arancia rossa di Sicilia" (Red Sicilian orange), grown in Sicily only in a few areas around the cities of Catania, Siracusa and Enna. The culture must be done according to the "Product specification for the PGI Red Orange of

Sicily", regulated by the Circular of the Ministry of Agriculture - Gazette No. 240 of 14 October 1997, which led to the Entry in the "Register of protected designations of origin and protected geographical indications" within the meaning of Reg. 1107/96.
It is characterized by a dark red pigmentation due to its high phenolic compounds content. The pigments are present both on the skin and in the pulp (89 mg/100g fp in the skin, 125 mg/100g fp in the pulp (INRAN, 2011)). This fruit is commonly present on the Italian market from January to April. It is important to note that the fruit pigmentation is the result of both a genetic factor and a climatic condition (Cutuli and al., 1985). In facts, biosynthesis of anthocyanins is a cold-regulated pathway (Crifò et al., 2012). For this reason, in early or late crops pigmentation is not developed and not even, in fruits grown outside the typical area located in the oriental Sicily, a triangle outlined by the cities of Adrano, Scordìa and Paternò, with the exclusion of a small area in California (U.S.A.).

3.1.2.3 Research goals

The aim of study is to obtain by means of a miniaturized plant, a particular kind of citrus derivate, produced in an artisanal scale part of a short supply chain context. The product should have to be a type of marmalade characterized by a high retention of the natural polyphenol compounds present in the raw material, poor in added sugar, made by a particular and typical raw material. The technological comparison has regarded two different conditions of concentration and their consequences on the products obtained.

3.1.2.4 Materials and methods

3.1.2.4.1 Production method

Fifty kg of organic pigmented Sanguinello organic oranges were collected by a Sicilian producer and immediately delivered and processed. The pulp has been added of fresh squeezed lemon juice, sucrose, and concentrated under a vacuum (samples SV) or at ambient pressure (samples PA). Once reached a soluble solids content of 57±0.5°Brix, the mass have been heated until reached 90°C and then hot bottled in glass jars (with a volume of 390 ml).

Fig 9. A view of Sanguinello orange marmalade type 1 samples.

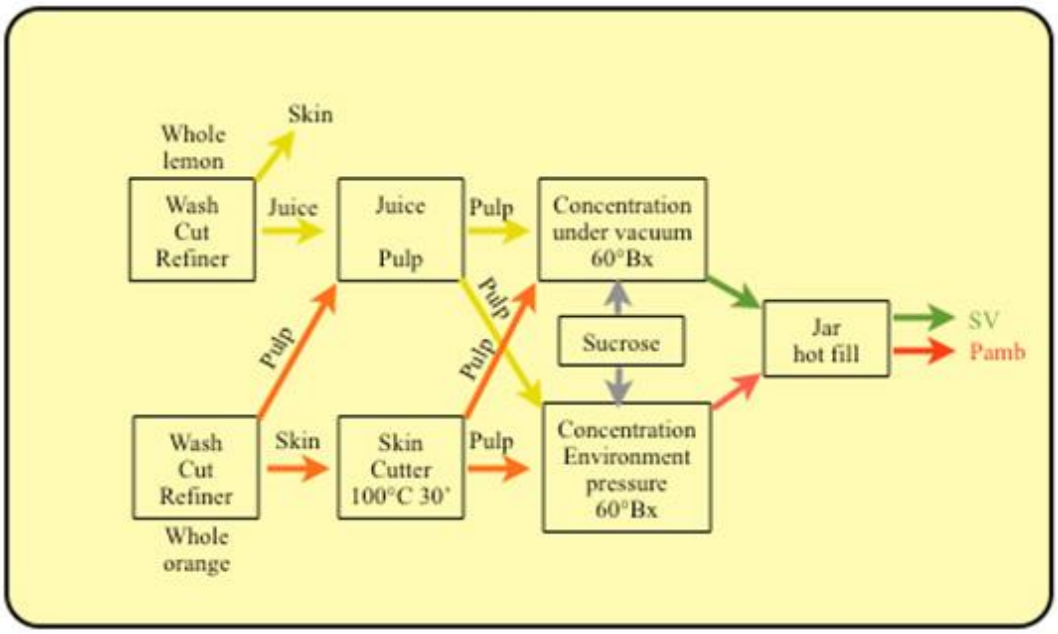

Diagram 2. Sanguinello orange marmalade type 1 production scheme. The different colours of the arrows indicates the technological path of every thesis, subjected to different treatments or conditions.

3.1.2.3.2 Product description

The marmalade developed contains orange pulp and a low sucrose amount. It is strongly pigmented because of the high content of natural pigments mainly represented by anthocyanins).

The comparison parameter has been the pressure of concentration: Pamb (thesis concentrated at ambient pressure) *vs* UV (thesis concentrated under vacuum).

	%	Sd
Orange pulp	45,16	0,53
Orange skin	15,61	2,11
Lemon juice	8,39	0,12
Sucrose	30,85	1,45

Tab. 10. Average initial composition of Sanguinello marmalade type 1.

3.1.2.3.3 Analytical methods

The analytical approach for the processing effect on the product quality was carried out by measuring the final product following quality parameters vs the initial material composition.

Ascorbic acid content was measured in according to Picchi et al. 2012 as a first heat treatment marker. The following modifications were introduced in the sample preparation step: 2g of marmalade were extracted with 4 ml of 6% metaphosphoric acid (at 4°C) and 4 ml of water (at 4°C), homogenized and centrifuged at 9,000rpm for 15 min at 4°C, and immediately analyzed.

1 g for each sample were extracted in 9 ml of , HCL0,02N 1:1 solution, mixed with a Vortex equipment for 2 min, than centrifuged al 10000 rpm for 10 min. The supernatant were stored at -80°C for further analysis.

The total anthocyanin index was measured following the pH differential method according to Rapisarda et al. (2000): marmalade extracts were diluted 25 folds with pH 1.0 and pH 4.5 buffers, respectively, their absorbances at 510 nm were read and the total amount of anthocyanins was evaluated as equivalents of cyanidin-3-glucoside according to the following formula: $C=(A_{pH1.0}-A_{pH4.5})$ x 484.82 x 1,000/24,825 x DF where C represents the concentration (mg/100 g f. w. tissue), A the absorbance, 484.82 the molecular weight of cyanidin-3-glucoside, 24825 its molar extinction coefficient and DF the dilution factor.
Class Polyphenols content have been evaluated by spectrophotometric scan in the UV-VIS from 275 nm to 600 nm, as described by Di Stefano and Cravero (1991). An extract solution diluted 10-fold, has been analyzed as follows: total phenolics at 280 nm, total cinnamates at 325 nm, flavonols at 360 nm and total anthocyanins at 520 nm. The system was calibrated with (+)catechin at 280 nm, caffeic acid at 325 nm, quercetin at 360 nm and the molar extinction of malvidin ($\varepsilon = 37200$, Lee et al., 2005) was used for the anthocyanin determination.
Total polyphenols index has been evaluated by the Folin-Ciocalteu reaction, as described in Singleton and Rossi (1965) on samples diluted 5 folds v/v.
RSR, pH, titrable acidity, were analyzed according to AOAC, 1980.
Free radical scavenging properties were measured by EPR analysis by means of TEMPO and Fremy'salt probes, using a Miniscope MS 200 Magnettech (Berlin, Germany). All measurements were performed in triplicate.

TEMPO assay.
1g of marmalade were extracted in 10 ml of methanol acidified with 10 µl of HCl3N, vortexed for 3 min than centrifuged at 10000 rpm for 10 min. the supernatant were put in eppendorf and stored at -80°C for further analysis. A 10 mmol/lsolution of 1-hydroxy-2,2,6, 6-tetramethyl-4-oxo-piperidine (also known as TEMPO) dissolved in methanol was used to determine samples scavenging activity. The control reaction was prepared with 50µl of TEMPO solution diluted 100 v/v, mixed with 250 µl of PBS and 200 µl of acidified methanol. The scavenger reaction consisted 50µl TEMPO solution diluted 100 v/v, mixed with 250 µl of PBS and 200 µl of marmalade extract. The system was calibrated with an Amadori product solution obtained as follows: an equimolecular solution of glucose (2%) and glicyne, in PBS 0,1M have been heated at 100°C for 2 hours in a climatic chamber. The total glucose consumption by the reaction was checked by HPLC with detection by refractive index (López-Tamames et al., 1996). The Amadori product solution was diluted 10 v/v, 20v/v, 40v/v, 100v/v folds. EPR instrumental conditions were set at 3,350 G as field set, scan range 100 G; scan time 30 s; modulation amplitude 2000 mG; microwave attenuation 5 dB; receiver gain 100. The EPR spectrum consisted of a symmetric triplet, and the measure of intensity in the absence and in the presence of marmalade extract was made on the signal at 3,336.01 G after exactly 1 min of reaction at 25°C. The scavenging activity is expressed in percent activity compared to the control.

Fremy's salt assay.
1g of marmalade were extracted in 10 ml of methanol acidified with 10 µl of HCl 3N, vortexed for 3 min than centrifuged at 10000 rpm for 10 min. the supernatant were put in eppendorf and stored at -80°C for further analysis . The free radical scavenging activity of marmalade samples was measured by EPR with the inhibition of marmalade extracts of a solution of a stable N-oxide free radical, potassium nitrosodisulfonate, worldwide known as Fremy's salt (GARDNER et al., 2000). The control reaction was prepared with a 10 mmol/l solution of Fremy's salt dissolved in PBS pH 0,1 M (25µl, mixed with 500 µl of methanol and 200 µl of acidified methanol). The scavenger reaction consisted 25µl Fremy's salt solution, mixed with 500 µl of ethanol and 200 µl of marmalade extract. Calibration was performed with a solution of 6,7 mg of Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) in 10 ml PBS 0,1M, diluted 5v/v, 10 v/v, 20v/v, 40v/v, 100v/v folds. EPR instrumental conditions were set at 3,350 G as field set, scan range 100 G; scan time 30 s; modulation amplitude 2000 mG; microwave attenuation 5 dB; receiver gain 5. The EPR spectrum consisted of a symmetric triplet, and the measure of intensity in the absence and in

the presence of grape extract was made on the signal at 3,336.01 G after exactly 1 min of reaction at 25°C. The scavenging activity is expressed in percent activity compared to the control.

3.1.2.4 Results and discussion

Sanguinello 1

The table 11 shows the values of RSR, pH and titratable acidity of the starting material and of the two samples processed. As can be seen in table 12, the ascorbic acid loss in the sample Pamb is much greater than that found in sample SV. A similar trend can be seen for the total anthocyanins, although with a better retention in the sample SV. Both results can be explained by the strong temperature difference which is applied to the two production techniques. Fig 10 shows the data of EPR with probe TEMPO. It is evident that a high-temperature process results in a strong increase in the formation of compounds with antioxidant activity, such as the Maillard reaction products. The same behavior can be seen in fig 11, which contains data related to the EPR probe Fremy's salt.

	RSR (°Bx)	*sd*	pH	*sd*	titratable acidity (mEq %)	*sd*
Starting material	13,3 e	*0,60*	3,61 c	*0,22*	15,15 d	*1,20*
Pamb	54,8 b	*0,70*	3,56 c	*0,12*	11,10 f	*0,87*
SV	55,4 b	*2,30*	3,53 c	*0,55*	11,74 f	*1,98*

Tab. 11. Sanguinello marmalade type 1: RSR, pH and titratable acidity before and after the processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

	AsA			Tot ATH		
	mg/100g fp	sd	% loss	mg/100g fp	Sd	% loss
Starting material	83,10 b	12,10		166,90 e	14,40	
Pamb	35,00 c	7,40	-57,88	70,20 b	5,20	-57,94
SV	48,90 f	5,30	-41,16	125,80 a	16,40	-24,63

Tab. 12. Sanguinello marmalade type 1: ascorbic acid and total anthocyanin before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

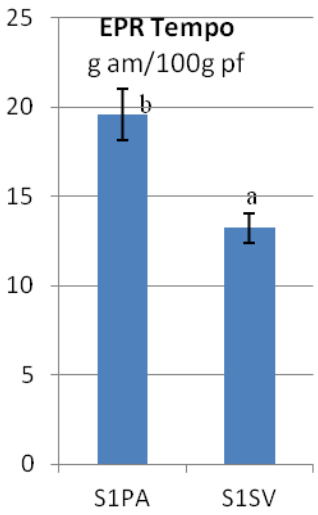

Fig. 10. Sanguinello marmalade type 1: EPR with probe TEMPO after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

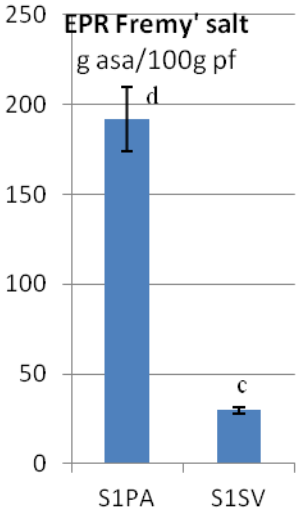

Fig. 11. Sanguinello marmalade type 1: EPR with probe Fremy's salt, after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.1.2.5 Conclusions

The purpose of this research was achieved because the product obtained complies with the specifications outlined. The two variants of the product are clearly distinguishable to the naked eye due to a strong colour difference: the sample obtained under vacuum presents a colour very similar to the one typical of sanguinello orange juice harvested during the top pigmentation ripening time. The sample concentrated at room temperature has a brownish coloration. The biochemical tests showed that samples obtained under vacuum have a retention of ascorbic acid and anthocyanins significantly greater than the product Pamb.

Informal sensory analysis showed a good acceptance of the product and a clear preference toward the sample obtained SV. Moreover, after some informal consumer tests, it have been noted that even if the overall liking test was clearly positive, the intense red color characterizing this product often has induced consumer confusion, creating an expectation concerning another product, such as strawberry or cherry jam.

3.1.3 Sanguinello orange marmalade type 2

3.1.3.1 Raw materials description and peculiarity

The starting material is the same used for the Sanguinello orange marmalade type 1, described in § 3.1.2.1.

Contrarily to the oranges used for the marmalade type 1, here were used two groups of fruits, differing because of the harvesting time: fruits deriving from a late crop, thus not pigmented (see § 3.1.2.1) have been used to obtain the pulp, while, fruits deriving from an optimal harvesting time were used in order to obtain the pigmented skins. The vegetal material had been previously separated and frozen.

3.1.3.2 Research goals

The aim of study is to obtain by means of a miniaturized plant, a particular kind of citrus derivate, produced in an artisanal scale part of a short supply chain context. This product was developed in order to obtain a marmalade using late crops of sanguinello orange, but as much as possible rich in natural anthocyanins. A second aim was to test two different acidifying media: fresh squeezed lemon juice or a citric acid solution.

3.1.3.3 Materials and methods

3.1.3.3.1 Production method

During January 2013 around 25 kg of pigmented organic Sanguinello organic orange fruits (oranges 1) were collected by a Sicilian producer. After delivery the fruits have been immediately processed through a pulp refiner, obtaining pulp and skins separation. This two semiprocessed products have been packed in PET bags and frozen by means of an air flow freezing tunnel. Freezing conditions were: -50°C, with a 2 m/s air speed tangent flow.

During April 2013 around 25 kg of not pigmented organic Sanguinello organic orange fruits (oranges 2) coming from a late crop, were collected by a Sicilian producer. After delivery the fruits have been immediately processed. Pulp and skins were separated.

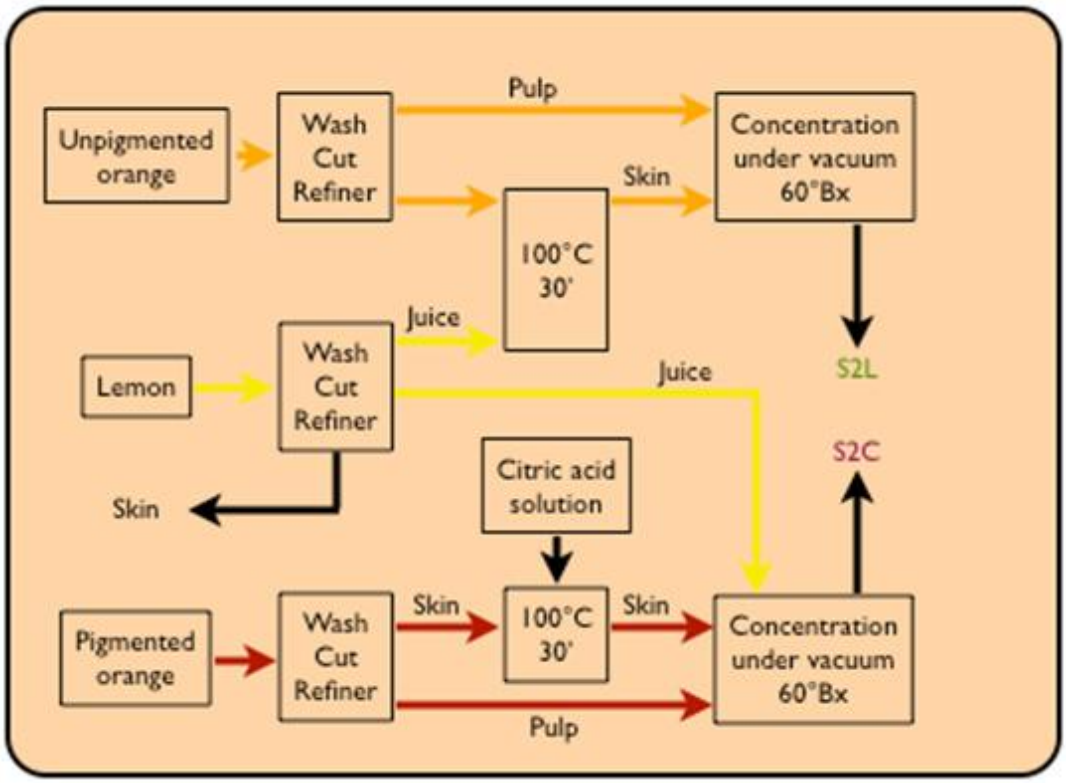

Diagram 3. Sanguinello orange marmalade type 2 production scheme. The different colours of the arrows indicates the technological path of every thesis, subjected to different treatments or conditions.

After thawing the skins deriving from oranges 1 have been added with the acidifying solution (lemon juice or a similar acidity citric acid solution) and cooked in boiling water, then chopped in around 7 mm side pieces, using a food cutter. The pulp of oranges 2 have been added of the cooked skins, sucrose and (only LEM samples) lemon juice. The mixture have been concentrated under a vacuum (approximately P=-0.94 atm), at 41±2°C until reaching 57±2 °Brix as soluble solids content. Thermal stabilization has been carried out by heating the product up to 90°C, followed by a hot filling in 390 ml glass jars.

3.1.3.3.2 Product description

The marmalade developed shows an orange coloured matrix in which are dispersed small bits of dark red pigmented skin. Samples compared are: S2Clem (acidified with fresh squeezed lemon juice) *vs* S2Citr (acidified with a 100 g/l citric acid solution).

	%	sd
Orange pulp	45,58	0,46
Orange skin	13,58	0,01
Lemon juice	9,03	0,03
Sucrose	31,59	0,12
(Citric acid)	(0,45)	///

Tab. 13. Average initial composition of Sanguinello marmalade type 2.

Fig 11b. A view a of Sanguinello marmalade type 2 sample.

3.1.3.3.3 Analytical methods

1 g for each sample were extracted in 9 ml of , HCL0,02N 1:1 solution, mixed with a Vortex equipment for 2 min, than centrifuged al 10000 rpm for 10 min. The supernatant were stored at -80°C for further analysis.

RSR, pH, titrable acidity, were analyzed according to AOAC, 1980.

Free radical scavenging properties were measured by EPR analysis by means of TEMPO and Fremy'salt probes, using a Miniscope MS 200 Magnettech (Berlin, Germany). All measurements were performed in triplicate. For methods description see **§** 3.1.2.3.3.

3.1.3.4 Results and discussion

Fig 12 shows the data of EPR with probe TEMPO. It is evident that a high-temperature process results in a strong increase in the formation of compounds with antioxidant activity, such as the Maillard reaction products. The same behavior can be seen in fig 13, which contains data related to the EPR probe Fremy's salt. In Sanguinello 2 matrix, significantly poorer in anthocyanins than the Sanguinello 1 matrix, the probe Fremy's salt order of magnitude is significantly smaller. This result can be explained as the Fremy's salt is particularly sensitive to phenolic compounds, much less represented in Sanguinello 2 matrix than in Sanguinello 1, since the pulp used for this product was not pigmented.

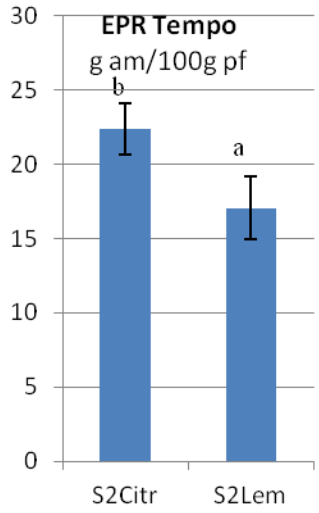

Fig. 12. Sanguinello marmalade 2: EPR with probe TEMPO with 2 different acidifying media: citric acid solution *vs* lemon juice In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

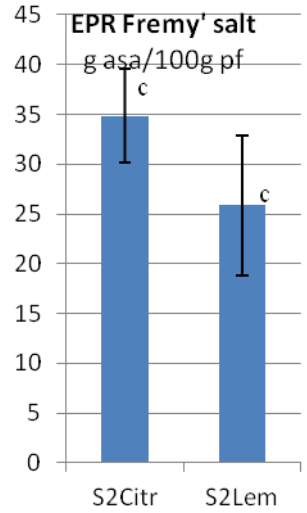

Fig. 13. Sanguinello marmalade 2: EPR with probe Fremy's salt with 2 different acidifying media: citric acid solution *vs* lemon juice. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.1.3.5 Conclusions

The product obtained confirms the achievement of the purposes. The marmalade developed shows an orange coloured matrix in which are dispersed small bits of skin dark red pigmented. The two variants of the product obtained are not distinguishable to naked eye, not even by taste tests. The biochemical analysis suggest a greater presence of degradation compounds in the sample acidified with citric acid. Furthermore, its development provided an alternative citrus derivate that do not presents the problems of consumer confusion showed by Sanguinello orange marmalade type 1 (§ 3.1.2.5).

3.1.4 Tarocco dal muso orange marmalade

3.1.4.1 Raw materials description and peculiarity

Citrus sinensis L. var. Tarocco dal muso belongs to the PGI "Red Sicilian orang" group (see § 3.1.2.1). The fruits used for this study are from a not pigmented late crop (see § 3.1.2.1).

3.1.4.2 Product description and research goals

This product stems from the need to obtain by means of a miniaturized plant, a marmalade, using very late harvest of oranges Tarocco dal muso. Its production had to be obtained in an artisanal scale, belonging to a short supply chain context. The marmalade had to be made from the whole fruit.

3.1.4.3 Materials and methods

3.1.4.3.1 Production method

During May 2013, approximately 25 kg of *Citrus sinensis* L. var Tarocco dal muso organic fruits were collected from a Sicilian producer and processed soon after delivery, at CRA-IAA.

Oranges, after washing, brushing, drying and removal of the poles were prcessed by a shredder / refiner, with the aim to separate pulp from solids (skins and seeds). The skins were cooked in boiling water and then switched to a cutter, to ensure uniform size.

Cooked skins, pulp, lemon juice and crystalline sucrose were introduced into the concentration boule. The concentration process was performed at a pressure of about -0.94 atm, thus to a correspondent boiling temperature of 41 ± 2°C. The process was run until it reached a title soluble solids of 58° Brix. At the end of concentration, the product was heated up to 90°C, at atmospheric pressure and subsequently transferred in 390 ml glass jars.

3.1.4.4 Results and discussion

After development the marmaladet has been subjected to informal sensory sessions in order to define informally its overall liking reporting positive evaluation.

3.1.5 Multi-Purpose Industrial Sugar Substitute

3.1.5.1 Raw materials description and peculiarity

The grape types used for this study are *Vitis vinifera* L. var. Italia and var. Red Globe. The former is a common non pigmented table grape, while the latter is a pigmented table grape. The red skins pigmentation is due to phenolic pigments (Yilmaz, Y. & Toledo R. T.,2004) and phenolic compounds have been correlated with a strong antioxidant activity (Bertolomè et al., 2003). Moreover, since has been proved that thermal treatments (in addition to other advantages such as enzyme denaturation, microbial decontamination, etc.) can be used in order to enhance the antioxidant potential (Lo Scalzo et al., 2004), has been performed a blanching pretreatment of a half of each type of grapes.

Unfortunately, due to unexpected technical problems, the trials could not start at fall 2012 as planned but at the end of December 2012. The only pigmented starting material available on the market have been a grape harvested at the end of October and cold stored until the purchase. The principal consequence have been that the starting material vitality and its starting content of bioactive compounds was lower than fresh harvested grape.

3.1.5.2 Research goals

Purpose of this product development was to obtain a semifinished product derived from grapes pigmented and non-pigmented. The semifinished product had to be a sugar substitute for use in the development of other products. The product had to preserve as much as possible the nutritional value of the raw material and had to be achieved in a craft dimension, within the context of a short chain, using a miniaturized processing equipment.

3.1.5.3 Materials and methods

3.1.5.3.1 Production method

About 50 kg of two commercial table grape *Vitis vinifera* L. variety Italia (unpigmented samples, called B) and variety Red Globe (pigmented samples, called N), , were purchased on the market. The berries were selected for uniformity and visual absence of defects, cleaned with water, dried, and then cut into small bunches of 3-5 berries each. They were then randomly divided into two batches of each variety, one aliquot processed to juice without treatment (NT) and the other processed after blanching in boiling water for 2 min (water-grape ratio 10:1) and then quickly cooled in a water-ice bath (see Fig. 14 for the temperature trend model in a grape berry). Four samples were obtained: two white grape (BNT and BBL) and two black grape (NNT and NBL) samples.

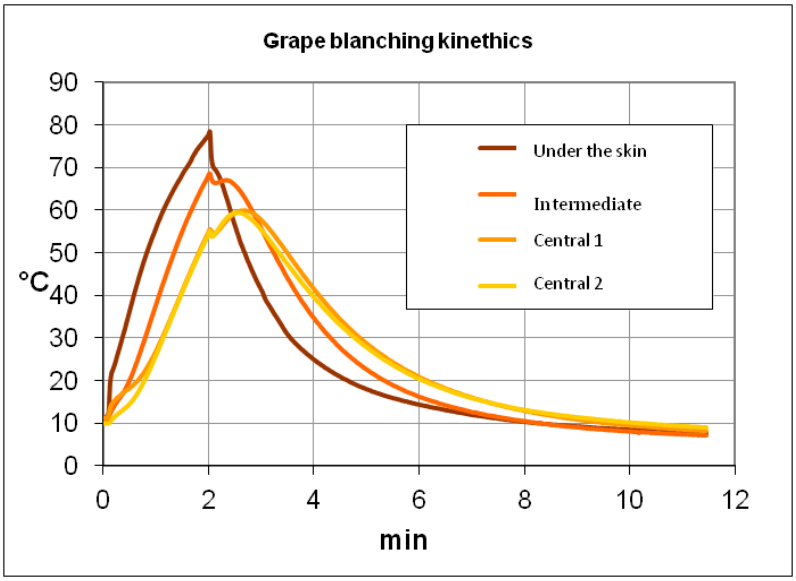

Fig. 14. Temperature trend model in a grape berry at different levels of deepness.

Each group was then squeezed to raw juice, which was conditioned at 3°C for 72 h to separate larger solid particles then decanted and simultaneously cleaned by filtering through a nylon cloth of approx. 7 mesh porosity and afterwards centrifuged at 7000 rpm through a finishing cloth of approx. 150 mesh porosity to obtain the refined juice. The refined juice was vacuum-dried at 43±2°C at a pressure of ≈-0.93 bar. The degree of dryness was evaluated by the increase of °Bx in the processed product to a constant value (tab. 14).

	Initial °Bx	**Final °Bx**	**ratio**
BNT	14,8	86,7	5,9
BBL	14,1	85,9	6,1
NNT	17,6	84,0	4,8
NBL	16,4	84,2	5,1

Tab. 14. Values of °Bx in starting and final grape juices.

The final product's water activity level was measured with a dew point water activity meter AquaLab 4TE, and the results (average of two replicates) were expressed in percentage.
The full production process is shown schematically in diagram 4.

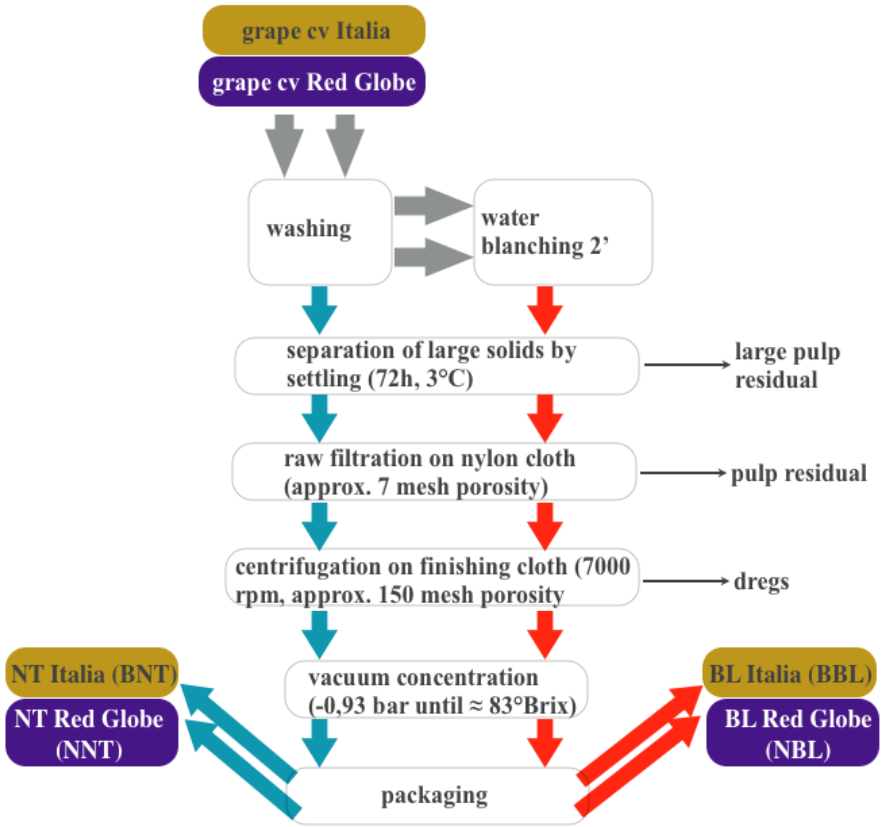

Diagram 4. Sugar substitute production process scheme. The different colours of the arrows indicates the technological path of every thesis, subjected to different treatments or conditions.

3.1.5.3.2 Analytical methods

The analytical approach for the processing effect on the product quality was carried out by measuring the final product main quality parameters *vs* the initial material composition.
The initial grape juice was divided in a number of aliquots and centrifuged at 10.000 rpm for 10 min. The final products have been reconstituted to the starting concentration according to the concentration ratio factor shown in Table 1 and treated as the initial juice. The resulting solutions have been used for glucose and fructose analysis, made by HPLC with detection by Refractive Index (López-Tamames et al., 1996) and the total acidity measurement (AOAC, 1980).
As for the phytochemical analysis, the supernatants have been diluted 10 folds with a EtOH/HCl 0.02N 1:1 and stored at -20°C for further analysis. Total polyphenols index has been evaluated by the Folin-Ciocalteu reaction, as described in Singleton and Rossi (1965). The polyphenols single classes have been evaluated by spectrophotometric scan in the UV-VIS from 275 nm to 600 nm, as described by Di Stefano and Cravero (1991). An extract solution diluted 10-fold , has been analyzed as follows: total phenolics at 280 nm, total cinnamates at 325 nm, flavonols at 360 nm and

total anthocyanins at 520 nm. The system was calibrated with (+)catechin at 280 nm, caffeic acid at 325 nm, quercetin at 360 nm and the molar extinction of malvidin (ε = 37200, Lee et al., 2005) was used for the anthocyanin determination.

3.1.5.4 Results and discussion

A total sugar content decrease has been the first blanching process effect on the product composition (tab. 15), given by the leaching induced due to blanching. Data regarding the water activity (tab. 15) on the final products showed a lower value in the products derived from black grapes, with no effects induced by the blanching process.

					Processing effect (blanching)		
	INITIAL	std dev	FINAL	std dev	% variation	initial	final
	°Bx on dw						
BTQ	84,8	0,3	85,1	0,2	100		
BSC	85,1	0,7	84,7	1,3	99	100	100
NTQ	83,2	0,2	83,4	1,2	100		
NSC	81,2	1,6	80,1	0,4	99	98	96
	titratable acidity mEq%						
BTQ	20,0	0,3	25,2	1,1	126		
BSC	21,8	0,2	21,9	2,1	100	109	87
NTQ	24,3	0,4	23,9	0,4	98		
NSC	27,6	0,9	25,8	1,6	93	113	108
	glucose g/100g dw						
BTQ	31,4 a	1,0	27,0 c	1,0	86		
BSC	31,5 a	0,9	28,5 c	4,7	91	100	105
NTQ	34,2 b	1,3	27,5 d	3,7	81		
NSC	34,1 b	2,7	26,5 d	0,5	78	100	96
	fructose g/100g dw						
BTQ	48,6 a	3,5	39,5 d	5,9	81		
BSC	50,0 a	0,9	38,7 d	4,3	77	103	98
NTQ	48,4 b	1,4	37,8 e	3,0	78		
NSC	45,9 c	0,5	40,6 e	4,8	89	95	108
	Water activity						
BTQ			48,6	0,1			
BSC			47,0	2,8			
NTQ			40,3	6,2			
NSC			42,0	1,2			

Table 15. Total acidity, glucose, fructose and water activity amount of initial and final processed grape juice, expressed on dry weight. The processing effect has been computed by the final percent ratio vs initial values. The blanching effect has been calculated by the blanched sample percent ratio vs the non treated. Comparison is made between samples couples TQ *vs* SC. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

The same consideration can be arisen from the total acidity content changes (tab. 15). The processing effect has some influence on the total acidity values, with an increase only in BNT. The processing effect on glucose and fructose amount resulted in a diminution for both of them, while no effect has been detected after blanching (tab. 15). No significant differences in this trend have been found between the two sugars. It is evident that some decomposition reaction has been induced by the vacuum concentration processing.

As for the phytochemicals amount (tab. 16), it can be noted that both total phenols and single phenol classes content have been strongly increased by the blanching, from two to four folds with respect to the NT samples, confirming previous results on blueberry juice processing (Rossi et al., 2003). The anthocyanins had an increase of about four folds in BL samples with respect to NT ones, probably due to their water solubility.

							Processing effect (blanching)		
	INITIAL	**std dev**		**FINAL**	**std dev**		**% variation**	**initial**	**final**
	total polyphenols index Folin reaction mg/100g dw catechin eq								
BTQ	82,1 a	0,3		137,9 e	8,9		168		
BSC	164,8 b	2,2		268,5 f	12,2		163	201	195
NTQ	180,1 c	1,9		237,1 g	11,1		132		
NSC	343,9 d	0,4		446,2 h	22,2		130	191	188
	total polyphenols index 275 nm mg/100g dw catechin eq								
BTQ	286,3 a	10,2		378,0 e	0,8		132		
BSC	697,5 b	1,5		979,7 f	58,4		140	244	259
NTQ	456,0 c	7,2		587,9 g	52,4		129		
NSC	867,4 d	23,9		1078,9 h	38,1		124	190	184
	total cinnamates325 nm mg/100g dw caffeic acid eq								
BTQ	129,9 a	6,3		13,8 e	0,3		11		
BSC	316,0 b	13,2		34,6 f	2,3		11	243	251
NTQ	134,1 c	1,6		14,4 g	1,8		11		
NSC	301,5 d	8,7		28,4 h	1,3		9	225	197
	total quercetins 360 nm mg/100g dw quercetin eq								
BTQ	52,7 a	0,5		6,1 e	0,0		12		
BSC	184,9 b	11,1		20,0 f	1,3		11	351	326
NTQ	70,7 c	1,6		7,4 g	1,0		10		
NSC	169,9 d	5,0		13,8 h	0,7		8	240	186
	total anthocyanins 520nm mg/100g dw malvidin eq								
NTQ	13,5 a	0,0		8,1 c	0,7		60		
NSC	47,0 b	1,1		34,5 c	2,8		73	349	428

Table 16. Total phenols and single polyphenols classes evaluated by a spectrophotometric method. The processing effect has been computed by the final percent ratio vs initial values. The blanching effect has been calculated by sample blanched percent ratio vs the not treated. Comparison is made between samples couples TQ vs SC. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

On the other hand the processing effect computed by the percent recovery in the final product with respect to the initial one (tab. 16), resulted in a different trend. The total phenols content index has been measured both by Folin reaction and by the absorbance of the extract at 280 nm. It resulted increased in all the final products, as demonstrated by the percent values higher than 100% (tab. 16). Within the two grape types, an higher increase was found in white grape.
The other polyphenols classes (monitored at 325 and 360 nm) showed about 90% of loss (probably due to the processing) with an average retained value of 10%, while the red pigments, evaluated at 520 nm, have been retained by 65%. It's possible that the processing temperature, together with the acidity increase due to the concentration process, lead the original grape conjugated phenols to a decomposition, such as the tartaric acid esters of hydroxycinnamics. This reaction produced other simpler phenols, able to react at 280 nm and present in an higher concentration than the starting samples. These simpler phenols correspond to an high biological value and gave a relevant index of

chemical reduction, that completely followed the spectrophotometric results, as demonstrated by the Folin test data.

3.1.5.5 Conclusions

The product obtained fulfills completely with the aims. Its texture is honey-like and it showed the abilities to sweeten, colour, acidify and provide a good retention of the original bioactive compounds present in the row materials. The product obtained has characteristics that could allow its use as a sucrose substitute in development of new products. Due to its texture and acidity (in addition to good shelf life at room temperature), it could find applications in the dairy sector in the yogurt and ice cream formulation. Biochemical analysis showed that the blanched samples better tolerated the processing than those not blanched.

3.1.6 Creamy plain yogurt

3.1.6.1 raw materials description and peculiarity

For these tests was used raw whole cow's milk, from CRA-FLC farms, in Lodi. The title of protein and fat was respectively 3.36% and 3.6%.

A common commercial plain yogurt (a viable culture of *Lactobacillus bulgaricus* and *Streptococcus thermophilus*), was used as inoculum.

3.1.6.2 Research goals

The test purpose was to verify the possibility to realize the entire production cycle of creamy plain yogurt by means of a multi-functional processing line, used in an artisanal context of short supply chain.

3.1.6.3 Materials and methods

3.1.6.3.1 production method

25 l of raw milk were introduced into the concentration boule, and heated up to 90°C. In order to obtain a strong pasteurization it was maintained at this temperature for 20 min. Subsequently, the milk was cooled to 42°C. During cooling the milk was concentrated under vacuum until reaching a title of protein equal to approximately 3.9%. As soon as the temperature reached 42°C, 1 kg of inoculum was introduced. During 60 min prior to inoculation the inoculum was slowly heated up to 40°C. The product maturation took place for 24 hours in the concentration boule where the product was maintained at 42°C and under continuous stirring by means of a rotating blade. Spent the maturation phase, the product was transferred into 100 ml glass jars, previously sterilized and than stored in a cell at 4°C.

3.1.6.3.2 Product description

The product obtained is a creamy plain yogurt with title in proteins 3.87%.

3.1.6.4 Results and discussion

The production test has given a positive outcome, as the product obtained presents visual and sensory typical characteristics.

The product obtained was evaluated by means of informal sensory sessions, always obtaining positive evaluations.

3.1.7 Compact plain yogurt

3.1.7.1 raw materials description and peculiarity

Raw materials used are the same described in § 3.1.6.1.

3.1.7.2 Research goals

The test purpose was to verify the possibility to realize the entire production cycle of compact plain yogurt by means of a multi-functional processing line (excluding the final maturation), used in an artisanal context of short supply chain.

3.1.7.3 Materials and methods

3.1.7.3.1 production method

25 l of raw milk were introduced into the concentration boule, and heated up to 90°C. In order to obtain a strong pasteurization it was maintained at this temperature for 20 min. Subsequently, the milk was cooled to 42°C. During cooling the milk was concentrated under vacuum until reaching a title of protein equal to approximately 3.9%. As soon as the temperature reached 42 ° C, 1 kg of inoculum was introduced. During 60 min prior to inoculation the inoculum was slowly heated up to 40°C. After inoculation, the milk was kept at 42°C for 30 min, under continuous stirring by means of a rotating blade. Subsequently, the inoculated milk was transferred into 100 ml glass jars, previously sterilized, and then placed into a climatic chamber at 42°C for 24 hours, where was held the product maturation. Spent the maturation phase, the jars were stored into a cell at 4°C.

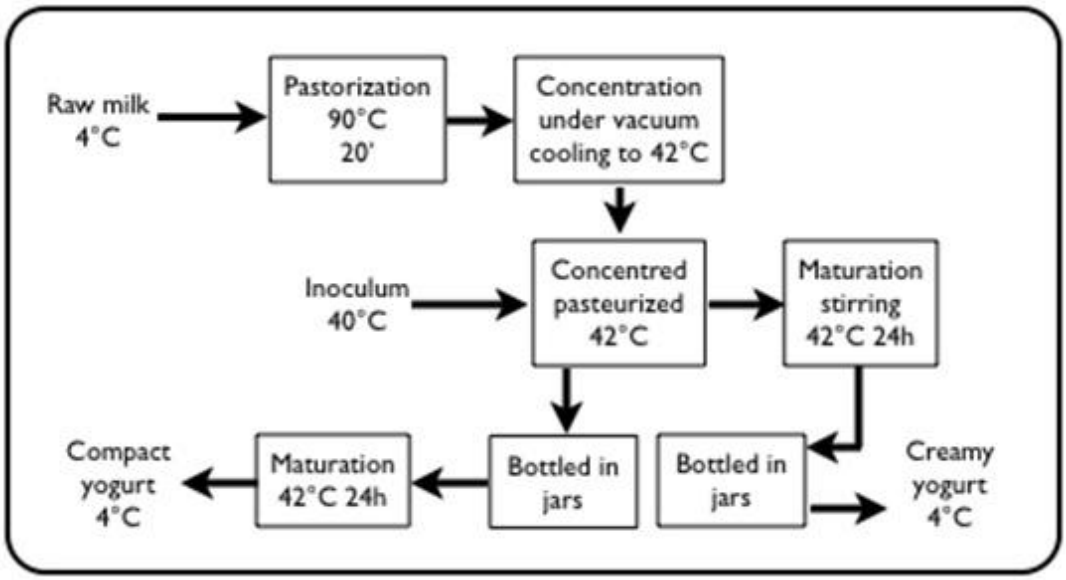

Diagram 5. Creamy and compact yogurt production process scheme.

3.1.7.3.2 Product description

The product obtained is a compact plain yogurt with title in proteins 3.87%.

3.1.7.4 Results and discussion

The production test has given a positive outcome, as the product obtained presents visual and sensory typical characteristics.

The product obtained was evaluated by means of informal sensory sessions, always obtaining positive evaluations.

3.1.8. Conclusions of group 1

The products obtained by means of the miniaturized multifunctional processing line meet the project requirements and showed a quality that can be considered superior to that which characterizes the normal handicraft production. Thanks to a good qualitative markers retention, that was almost always found, these products can provide a natural product and rich in bioactive compounds for a period longer than the fruit commercial life and in a area wider than its usual sales area. In particular, the study of citrus marmalade allow to obtain:

- A quality product, characterized by a good retention of bioactive substances and positive informal sensory evaluations
- A good production yield, waste reduction, since almost all studied products are obtained by the whole fruit
- increase in a novel way the value of lower quality crops, such as early or late pigmented citrus crops (which, in fact, are not pigmented).

The study of the sweetener has allowed to obtain an innovative industrial semi-finished product, able to sweeten, colour, acidify and provide a good amount of bioactive compounds.

The production of yogurt in two different textures was optimal. It can also be performed by means of alternative energy sources. Its production can also be associated to a semi-processed fruit production (such as orange marmalade, or other fruits), used for flavoring.

3.2 Group 2: Products obtained by means of a solar drying system

In the last few years there has been an increasing demand for innovative products responding to changing lifestyle, leading to a strong increase of out-of-home food consumption. Consumers are also becoming more interested in consuming healthy, natural and tasty foods. Dried food products make up an important market area of innovative snacks, in particular F&V based products.
Drying is one of the oldest techniques of conservation. It is extremely simple and is based on the decrease of the amount of free water present in the raw materials, until is exceeded the stability threshold (fig. 15).

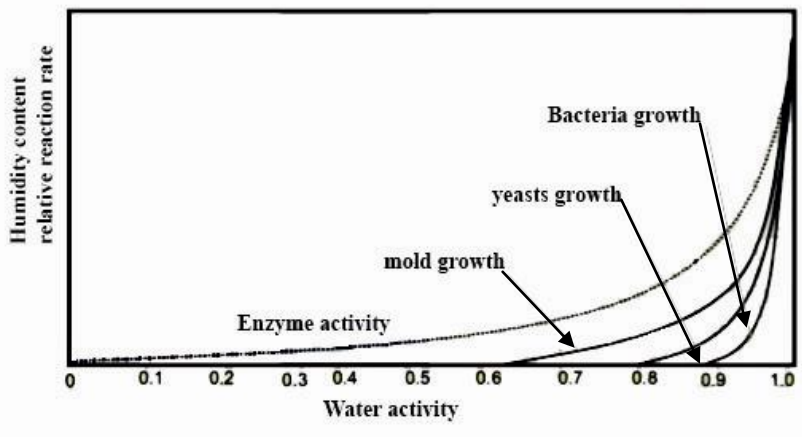

Fig. 15. Microorganisms' growth vs water activity (image taken from the website www.aqualab.com, modified).

Drying was traditionally carried out by exposing to air or solar radiation, the products to be processed, whole or portioned, for the time required to obtain its stability. The drying time depended on the local weather and was thus operated in unpredictable conditions related to factors not directly, or effectively, controllable.
Conventional drying techniques employed by the food industry are based on the water removal from the food through the use of dryers (commonly electricity powered). In such equipment the raw materials are exposed to the action of a hot dry air current. This technique is very effective from a technological point of view, allowing to reach the desired a_w within very short processing time, but it is characterized by a very high energy cost (electricity consumption).
The newly designed solar drying systems allows the use of sun radiation, reducing most of the traditional techniques defects.
The dehydration process represents an important opportunity both for food industry and small producers. Exploiting renewable energy sources seems to be a winning path in a more sustainable production context. The use of thermal and photovoltaic energy has become particularly prominent. Though big industry's needs (in terms of production times and costs) still make not possible the use of renewable energy sources, small and local craft producers can make a profit by using solar energy.
The research focuses on Mediterranean fruit (orange and lemon) and vegetable (Senise pepper) which, after drying, can be exploited by direct consumption or as ingredients in other processed foods.
The products here studied are stable dried citrus and pepper derivates. They have been obtained using a solar drying system (see § 1.1.3.2) without any energy source except the solar radiation.

Processing of these products require a longer processing time rather than the conventional method, but the energy saving is high indeed.

3.2.1 Tarocco orange and Femminello Zagara Bianca lemon dried slices

3.2.1.1 Raw materials description and peculiarity

For *Citrus sinensis* L. var Tarocco description see § 3.1.2.1.
Citrus lemon L. var. Femminello Zagara Bianca Nucellare 356 is a commercial lemon typical from Sicily.

3.2.1.2 Research goals

The aim of this research is to obtain a high quality dried product using a solar drying system used in an artisanal dimension and belonging to a supply chain context. The product should have to be a citrus derivate developed allowing to use it by direct consumption (as a snack), or as an ingredient in other foods. In addition, two drying techniques have been compared: a solar drying system prototype (see § 1.1.3.2) and a conventional air-drying system whose processing conditions are described here below.

Fig. 16. Orange slices on solar drier tray during the processing.

3.2.1.3 Materials and methods

3.2.1.3.1 Production method

Around 15 kg of *Citrus sinensis* L. var Tarocco Meli organic oranges and around 15 kg of *Citrus lemon* L. var. Femminello Zagara Bianca Nucellare 356 organic lemons were purchased by a Sicilian producer. After washing, brushing and drying, the fruits were cut into 0.5 cm thickness slices by means of a professional rotary blade slicer. The oranges' slices average weight was 16.1±1.5 g, while the lemon's was 10.7±1.4 g. The half of each group have been added of sugar "dipping" the slice into crystalline sucrose and then carefully put on the drier tray. The average sugar amount was 3.4±0.9 g for each orange slice and 2.2±0.9 for each lemon's one.
An equivalent number of slices with or without sugar, for each citrus type, were dried using the solar drying system described in § 1.1.3.2. Solar drying was carried out in Sicily, at Acireale Research Agriculture Council CRA-ACM (37°37′17.97″N, 15°09′51.99″E) during April 2012, while conventional drying took place in Milan at Research Agriculture Council CRA-IAA. The conventional drying conditions were: 45°C, 2m/s air speed, tangent flow.
Drying has been considered finished when the product reached constant weight, with both drying systems.

3.2.1.3.2 Product description
The product consisted of round slices obtained by slicing the whole fruit (thus including skin). For each citrus type, two kinds of product have been studied: slices added of sucrose and slices without sucrose added. The dried slices, once powdered, have also been used as flavouring agents (see § 3.3.2).

3.2.1.3.2 Analytical methods
1 g for each sample were extracted in 9 ml of ethanol, HCL0,02N 1:1 solution, mixed with a Vortex equipment for 2 min, than centrifuged al 10000 rpm for 10 min. The supernatant were stored at -80°C for further analysis. Ascorbic acid content was measured in according to Picchi et al. 2012.
Total polyphenols index has been evaluated by the Folin-Ciocalteu reaction, as described in Singleton and Rossi (1965) on samples diluted 10 folds v/v.
Residual humidity content was determined by Karl Fisher titration (tab. 17), using the official method provided by the patent owner (Mattler Toledo, www.mt.com).
Free radical scavenging properties were measured by EPR analysis by means of TEMPO and Fremy'salt probes, using a Miniscope MS 200 Magnettech (Berlin, Germany). All measurements were performed in triplicate. 30 mg of powdered sample (powdered in a hammer mill for 30 sec) were added to 1 ml of HPO_3 3%, vortexed for 30 sec, centrifuged at 10000 rpm for 10 min; the supernatant was transferred in vials and stored at –80°C for further analysis. Before analysis, all samples were diluted 10 v/v with HPO_3 0,02 N.
The methods are reported in § 3.1.2.3.3, with the following differences:

- TEMPO probe: the control reaction was prepared with 50µl of TEMPO solution diluted 100 v/v, mixed with 350 µl of PBS and 100 µl of acidified methanol. The scavenger reaction consisted 50µl TEMPO solution diluted 100 v/v, mixed with 350 µl of PBS and 100 µl of marmalade extract
- Fremy's salt probe: samples were diluted again 4 v/v. Calibration was performed by means of the following solution: 10mg of ascorbic acid were diluted in HPO_3 3%.

Photochem is an automatic system (by Analytikjena AG), capable to quantify the antioxidative capacity by means of a photobioluminescence reaction using Luminol and calibrated with a Trolox solution. 20g of sample were pounden in a mortar, 0.5g of powder were added to 20 ml of methanol, shaked with a Vortex equipment for 3 min, centrifuged at 13200 rpm for 2 min. The supernatant was instantly analyzed. Preparation of calibration curve was performed as described in the standard protocol kit, using volumes as displayed in the scheme reported in tab. 18 (§ 3.2.2.3.3). Calibration molecule was ascorbic acid. All solution (R1, R2, R3, R4 are covered by a patent and sold by Analytikjena AG). Photochem equipment realize automatically the measurement.
RSR, pH, titrable acidity, dry matter were analyzed according to AOAC, 1980.

3.2.1.4 Results and discussion
Antioxidant profile
In the following charts is represented the drying method effect (solar *vs* conventional) and the effect of sucrose presence during processing (TQ samples *vs* samples sweetened SU). The reference data is represented by the value of the freeze dried starting material.

3.2.1.4.1 Lemon
The ascorbic acid content values (Fig. 17) seem to follow directly the time of treatment duration. The longer treatments correspond to the conventional sweetened and the two solar dried samples: TQ conv is the shortest, then follows the SU conv, the two solar dried samples record the longest drying time, that is the same for both. Also the EPR probe TEMPO (Fig. 18) shows a trend similar to that of AsA (correlation 0.908), with a value of SU conv greater than the two solar dried, but lower than the sample TQ conv. The EPR probe Fremy 'salt (Fig. 19) shows a completely different

trend. The lowest values correspond to the absence of treatment (freeze-dried), and unsweetened samples. Such an effect could be explained by the fact that the formation of Maillard compounds, due to their high reactivity with the radical, is enhanced by both the presence of sugars, and by the treatment length: in fact, the highest values derive from sweetened samples also characterized by the two greater treatment times.

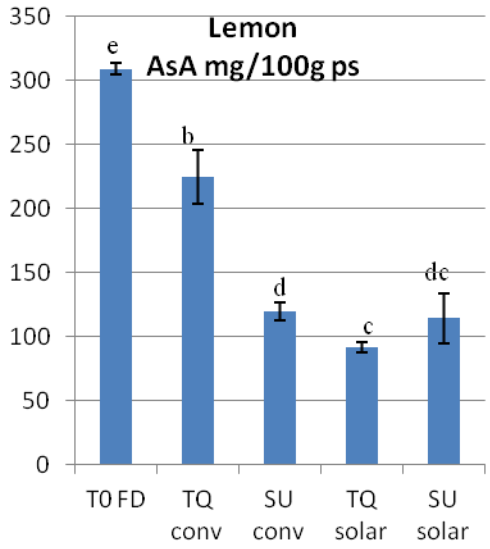

Fig. 17. Lemon dried slices. Ascorbic acid content before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

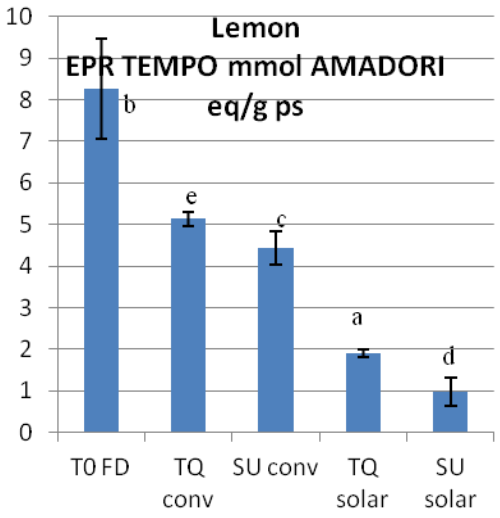

Fig. 18. Lemon dried slices. EPR with probe TEMPO before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

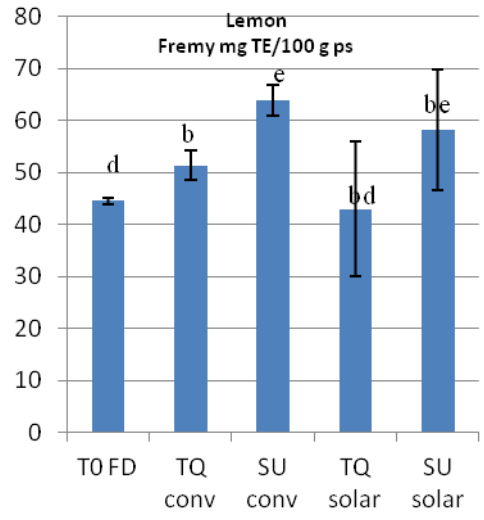

Fig. 19. Lemon dried slices: EPR with probe Fremy's salt before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

In this case, the Folin Ciocalteu test (Fig. 20) is influenced both by the presence of AsA (especially the fd sample), and both the presence of degradation compounds caused by the presence of carbohydrates, and by the treatment length: the two sweetened samples show higher values than the two unsweetened.

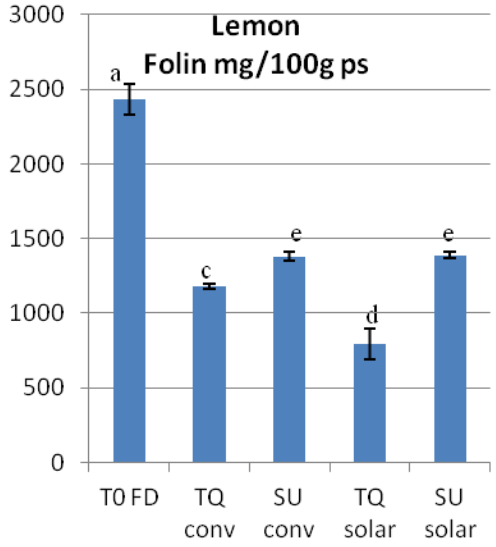

Fig. 20. Lemon dried slices: Total polyphynols before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.2.1.4.2 Orange

By the AsA trend (Fig. 21), it might be expected that the presence of sugar increases the effect of AsA degradation since the two solar dried samples have equal drying time. The EPR Fremy 'salt (Fig. 24) and EPR TEMPO (Fig. 22) results show a good correlation value with those of the AsA (respectively 0.730 and 0.882). The Folin Ciocalteu index, being very sensitive to the degradation compounds induced by the processing (Fig. 23), assumes as higher values those related to the most favorable conditions for Maillard reactions: such as longer processing times and sugar presence (samples SU conv and SU solar). It is known that that the AsA presence strongly contributes to a Folin Ciocalteu index increase: this fact could explain the high value shown by freeze dried sample.

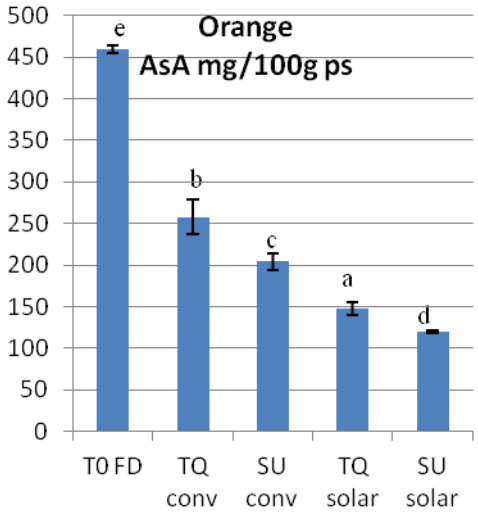

Fig. 21. Orange dried slices: Ascorbic acid content before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

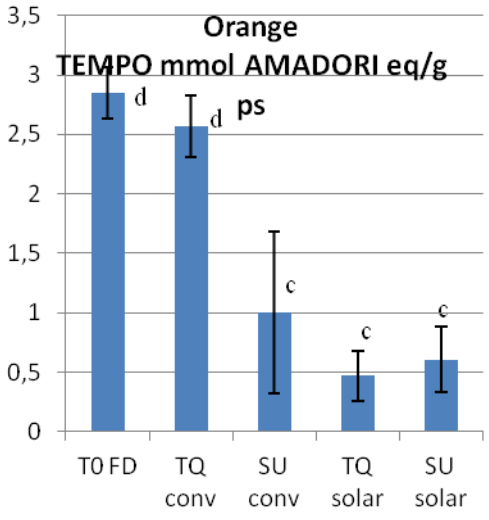

Fig. 22. Orange dried slices: EPR with probe TEMPO before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

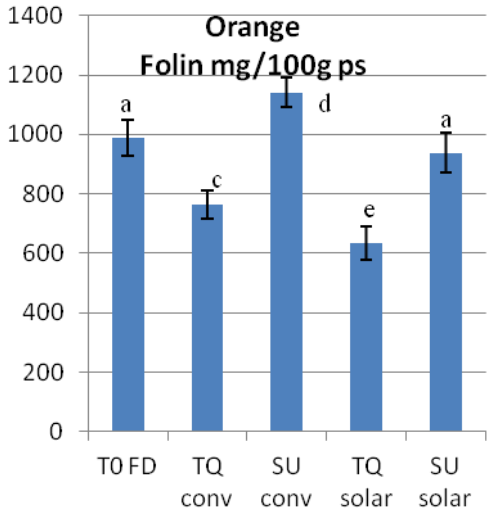

Fig. 23. Orange dried slices: Total polyphynol content before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

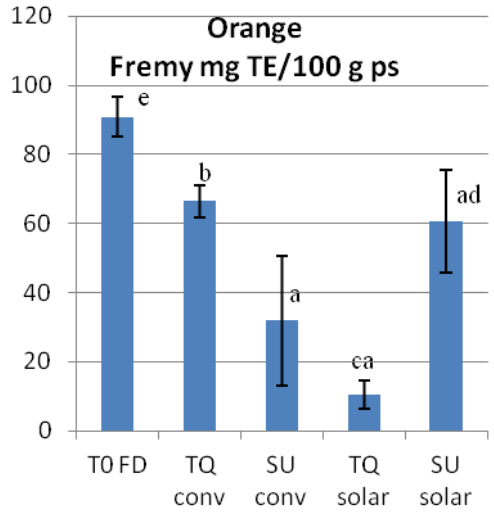

Fig. 24. Orange dried slices: EPR with probe Fremys' salt before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

The residual humidity values (tab. 17) reached by the two drying systems show a good efficiency of both the drying systems. Only the sample TQ solar shows a relatively high value (remaining within the stability range) due to persisting bad weather conditions during the drying.

It is also important to take into account that in this study the conventional drier have been used with different settings than those commonly used by drying industry. Temperature never exceeded 45°C, in the intent to obtain a less heat damaged product. This setting resulted in a substantial lengthening of drying time

	Lemon		***Orange***	
	% H2O	*sd*	*% H2O*	*sd*
T0 FD	4,89	0,276	4,82	0,311
TQ conv	5,39	0,269	5,54	0,185
SU conv	4,83	0,095	4,64	0,358
TQ solar	6,53	0,104	16,70	0,068
SU solar	6,92	0,540	8,78	0,607

Tab. 17: Karl Fisher titration: residual humidity values in orange and lemon samples after processing.

3.2.1.5 Conclusions

Products made from lemon are not directly consumable as a snack because of their hardness and their bitter and sour taste (which is typical of fresh lemon that, in this case, resulted very boosted). May instead be used as flavouring agent in the formulation of other food products. Biochemical assays suggest that the samples unsweetened, dried conventionally, show a better retention of bioactive compounds. Sensory analyzes show (§ 3.3.2.4) a difference in the perception of the two different drying techniques, with a preference towards the sun drying ones. Orange dried products can be consumed directly as snacks, as indicated by informal sensory tests, during which was also expressed particular appreciation to their very "natural" appearance. Biochemical assays have not given results that can be described in a general way. Their use as ingredients in flavored yoghurt showed a high liking value and a preference for the solar dried samples (§ 3.3.2.4).

3.2.2 Dried Peperone di Senise

3.2.2.1 Raw materials description and peculiarity

Capsicum annuum, L. var Senise is the first Italian PGI vegetable (EC Regulation no. 1263, 01.07.1996, Official Journal EC L 163, 02.07.1996). Its growing area is 120 km south-east from Potenza, between the cities of Potenza and Matera, in the Basilicata region. It is sold fresh or dried.
In this study, the PGI product from Senise (40° 8' 3.71"N, 16° 17' 0.10E) has been compared with berries grown at different latitudes in the north and in the south of Italy: Montanaso Lombardo (45° 20' 33.58"N, 9° 26' 50.18"E) and Battipaglia (40° 35' 34.28"N, 14° 59' 1.20"E).

3.2.2.2 Research goals

The purpose of this study was to compare the same raw material, dried by three different ways: by a solar dryer, by a conventional dryer, by the traditional method (using PGI product purchased on the market). In addition, it was intended to make a comparison between the same type of pepper berries grown in different places, with the aim of verifying the existence of detectable differences in the dried products. Even in this case have been employed both solar and conventional drying techniques. The reference used for comparisons was the fresh product.

3.2.2.3 Materials and methods

3.2.2.3.1 Production method

Berries of *Capsicum Annuum* L. var. Senise pepper were grown at the Agricultural Research Council CRA ORT in Battipaglia and CRA ORL in Montanaso Lombardo. After harvesting the berries were washed, dried, cut in halves and dried both in a solar drying system and in a conventional one. The end of the processing was determined by reaching of the product's constant weight.

3.2.2.3.2 Product description

In this work berries grown in two different Italian regions have been dried using two different drying systems: a solar drier and a conventional drier, while the dry PGI product was purchased on the market (where it's available in whole berries or in powder). This traditional product is dried by direct exposure to air and sunlight for several weeks.
The dry PGI product can be consumed directly or as an ingredient in many typical foods.

3.2.2.3.3 Analytical methods

1 g for each sample were extracted in 9 ml of ethanol, HCL0,02N 1:1 solution, mixed with a Vortex equipment for 2 min, than centrifuged al 10000 rpm for 10 min. The supernatant were stored at -80°C for further analysis. Ascorbic acid content was measured in according to Picchi et al. 2012.
Total polyphenols index has been evaluated by the Folin-Ciocalteu reaction, as described in Singleton and Rossi (1965) on samples diluted 10 folds v/v.
Free radical scavenging properties were measured by EPR analysis by means of TEMPO and Fremy'salt probes, using a Miniscope MS 200 Magnettech (Berlin, Germany). All measurements were performed in triplicate. Samples extractions and methods are described in § 3.2.1.3.2.
Photochem is an automatic system (by Analytikjena AG), capable to quantify the antioxidative capacity by means of a photobioluminescence reaction using Luminol and calibrated with a Trolox solution. 20g of sample were pounden in a mortar, 0.5g of powder were added to 20 ml of methanol, shaked with a Vortex equipment for 3 min, centrifuged at 13200 rpm for 2 min. The supernatant was instantly analyzed. Preparation of calibration curve was performed as described in the standard protocol kit, using volumes as displayed in the scheme reported in tab 18. Calibration substance was ascorbic acid. All solution (R1, R2, R3, R4 are covered by a patent and sold by Analytikjena AG). Photochem equipment realize automatically the measurement.
RSR, pH, titrable acidity, dry matter were analyzed according to AOAC, 1980.

Reagent	R1 (µl)	R2 (µl)	R3 (µl)	R4 (µl)	Sample (µl)
Blank	1500	1000	25	0	0
Calibration	1500-x	1000	25	x	0
Measurement	1500-y	1000	25	0	y

Tab. 18: Pipetting scheme for Photochem measurements (from Analytikjena official method).

Carotenoids were analyzed as follows: 50 mg of powder was extracted in 0.8 ml isoctane, 0.1 ml acetone and 0.1 ml BHT solution (1% butylated hydroxytoluene in ethanol), by vortexing for 30 sec. Samples were then centrifuged at 10000 rpm for 5 min. The pellet was extracted

twice. Extract absorbance at 450 nm was measured in a 1 cm path length cuvette (UNICAM UV/Vis spectrometer), and total carotenoids were expressed as β-carotene equivalents at 450 nm (mg β-car. eq/100 g fw) by using the calculated absorption coefficient ($A_{1\%}$ = 2786.4) of a pure β-carotene commercial standard solution, according to the Beer Lambert law.

3.2.2.4 Results and discussion

Ascorbic acid (AsA) is strongly represented in *Capsicum annuum* L, especially in the varieties grown in southern Italy (Perrone et al., 2011).

The following charts allow to study the behaviour of two drying techniques (solar *vs* conventional) and the behaviour of the same cv grown at three different latitudes (Montanaso Lombardo, Battipaglia, Senise PGI). The reference data is the value provided by the freshly harvested starting material immediately freeze dried.

Fig. 25 shows the evolution of the AsA. The two fd samples show a similar value, significantly higher than the others. The conventional dried samples (Battip conv and Mont conv) are always greater than the corresponding solar dried (Mont solar and Battip solar), while the PGI product shows the lowest retention. A similar trend was expected and mainly reflects the treatment length effect on ASA degradation: the shorter treatment is the conventional, followed by the conventional with sweetened samples, while the solar tq and with sweetened samples required the longest time (which is the same for both).

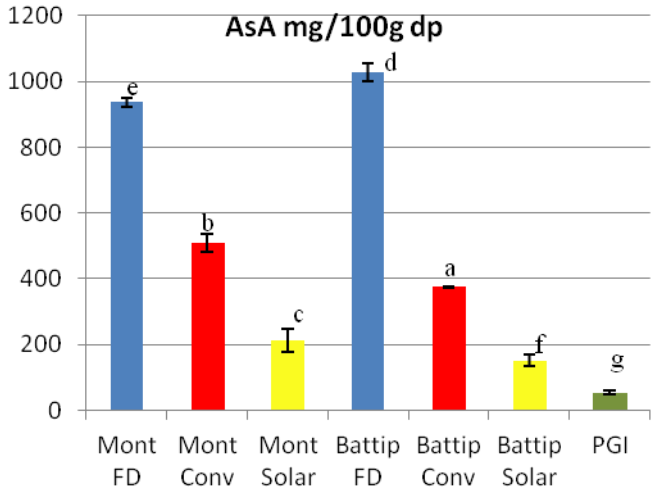

Fig. 25. Dried Senise pepper: evolution of ascorbic acid before and after the processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

PGI samples have a very low retention of AsA since the traditional drying method involves several weeks of exposure to sun radiation. The antioxidant capacity trends of the assays by EPR Fremy 'salt, EPR TEMPO and Photochem are similar to that of AsA, in fact the methods show a good level of correlation (Tab 19).

Method	Correlation
TEMPO vs AsA	0,837
FREMY vs AsA	0,898
FREMY vs PHOTOCHEM	0,793

Tab. 19. Dried Senise pepper: Correlation among the different methods used for antioxidant capacity measurement.

The Folin Ciocalteaeu reaction (Fig. 26) shows a different trend. The fd samples have smaller values, while the largest are the two conventional dried samples, which have values very close to the Battip solar and PGI samples. The Folin Ciocalteu test is sensitive to a broad number of molecules including AsA and Maillard compounds. In this case it appears that the AsA contribution to the index variation is very low, if compared with a very high effect due Maillard compounds presence. The neo-formation of the latter compounds is promoted both by high temperatures (conventional drying), and by high concentration of carbohydrates.

	DM	sd
Mont fresh	14,28	0,35
Battip fresh	17,00	0,25

Tab. 20. Initial dry matter content in fresh Senise peppers from north (Montanaso Lombardo) and south (Battipaglia) of Italy.

In Table 20 is shown that Battipaglia pepper presents a soluble solids content considerably higher than Momtanaso pepper. Such a composition variation may explain the high value of polyphenol index shown by Battip solar and IGP samples.
The carotenoids content trend (Fig. 27) expresses a situation of general stability, with respect to previously considered changes. This result was expected, as this type of molecules has a good stability and resistance to heating if compared to AsA.

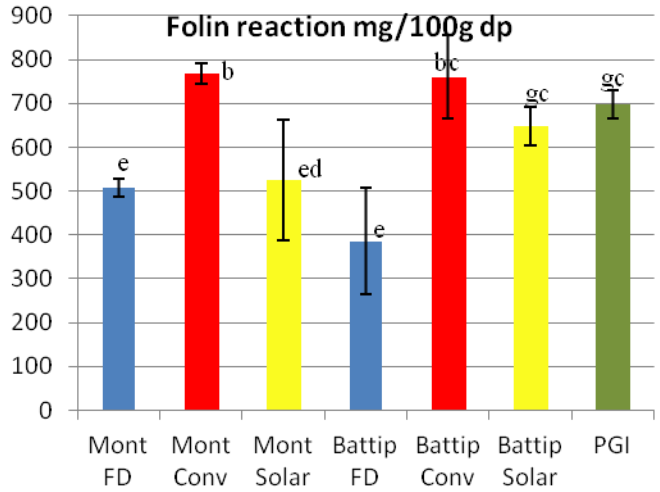

Fig. 26. Dried Senise pepper: total poliphynol index before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

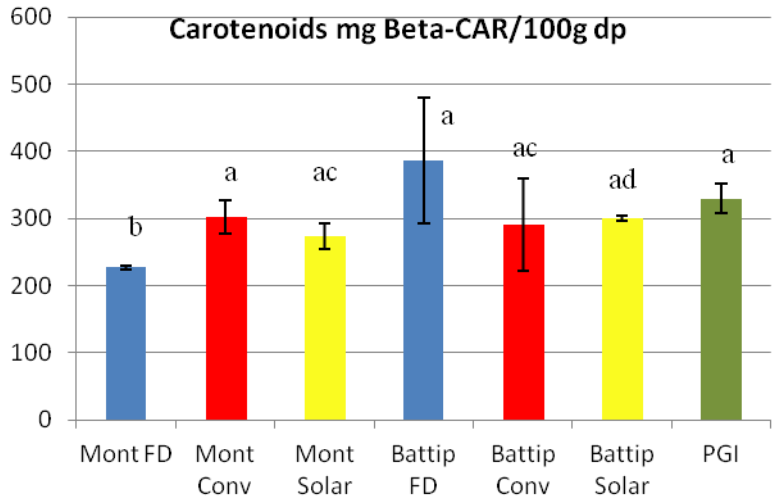

Fig. 27. Dried Senise pepper: carotenoids content before and after processing. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.2.2.5 Conclusions

The drying techniques gave significantly different results when compared between each other, both when compared with the commercial PGI product.

Almost always the solar dried products showed intermediate characteristics between the conventional dried products and the dried PGI products. The latter showed as the most degraded by processing.

From the second comparison could be assumed that the peppers area of cultivation may affects in a perceptible measure the degradation level of the dried products. In fact, the peppers grown in northern Italy (that is not the vocation area for growing) develop a smaller quantity of sugars compared to what happens in peppers grown in their area of vocation, thus contributing to a minor extent in the non-enzymatic degradation reactions.

3.2.3 Conclusions of group 2

The products obtained by means of the solar drier are characterized by the following reasons:

- produced using only solar energy
- can be consumed either directly, or as ingredients in other food products
- have a long shelf life.

3.3 Products obtained by means of combined techniques

However it is important to stress the fact that products obtained by means of the prototype plants here studied are also suitable to be used as ingredients in other food developments of products that can be considered complex from a technological point of view.
In this section are shown two products obtained by a combination of different techniques, meaning that an ingredient or a process step is realized through one of the prototype plants used during this work.
The goal was to develop at least two products characterized by the inclusion in the processing flow of common products, one or more steps or ingredients obtained as result of a combined use of the machines available for this work (the miniaturized processing line and the solar drier).

3.3.1 Apple candies

Apple candies have been the first product developed in this section. Their production involves the preparation of a semifinished product (obtained by the processing line), then dried by the solar drying system.
In the present research common apples were used in order to obtain candies using a traditional recipe using an innovative drying system. The product here studied is similar to "cotognata", a sweet preparation obtained by apple cv Cotogna. In the traditional recipe (Artusi, 1891) the semifinished drying is obtained through direct solar exposure, which provides a fast superficial water loss, but gives no UV radiation and parasites/environmental protection.

3.3.1.1 Research goals

The purpose of this work is to develop a confectionery product based on apple. Is required a comparison among three different drying methods: by direct exposure to solar radiation (traditional system), through a solar drier and by means of a conventional dryer. Possible differences perceived by the consumer between "traditional" dried candies and solar dried, will be assessed by a triangle test. It also sought to verify the behaviour of texture and colour after a 6 months storage period at 20°C. Finally, the electricity consumption related to the processing will be measured.

3.3.1.2 Materials and methods

3.3.1.2.1 Production method

Due to logistic reasons, the semifinished product processing did not take place through the use of the multi functional processing line, but in a smaller scale, in an experimental kitchen at the CRA-IAA. Even if it has not been done, it's important to note that the line's features do not present any limitation for this kind of production.
Whole organic apples cv Pink Lady® purchased at the local market (12,1°Bx) were washed, decored, cut in pieces (approximately 30 g each), then added of water and cooked in a professional cooking machine (Zanussi, Italy) for 15 minutes. The cooked fruit was blended for 3 minutes and the solid particles were removed using a 2 mm sieve. The fluid obtained was added of sugar, transferred to a 60 cm stainless steel pan an kept boiled, until the mass reached 55°Bx of soluble solids content. The product obtained (the semifinished product) has the appearance of a viscous fluid, and was poured into a stainless steel mould (400 x 200 x 18 mm). The semifinished product has been dried using three different techniques: samples "UV", by direct sunlight exposure (traditional method); samples "S" by using a solar drying system; samples "E", by using a conventional drier (70°C, air 3m/s air speed, tangent flow).
The semifinished product drying (for each of the three techniques used) took place in two different phases: the first was performed keeping the fluid semifinished product in the mould. It lasted until the initial fluid has reached a gelatinized consistency strong enough to be able to maintain its

geometry after removal from the mold. Afterwards the gel block were cut into 18 mm cubes for the second drying phase, lasted until it reached the weight stability.

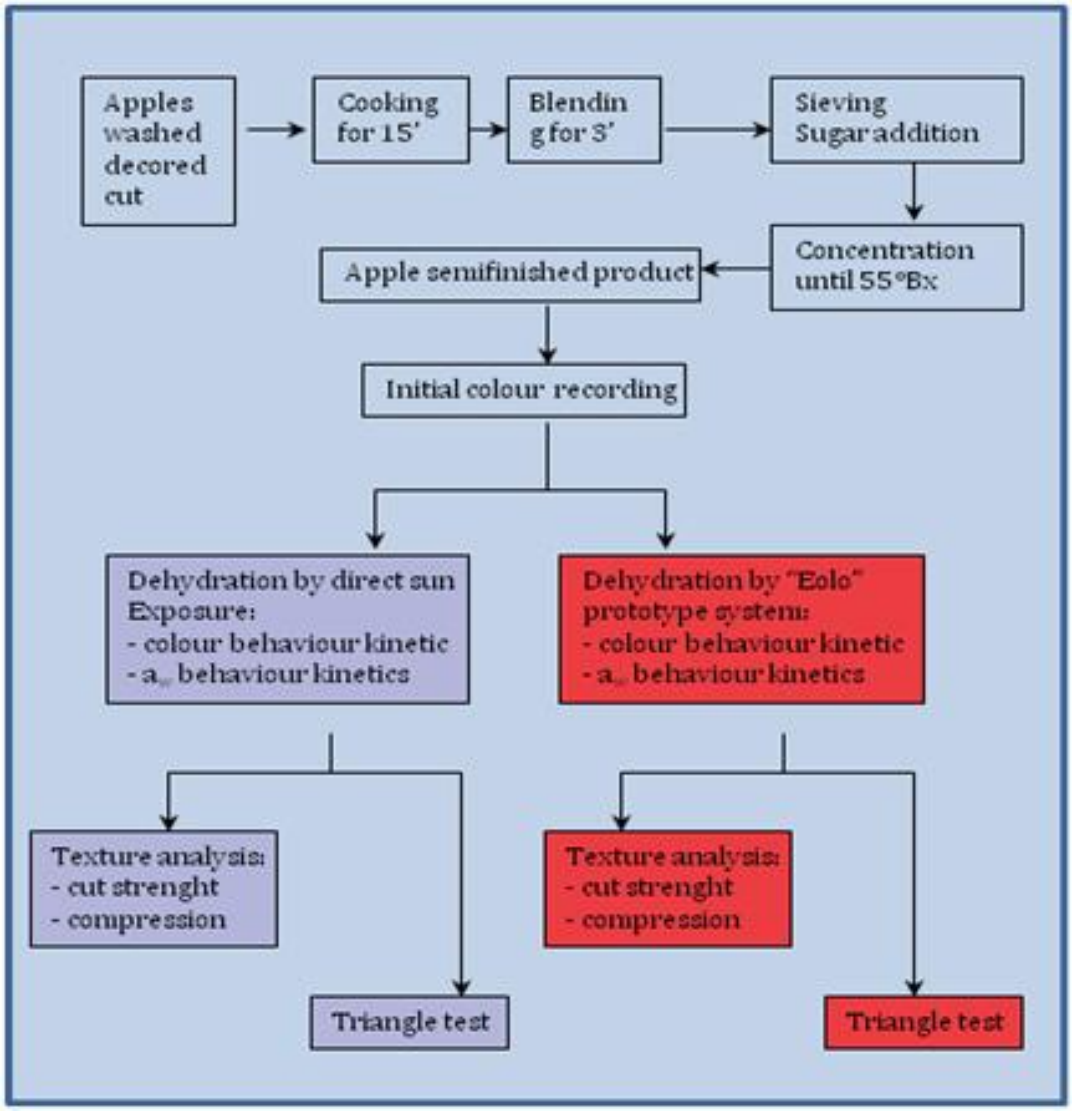

Diagram 6. Apple candies production scheme and analyses steps.

3.3.1.2.2 Product description

The product obtained is a candy showing a translucent aspect and an intense coloration. The surface is glossy but also sticky, so not suitable for a packaging that does not include the wrapping of the individual pieces.

Fig. 27. A view of Apple candies.

41,0 %	apple slices with skin
31,0 %	Sucrose
25,0 %	Water
1,5 %	lemon peel
1,5 %	lemon juice

Tab. 21. Apple candies initial composition.

3.3.1.2.3 Analytical methods

During drying, were monitored the following parameters: temperature and relative humidity, colour coordinates, water activity (a_w); texture analysis was performed on the finished product. A consumer test was also performed by means of a triangle test.
For shelf life evaluation were considered colour and texture evolution in a 6 months storage at 20°C in darkness. The product was packed in plastic trays containing 24 pieces each, inserted in a PET bag closed with a string.
The power consumption of the conventional process was recorded (see § 3.4.3).

Colour coordinates: determined using a D65 illuminant/10° observer reflection colorimeter (Minolta Chroma Meter CR 200 – Minolta Camera Co. Ltd., Japan). The initial colour recording was determined by using an optical glass cell (5 cm diameter, covered with a standard white standard plate) containing a 18mm layer of semifinished product (before pouring it in the mould). The colour of the semifinished product has been used as reference colour. For all the other samples the analysis was carried out by positioning the product cube directly on the colorimeter probe, keeping the white standard plate behind it.The CIE L a*b* coordinates were simultaneously measured. Results are the means of 10 determinations.
Texture: by cut strength test, using a Stable Micro System TA XT II plus, fitted with a 5 kg cell and a Warner - Blatzer blade. The maximum force peaks were directly compared. Results are the means of 10 determinations
by compression, using the above mentioned instrument, fitted with a 5 kg cell and a 2,5 cm diameter compression plate. The maximum force peaks were directly compared. Results are the means of 10 determinations

Triangle test: a standard triangle test (UNI, 2001) was carried out using an integrated Fizz system. The test was applied to determine if a consumer detectable difference existed between the samples. The test was carried out in a dark room, due to the evident colour difference among the samples. The test has been performed only on samples S and UV.
Water activity (a_w): by an electronic hygrometer (Aqua Lab. CX-2 – Decagon Devices, Pullman, USA). Results are the means of 6 determinations.

3.3.1.3 Results and discussion

The weight reduction behavior during the drying process (monitored by the variation of a_w) does not show significant differences between the two techniques used (see Fig. 29) between UV and S samples.
Texture: Compression test evidence a similar behavior of S and UV samples, wile sample E results harder. Cut test (fig. 30) does not show significant differences of cut strength values among the samples lower than S samples. Nevertheless, sample S shows a tendency to higher values.
Colour: L values analysis (Fig. 31 a) show all samples are different: UV is the lighter and follow S, E, reference. Analysis of a* values (Fig. 31 b) shows that E and UV samples ari higher than reference, but no differ between them, while sample S is the higher. Analysis of b* values (Fig. 31 c) shows two groups: reference and E samples; S and UV.
Triangle test: a perceptible difference exists between the samples, as shown in Tab. 32.

3.3.1.3.1 Shelf life results

Colour: the thesis shown the same behavior during the storage. After 6 months was detected a decrease of all L, a*, b* coordinates, but probably not perceptible to eyesight due to the narrow variation interval (see tab. 23).
Texture: After a 6 months storage was detected a significant amount of both compression and cut forces (see fig. 32 a, 32 b). The thesis show a similar behavior to the tests: E tends to have lowest values, while solar shows always the highest.

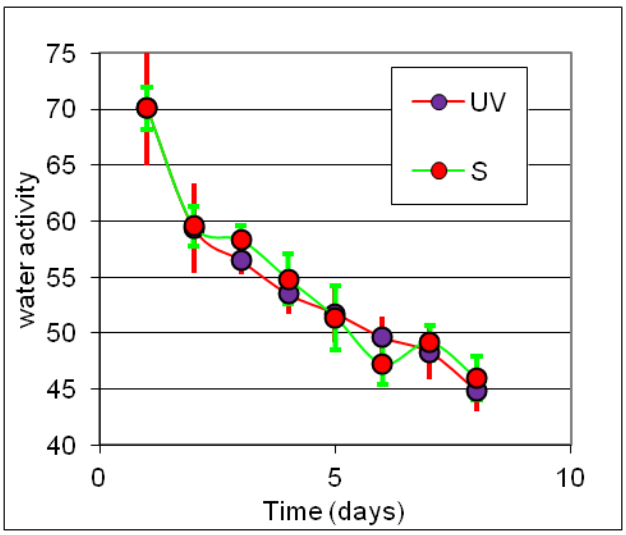

Fig. 29. Apple candies: a_w Kinetics samples UV and samples S during dehydration process.

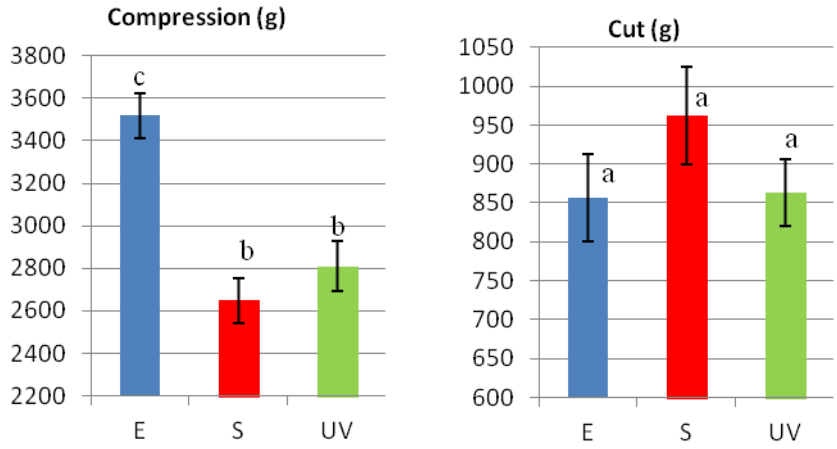

Fig. 30. Apple candies: texture analysis. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

Test	Without answer	Answers taken	Answers right	Signif. (risk)
P1/P2	0	33	27	<0.0001

Tab. 22: Triangle test results for Apple candies S *vs* UV samples.

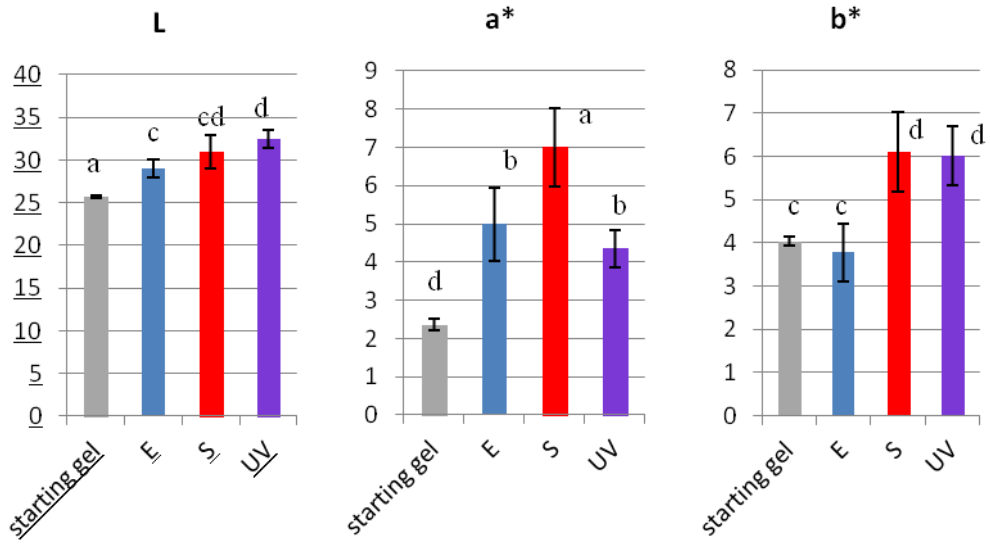

Fig 31 a, b, c. Apple candies: comparison of initial colour data L a*b*. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

Months	Le	sdLe	Ls	sdLs	LUV	sdLUV
0	29,02 a	1	30,99 b	1,93	30,99 c	1,93
2	28,99 a	1,19	30,87 b	0,9	32,18 c	1,08
4	29,35 a	1,04	32,89 b	1,19	32,89 c	1,19
6	29,4 a	0,83	30,19 b	0,58	30,19 bc	0,58
	a*e	**sda e**	**a*s**	**sda s**	**a*UV**	**sda UV**
0	4,99 b	0,96	7 d	1,03	7 c	1,03
2	6,82 b	2,07	5,88 d	1,18	5,75 c	1,69
4	9,09 bc	1,96	10,64 e	1,86	10,64 a	1,86
6	5,34 b	1,15	4,6 db	0,7	4,6 dc	0,7
	b*e	**sdb e**	**b*s**	**sdb s**	**b*UV**	**sdb UV**
0	3,78 e	0,66	6,12 d	0,92	6,12 d	0,92
2	3,78 e	0,97	5,38 d	0,96	6,64 d	1,58
4	4,59 e	0,95	8,5 f	1,66	8,5 d	1,66
6	3,16 e	0,51	4,06 fd	0,41	4,06 e	0,41

Tab. 23. Apple candies: colour component L a*b* variation during a 6 month storage at ambient temperature.

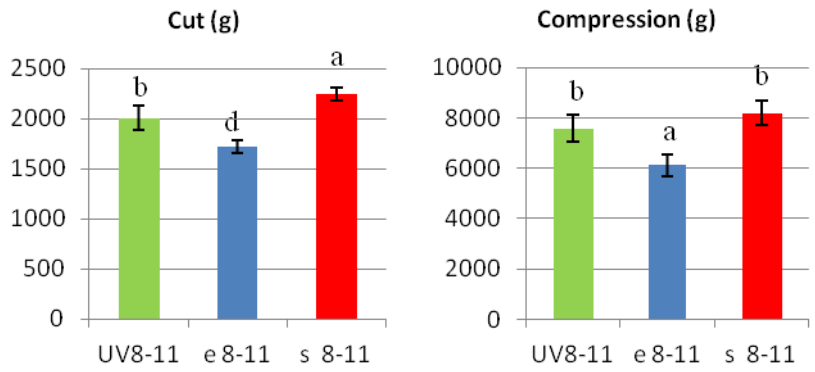

Fig. 32 a, b. Apple candies: texture analysis after a 6 month storage at ambient temperature. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.3.1.4 Conclusions

Drying foods by means of solar exposure using a protected system, such as the prototype used for this research, can provide significant benefits:

- more intense and consumer accepted product colour
- product softer but thicker at chewing
- improved product hygiene (the system protects the product from animal contamination and weathering)

- no energy required for production
- Shelf life behavior did not evidenced differences between the two different products, however a 6 months storage evidenced a significant increase of texture parameters.

3.3.2 Flavoured yogurt

The second product of this section have been developed at Tallinn University of Technology, Estonia, during a PhD internship which took place from September to December 2012, under the supervision of Prof. Raivo Vokk. The study goal was to develop a product flavoured through the addition of a solar dried semifinished product. At start, the choice has been oriented toward savory biscuits development. So three different savory biscuits, flavored with orange, lemon and pepper respectively have been prepared. Despite the three flavouring powders aromatical intensity were high, and even though were carried out some attempts with increased powder content and with different dough formulations, poor results were obtained. It resulted that the dough was not able to retain the flavour during the cooking step. So the snacks development has been stopped.
The choice was directed towards a dairy product. Among many option was chosen yogurt, especially by being able to be prepared from raw milk by means of the multi-functional processing line (see § 3.1.6 and 3.1.7).

3.3.2.1 Raw materials description and peculiarity

The products described in § 3.2.1 and 3.2.2 have been used as the flavouring agents for this product group. Because this study was developed in Estonia, it has not been possible to prepare the yogurt using the multi functional processing line. Commercial plain yogurt by whole cow milk (purchased on the market) has been used as product base.

3.3.2.2 Product description and research goals

The final yogurts developed contain different flavouring agent concentration but the same quantity of added sugar. In addition to the product development, the research studied through sensory analysis some product's characters linked to consumer perception and liking. In the study were compared if and how the consumer perceive the different drying techniques used to obtain the flavouring agents (solar or conventional for orange and lemon; solar, conventional, PGI product in the case of the Senise pepper). The whole sensory study has been realized in Tallinn, Estonia and in Milan, Italy (except the Napping test), in order to obtain a comparison between the product perception of two culturally far countries.
Flavoured yogurt's consume is thought as a common sweetened yogurt. The Senise pepper flavoured type, is also thought to be used as sauce for main dishes.

3.3.2.3 Materials and methods

3.3.2.3.1 Production method

By the use of a hammer mill the products described in § 3.2.1 and 3.3.1 have been powdered in order to obtain three flavouring agents.
Plain commercial whole yogurt have been added of 5% of crystalline sucrose and of the following amounts of flavouring powders (each thesis have been added of two different flavouring concentration):
- senise pepper grown in Montanaso Lombardo sun dried, conventional dried: 3 and 5%
- Senise pepper grow in Senise sun dried, conventional dried: 3and 5%
- Senise IGP dried pepper sun dried, conventional dried: 3 and 5%
- orange, lemon sun dried, conventional dried: 4 and 7%

Mixing of plain yogurt, powdered flavour, sucrose took place 12 hours before the sensory test. Product dosing in the test cup (*circa* 5 g each cup) took place immediately before the test.

3.3.2.3.2 Analytical methods

A method, called Napping®, was recently developed (Page`s, 2003, 2005a). It allows to collect directly an euclidian configuration for each subject in a unique session. It consists in collecting the sensory distance perceived among products by positioning the products on a sheet of blank paper in such a way that two samples are very near if they are perceived as identical and that two samples are distant from one another if they are perceived as different. Each judge chooses his own criteria and the relative importance that he wants to give: relative importance of the criteria is thus directly taken into account.

Napping (Risvik *et al*. 1994; Pagès 2005)

"The set of *I* products is presented to the panelists who are asked to position the products on a large sheet of paper (tablecloth) according to their similarity, i.e., two products are all the more close (on the tablecloth) as they look alike and all the more distant as they differ. For a given panelist, the data can be assimilated to the two coordinates of the products on the tablecloth.

For each of these procedures, panelists are informed of the overall character of the evaluation (hence, the term "holistic approach") and of the fact that they must use their own criteria, i.e., those which are the most important to them.

In addition, the three procedures have in common the quality of being nonverbal (Issanchou 1998). Nevertheless, in practice, categorization and napping are often enhanced by a collection of words in order to characterize the group (categorization) or the products (napping). These words are essential to interpret the differences between the products; in some cases, they can even lead to a sensory profile for each product, which value is due to its synthetic and spontaneous character (Perrin and Pagès 2009).

Some well-established methodologies can be used to analyze the data resulting from these procedures: the Individual Difference Scaling model (Carroll and Chang 1970) or the usual multidimensional scaling (Cox and Cox 1994) for the matrices of similarities; multiple correspondence analysis (MCA) for the categorization data (the products are the statistical units and the panelists are the variables, each one of them being assimilated to a partition; Cadoret *et al*. 2009); multiple factor analysis (MFA; Escofier and Pagès 2008) for the napping (each tablecloth defines a group of two unstandardized quantitative variables, the X-coordinate and the ordinate).

Probably because of practical considerations and its nonverbal character, the direct collection of sensory similarities is not often used. On the other hand, categorization and napping are becoming increasingly popular as can be testified by their availability in softwares dedicated to sensory analysis (Fizz software [Fizz 2009; Biosystemes, Courtenon, France], EyeQuestion [EyeQuestion 2009; Logic8, Wageningen, The Netherlands]). Since their objectives are identical, the choice between one and the other method depends on the importance granted to their characteristics by the end user (e.g., categorization is known to be simple, whereas napping is known for being not too categorical but on the contrary more smooth) but also on his own practices.

The two procedures can be combined by asking panelists to provide a tablecloth on which groups of products appear. The idea of this new mixed procedure, called "sorted napping," comes from:

(1) A"behavioural"origin:forthenapping,ithasbeenobservedthatpanelists often group their products as they build their tablecloth; the two tasks, napping and categorization, seem to be carried out jointly. In that sense, sorted napping task is not more complicated than napping task.

(2) A "technical" origin: one can think that the napping will bring nuances to the categorization and that the categorization will emphasize some aspects of the napping. This idea to combine qualitative and quantitative approaches has already been used in sensory analysis in the framework of products discrimination (Bradley and Harmon 1964)."

Estonian Panel (November 2012)

The panel was composed of 25 students (aged between 22 and 26), all Estonians. The test was carried out at the Tallinn University of Technology, Estonia.

Italian Panel (July 2013)
The panel was composed of 24 people (aged between 26 and 55), all Italians, most of them were experienced in sensory testing. The test was carried out at CRA-IAA.

Protocol
To each judge was given a paper sheet (29.7 X 29.7 cm) and a set of 16 samples (14 samples + 2 repeated controls). The set was randomized and lined up according to a balanced Williams design. They were asked to taste them following the presentation order, with the aim to place them on the sheet according to the criteria of similarity / difference described above (with the possibility to go back to an already tasted sample).
After the Napping were asked to group the samples into coherent clusters. It has also been asked to associate the clusters, or possibly each product, to some words belonging to a group of attributes previously agreed (during the pre-test briefing). At the end of Napping has been subjected to the participants a questionnaire consisting of four questions relating to: overall taste intensity, overall liking, bitterness, willingness to buy.

3.3.2.4 Results and discussion
PCA analysis (Fig. 33) shows well clustered samples into three groups comprising respectively orange, lemon and pepper flavored samples.
Fig. 34 shows the correspondence between comments and samples. It is evident a good level of congruence between the distribution in terms of comments and samples. Here are also shown clusters defined by the point of view of the relationship between sample type and associated sensory comment.

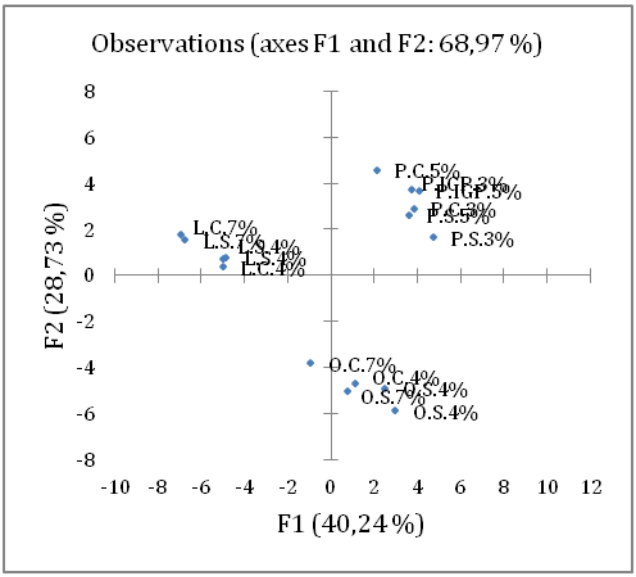

Fig. 33: score plot of PCA on yogurt samples.

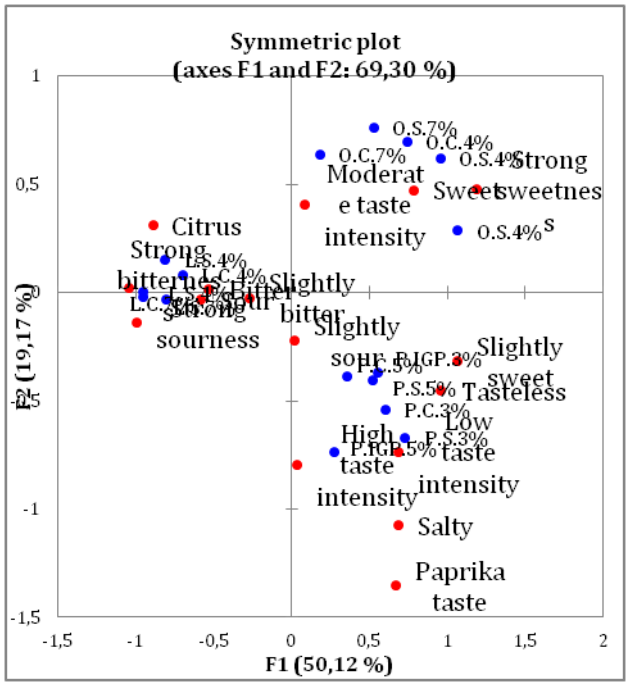

Fig. 34: correspondence between comments and samples of flavoured yogurts.

The questionnaire data are shown in the figures 35 and 36, which the numbers 1, 2, 3 represent the perception level respectively coded as: "too little ", " about right ", " too much". The graphs should be read "in pairs" because the drying technologies (solar *vs* conventional) are here compared.

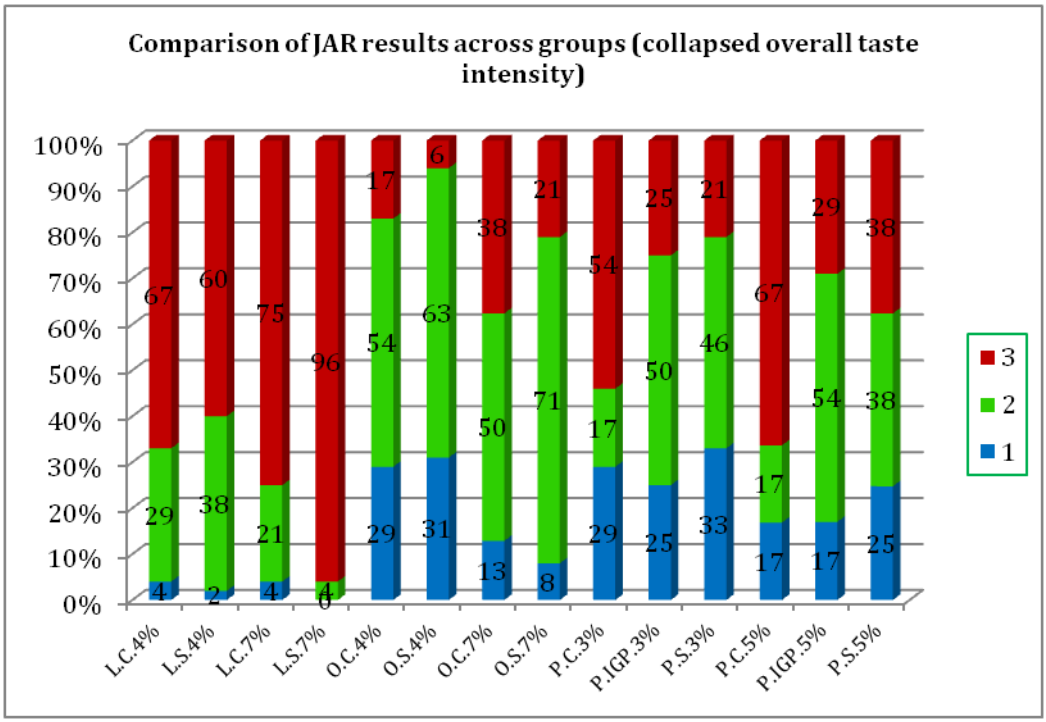

Fig. 35a: Perceived intensity of flavoured yogurts samples in Estonian panel.

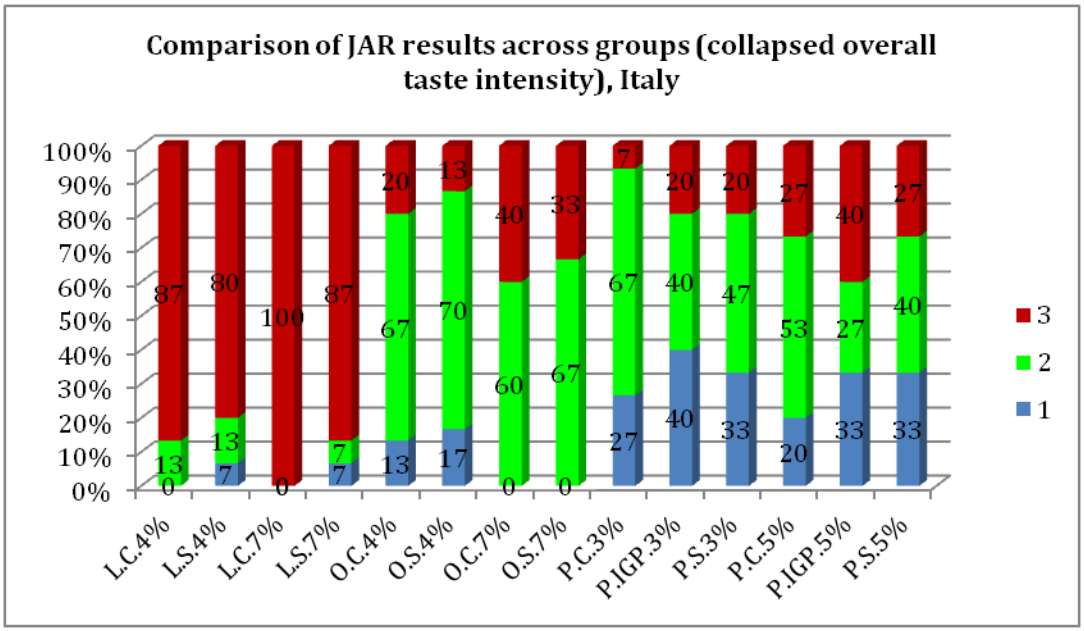

Fig. 35b: Perceived intensity of flavoured yogurts samples in Italian panel.

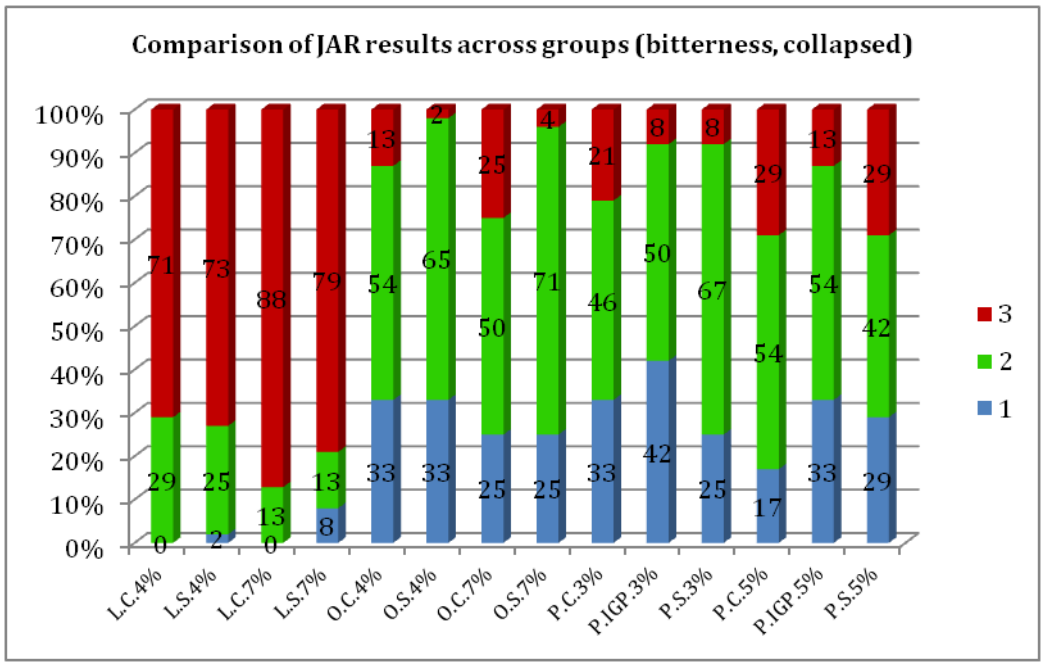

Fig. 36a. Bitterness Level of flavoured yogurts samples perceived by Estonian panel.

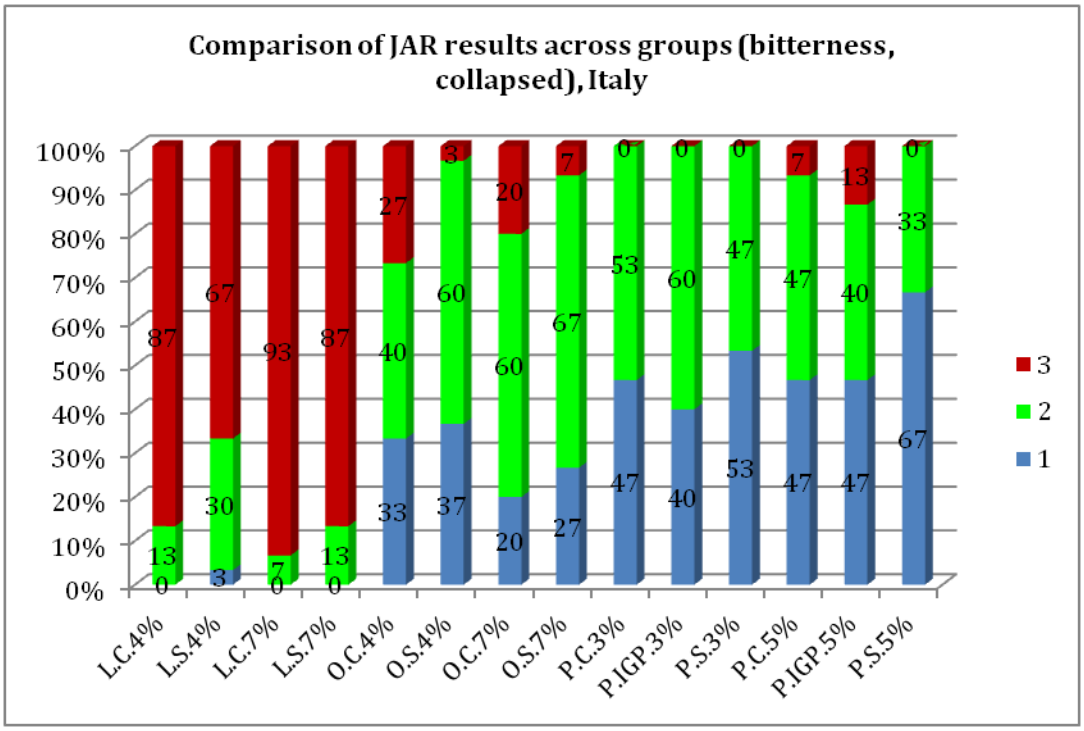

Fig. 36b. Bitterness Level of flavoured yogurts samples perceived by Italian panel.

With regards to the taste overall intensity (Fig. 35a, 35b) the samples flavored with lemon are generally classified as of "too much" and, in Italian results, it appears even more marked. In orange and pepper samples was noted a sharp increase in the perception of "about right" for all samples. In Estonian results it resulted a higher rating for samples of orange and pepper containing solar dried products. In Italian results is recorded the same result only for orange samples; on the contrary, samples containing pepper conventionally dried always show a rating higher than solar dried ones. Only in Estonian results, the samples perception of samples with PGI pepper results as better than those conventionally dried. By taking into consideration the Estonian bitterness perception (Fig. 36a), a similar consideration can be made, except for the samples containing 5% of pepper, for which the solar dried is perceived as "almost right" to a lower rating than the other two thesis containing the same powder concentration. Taking into account Italian bitterness perception (Fig. 36b), citrus samples flavoured with solar dried, result in a higher rating than conventional dried. This is not true for pepper, where conventional dried are perceived with the higher ranking. In general, seems that Italian panel shows a lower sensibility to bitterness perception: this appears very clear by comparing Italian and Estonian Pepper flavoured samples

The overall liking (Fig. 37) shows that in general: there is a tendency for Estonian assessors to give a higher rating to citrus products, than Italian assessors and to give a lower rating to pepper samples. Samples containing lemon are the least appreciated (especially those in higher concentration), the most appreciated are orange flavored, with a general preference for the solar dried, at both concentrations. Among the 3% pepper samples, in both Italian and Estonian results, the least popular are the PGI, while in 5% flavoured samples Italian accessors expressed a preference for the solar diried, and Estonians preferred the PGI (PGI is a solar dried). Fig. 38 shows the "willingness to buy". The orange flavored samples are the most "likely purchased", with a strong preference (at both concentrations) for the solar dried within the Estonian panel. Italian panel expressed a preference for conventional dried at 4% and for solar dried at 7%. Neither Italian nor the Estonian assessors would buy the lemon flavoured yogurt, at any concentration. Estonians would not buy even the pepper flavoured, while Italians results referred to pepper flavoured show an intermediate value which means they could reflect a "maybe I will buy" expression, with a preference towards the products containing a 3% of pepper powder.

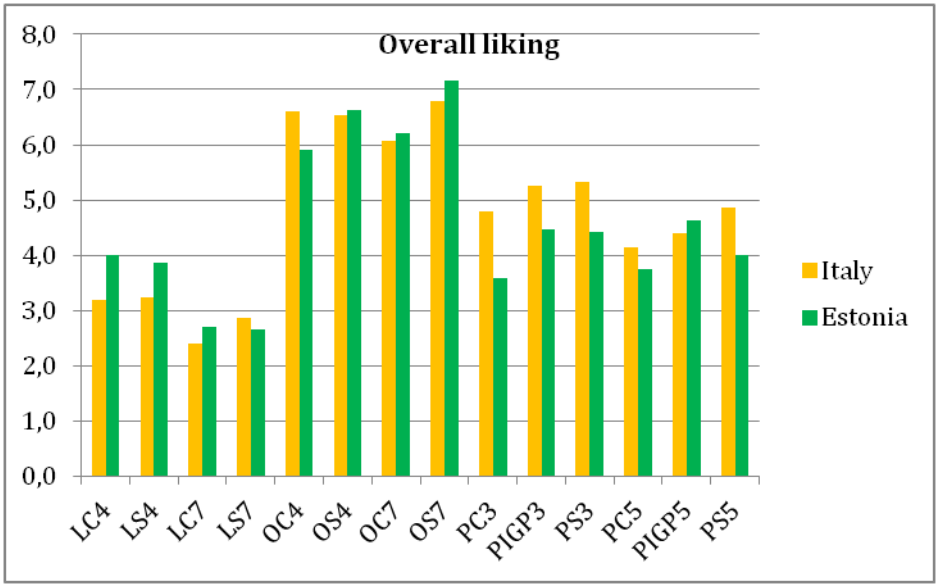

Fig. 37. Results of overall liking evaluation test of flavoured yogurts.

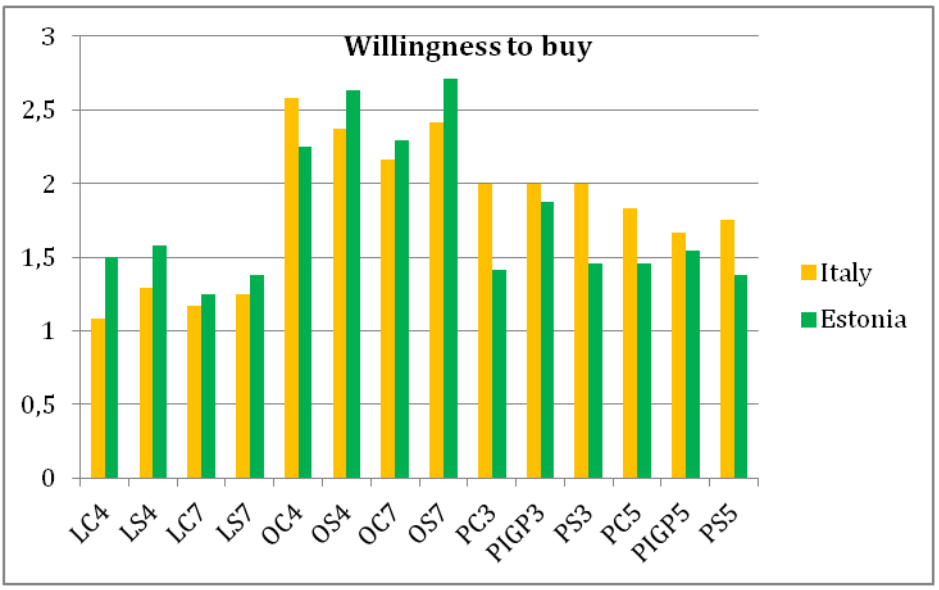

Fig. 38. Results of consumer's willingness to buy evaluation test of flavoured yogurts.

3.3.2.5 Conclusions

The products met a good level of consumer liking, even though the "willingness to buy" test results didn't reflect a real will to buy this product, except for the orange flavoured ones. In addition, the results showed 2 interesting trends: one depending by the nationality habits, one independent. The former shows a tendency by Italian panel (if compared with the Estonian), to over feel the taste intensity of the lemon flavoured products and under feel the bitter taste of the pepper flavoured samples. The latter shows a general tendency to associate a better feeling to products containing sun dried flavours.

It is important to stress that in this kind of tests, the data variation is very high due to judge variability. Thus the above considerations have to be meant as panel's possible tendency.

3.3.3 Conclusions of group 3

The combined use of techniques enables a good optimization of raw materials and energy consumption. Sensory tests showed that the products here obtained had a good appreciation by the consumer, often indicating a preference for the product obtained through the use of solar energy.

3.4 Use of renewable energy sources

The studies related to the use of alternative energy sources have followed two different paths, depending on the system used.
The production tests regarding the multi functional processing line were conducted during summer 2013. Since those trials have also coincided with the first tuning experiences of the renewable energy section of the prototype, their execution initially presented a number of technical problems then solved.
In addition to a set of experiments regarding the heating topic, the polyvalent production line has been used for experiments regarding the production of a fruit preserve. The goal was to realize the heating and evaporation phase by using solar energy as the only power source
During spring / summer 2011 and 2012 took place the experiments regarding the solar drier. They concerned the production of vegetal semi-finished and finished products obtained using solar energy as the only energy source (see § 3.2.1 and 3.2.2). During 2012 and 2013 were carried out the trials regarding the use of semi-finished dried products as ingredients in other processing fields e.g. dairy products or candies (see § 3.3.1 and 3.3.2).

3.4.1 Use of renewable energy sources by means of a miniaturized multi functional processing line

3.4.1.1 Sanguinello orange marmalade type 1

3.4.1.1.1 Raw materials description and peculiarity
See § 3.1.2.1

3.4.1.1.2 Product description
See § 3.1.2.3.2.

3.4.1.1.3 Research goal
The goal was to measure the difference of energy consuption during the processing through the comparison of a conventional processing cycle with another one, carried out in the same way but with an alternative energy source coupled to the processing line.

3.4.1.1.4 Materials and methods

3.4.1.1.4.1 Production method
During January 2013 about 50 kg of organics *Citrus sinensis* L. var Sanguinello (described in § 3.1.2.1) were washed, brushed and dried. Through a shredder / refiner, skins were separated from the pulp. The two semi-finished products obtained were packed in PET bags and frozen using a forced air freezing tunnel, at -50°C and 2 m / s air speed, tangent flow.
As already exposed, the test purpose was to measure and compare the electricity used to run two processing cycles. The two operations had the following characteristics: the samples called "WiRE" (with renewable energy) was processed using only electrical energy, while a thermal solar water heating system was coupled to the processing of samples called "WioRE" (whithout renewable energy). Therefore, for all other parameters, the two cycles were performed under the same conditions (including environmental and technological), with the same raw materials, used in the same proportions.
As mentioned above (§ 1.1.3.1), the heat transfer from the electrical resistors to the product during the processing is produced by the process water, stored in a tank and moved by a pump. The solar energy caught by the thermal solar panel is released to the process water by means of a thermal exchanger, located inside the process water tank. Inside the solar circuit flows softened water, moved by a small pump. If the process water temperature exceeds the solar circuit temperature, an

automatic control stops the solar system pump, in order to avoid dissipation of internal system thermal energy through the solar panel.
For the production method see § 3.1.2.3.1, with the following difference: in this case the starting material were two skin and pulp semi-finished products thawed at 4°C in about 24h (instead of the fresh harvested fruits).
Electricity consumption measurement was carried out through a counter (Lovato mod, DME D300 T2)

3.4.1.1.5 Results and discussion

The WiRE's concentration step was entirely realized without any use of electric powered heaters: the plant's electrical energy consuption is due to non heating devices: (in order of decreasing absorption) vacuum pump, process water recirculation pump, product stirrer, solar circuit recirculation pump.
As shown in fig 38. the WiRE samples production cycle duration has been significantly longer than WioRE samples. Two can be the reasons: due to system design, the power used for heating during WiRE samples processing is significantly less the one applied in the WioRE samples processing conditions (which uses two resistors 4kw each); for the same reason, the evaporation phase during the WiRE processing test was characterized by a ΔT Tprocess water/Tproduct, significantly lower than the one realized during WioRE processing test. Incident net radiation recorded during the testing days was approximately 560 w/m^2.

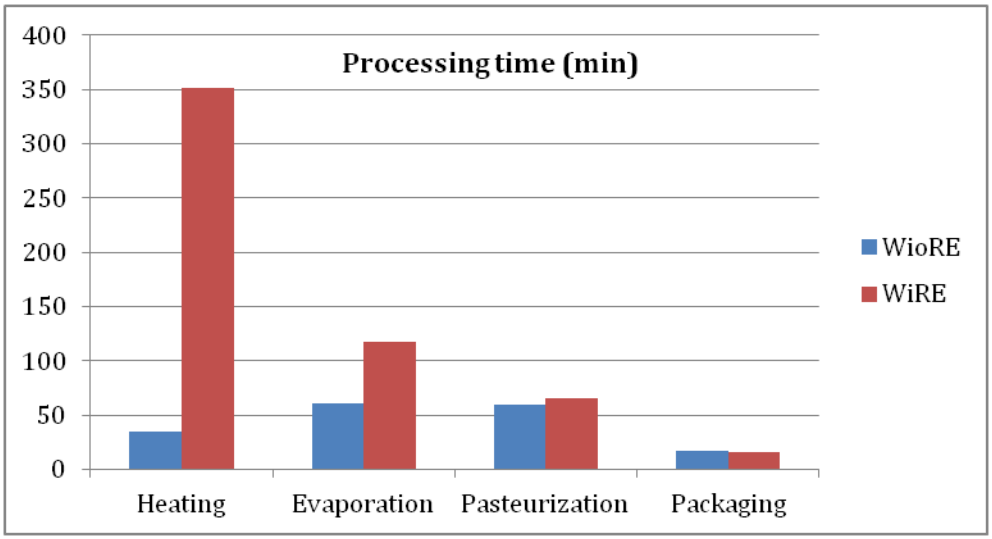

Fig. 38. Time length of each marmalade processing operation, with or without use of renewable energy.

Fig 39 shows the electric energy consumed during the different production cycle phases in function of the energy source type. In the heating and evaporation steps there is a net energy saving of respectively 42.9 and 17.5%. The net energy savings related to the entire production process is 17.1%.
Starting from the results obtained, it is important to make some considerations on the above discussed test:

- configuration plant: the one used for these tests is the minimum possible. By increasing the solar panel surface is possible to increase the heating rate and thus significantly reduce heating and evaporation time

- The geographical position: the test was performed in Milan (45°28 '28.59 "N, 9°14' 2.65" E). By varying the position it is possible to determine significant incident radiation increase or decrease
- weather conditions / season: have a dominant role on the heating power that can be reached, especially with the solar panel type used for the tests presented here.

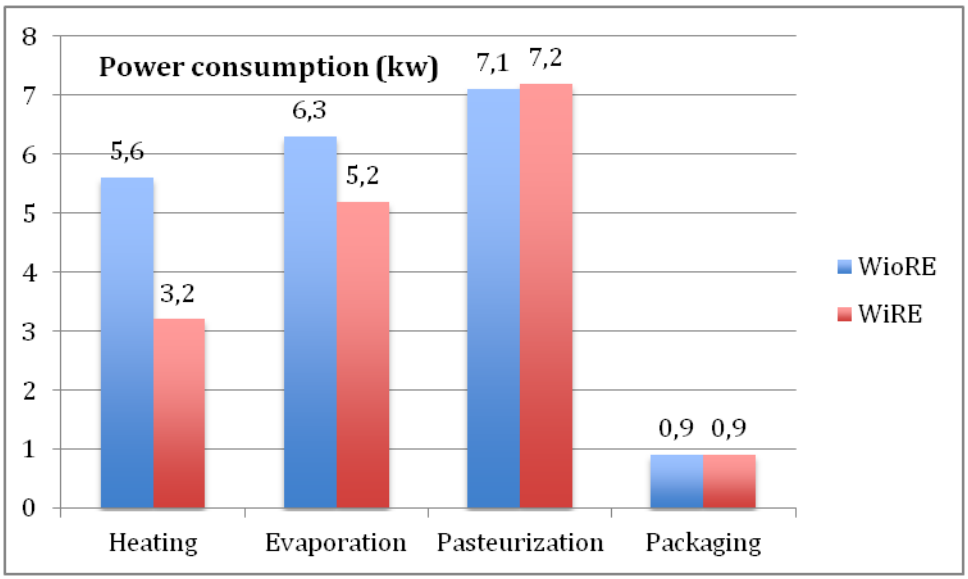

Fig. 39. Energy consumption during the different production phases of the marmalade processing cycle.

3.4.1.1.6 Conclusions

It can be concluded that the net energy saving rate was equal to 17.1%, which is clearly positive, despite the very limitant conditions under which the test was carried out. Therefore, it is possible to improve the result by enhancing one or more of the above mentioned conditions.

3.4.2 Use of renewable energy sources by means of a solar drying system

3.4.2.1 Dried whole slices of Tarocco Meli orange

3.4.2.1.1 Raw materials description and peculiarity

See § 3.1.2.1

3.4.2.1.2 Product description

See § 3.1.2.2

3.4.2.3.2 Research goal

The aim of this test is to quantify experimentally how much electrical energy can be saved by processing two types of dried products using a solar energy system (OR TQ sun samples, OR SU sun samples) or a conventional system (OR TQ conv samples, OR SU conv). The product used in the test are based orange Tarocco Meli dried with or without sugar. Products are described in § 3.2.1.3.2.

3.4.2.1.4 Materials and methods

3.4.2.1.4.1 Production method

See § 3.2.1.3.1.

3.4.2.1.5 Results and discussion

As expected, the solar dried samples required a time much greater than those conventionally dried. Both of the solar dried products (OR TQ sun and OR SU sun samples) required 339 hours (from April 19th 16:30 to May 3rd 18:00) as drying time. While samples conventionally dried ORTQconv required 94 hours, and ORSUconv samples required 125 hours. The figures 40 a, b show two different drying kinetics associated to the two drying systems used. It is also visible that the two samples types (with and without sugar) behave in a similar way. Fig 40 a (which refers to evaporation rate after 2 hours of drying) shows a faster water evaporation occurring during the first hours of treatment in the conventionally dried samples. After 24 h (Figure 40 b) the situation looks reversed. Such a behavior can be explained both by the fact that: inside the conventional dryer are present conditions which allow a more effective heat exchange than in the solar one. This fact initially allows to extract more water from the product, but also determines the formation of a crust which, in some way, isolates the product from the drying environment. On the contrary, the solar drier alternates conditions that allow an effective water extraction (during the solar irradiation), with conditions during which water migration is stationary or even negative (while the dryer is not exposed to direct sunlight).

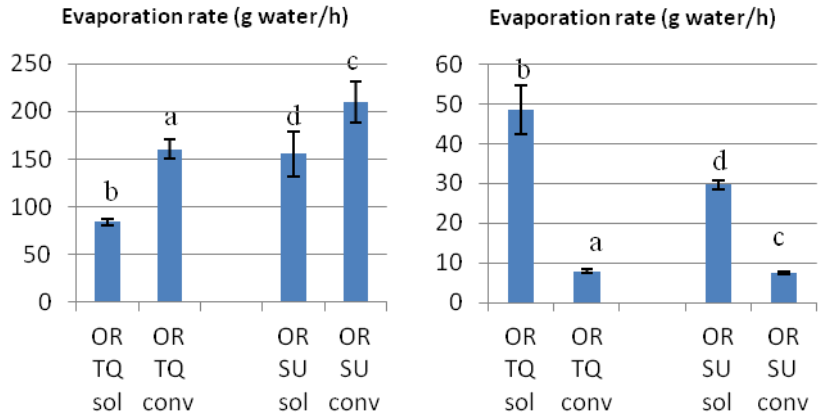

Fig. 40 a, b: Dried orange: evaporating rates after 2 and 24 hours of drying; samples ORTQsol with ORTQconv and ORSUsol with ORSUconv are compared separately in both charts. In each column different letters stand for significant differences (Tukey's test, $p<0.05$).

3.4.2.2 Conclusions

Considering that:

- Drying time by the solar drier includes also non sun radiation time
- The solar drier exposure time to direct sunrays was about 10 hours a day
- During the radiation time the average temperature was of 26.9 ± 4.1°C
- The solar drier average peak was 30.7 ± 1.2°C
- Drying of sweetened and unsweetened samples takes place in the same cell
- Conventional drying takes place at 45°C, constant
- Drying times with solar and conventional method for the orange slices are respectively of 339 hours and 94 hours

it is possible to hypothesize that during the exposure to sunlight, the vapour exchange effectiveness present in the solar dryer can be considered equivalent or even better than in conventional system. This result could be explained by the fact that the alternation of climatic conditions that cyclically occur in the dryer solar, prevents (or slows) the formation of a surface crust which disturbs the drying process.
During conventional drying, was measured an energy consumption of 32.9 ± 3.1 kw for unsweetened samples, and of 45.4 ± 2.3 kw for samples added of sugar. The difference is probably linked to the presence of sugar that, on the one hand facilitates the water migration from inside to outside of the product, but on the other hand facilitates the formation of a strongly hygroscopic surface crust, thus resulting in an appreciable lengthening of the drying time.
It is also important to take into account that in this study the conventional drier have been used with different settings than those commonly used by drying industry. Temperature never exceeded 45°C, in the intent to obtain a less heat damaged product. This setting resulted in a substantial lengthening of drying time.

3.4.3 Notes on apple candies

Also comparing the apple candies production times is found a clear difference between the conventional and the solar drying.

	Time (h)
E	56
UV	292
S	341

Tab. 25. Solar candies drying length (hours) of the three drying techniques. E means conventionally dried, UV stands for direct exposure to sun radiation, S means dried with the solar drier.

Nonetheless, the conventional process consumed 39.2 kw, compared to a reported zero energy consumption by the solar process.

3.4.4 Conclusions of session 3.4

The trials with the multi purpose processing line coupled with an heating solar panel here showed have to be intended as a reference model for other productions.
The tests performed have shown the possibility to use alternative energy sources for the preparation of products characterized by a processing high energy consumption, such as fruit preserves. The net energy savings obtained resulted to be good, despite the testing conditions were limiting. The energy saving performance can be easily improved.
The solar dried products are characterized by a long processing, but allow to obtain food of good quality associated to no energy cost.

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4 Dissertation conclusions

As partially anticipated in the specific conclusions regarding each product group (§ 3.1.8, 3.2.3, 3.3.3, 3.4.4), the aim of this PhD project has been fully achieved by obtaining a number of food products in accordance with all starting requirements: products quality, production's company context, link with the territory of origin, possibility of implementing alternative energy source and use.

Although this kind of research has not a well defined end, the results obtained allows to respond to the initial hypothesis. Therefore it is possible to affirm that quality products can be obtained in a craft context, belonging to a short supply chain, also employing profitably alternative energy sources. Products, processes and equipments used are not at all the only available alternatives: but instead they constitute what it was considered to be the best way to achieve the goals initially set (also taking into account the available resources). Further investigations can study the applicability of this approach to other food chains.

The transfer of knowledge from research to commercial world is the next step towards the uptake by consumers of the results obtained. One such innovation of small food producers involves the solution of a large amount of problems, mainly related to the technical and economical issues. The hope is that this work may be in some way to help in this difficult process.

Note

As already illustrated, the content of this thesis is based on the development of a number of food products. What perhaps was not explicitly expressed is that all experimentation activity has been carried out by the use of prototype machines. Insiders in research and development know how critical is shifting from the preliminary laboratory tests to pilot plant. In this case, the transition from pre-test to test on a prototype plant has generated many problems. In fact, often before even start to work on the product, it had been necessary to face and solve a variety of problems, which had not at all taken into account during the design of machinery. Understanding of the phenomena and solving of the related problems has required a great deal of patience, effort and, above all time. However, the work done in this direction is out of the scope of this PhD thesis, despite it is embedded in it and its amount has been huge.

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