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Development of food packaging systems that improve their conservation.

Desarrollo de sistemas de envasado de alimentos que mejoran su conservación.

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"La inteligencia es la habilidad de adaptarse a los cambios"
Stephen Hawking

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REPORT

CONTENTS

SUMMARY

Active packaging is one of the new packaging technologies that have emerged as a result of the innovation of the packaging industry to meet the challenges of the characteristics of the current market and the new demands of consumers. These packages extend the useful life of food, generating favourable conditions for its conservation through interaction with the product.

The purpose of this project is to develop an active packaging technology that improves food preservation from the incorporation of active ingredients that provide the appropriate effects for the packaged product. The type of product to be selected for this project is fruits and vegetables, since they are fresh and perishable foods, with a great tendency to decomposition.

The active packaging for fruits and vegetables that has been developed is based on two active systems: ethylene absorbers and emitters of antimicrobial agents. The first contains potassium permanganate as an active ingredient, and, the second, essential oils. The application system chosen for both is in sachets in which the adsorbed active substance is introduced into an inert support, specifically activated alumina spheres.

The production process of these impregnated spheres would consist of the dissolution of the active substance in a suitable solvent (water for potassium permanganate, and ethyl acetate for essential oils); the impregnation of said substances in the alumina spheres; a solid-liquid separation to separate the impregnated spheres; drying of the spheres; and, finally the dosage of the required amount of spheres in each sachet and the appropriate bagging of these for the protection of their properties.

The equipment selected for the process is: closed stirred and jacketed tank for dissolution, closed stirred and jacketed tank (of greater capacity than the previous one) for impregnation of spheres, and Nutsche filter for filtration and drying of impregnated spheres.

1. INTRODUCTION AND OBJECTIVES

1.1. FOOD PACKAGING DEVELOPMENT

In recent years there have been changes in the lifestyle and consumer habits of consumers that have generated the need to innovate to satisfy their new demands. On the one hand, the demand for food products that are minimally processed has increased since there is a greater concern for nutrition and healthier food (Yildirim et al., 2017).

On the other hand, because of the lack of time and a more frantic pace of life, the tendency to buy prepared dishes or foods that do not require a lot of preparation time and that are easy to consume at any time and place has increased considerably, but without having to give up quality or taste (Majid, Ahmad, Mohammad and Nanda, 2016).

In short, consumers look for foods that are safer, faster and more practical. In addition, the environmental concern has increased, which is why they demand more sustainable packaging that is respectful with the environment. These new preferences affect, not only the processing of food but also the way in which they are packaged (IAlimentos, 2015).

All these new demands from consumers, together with the growing demands in food safety, the increase of large commercial areas, new forms of logistics and distribution, among other aspects, are the origin of the evolution experienced by the packaging industry, sector that is in continuous progress (Techpress, 2012).

To face all the challenges that are presented to it, the packaging industry has had to innovate and generate new packaging solutions that adapt to the new requirements. With them, it is intended to obtain containers that prolong the useful life of the food, improving or maintaining its quality, conserving its organoleptic and nutritive properties, and that are environmentally, socially and economically sustainable (Majid et al., 2016).

Packaging performs an essential role in the food supply chain. As indicated in Directive 94/62/CE on packaging and packaging waste, a container is that product "*made of any materials of any nature to be used for the containment, protection, handling, delivery and presentation of goods, from raw materials to processed goods,*

from the producer to the user or the consumer". The main purpose of traditional containers is to contain and protect the product from damage, external contamination, in addition to facilitating its transport and storage. In short, they act as passive barriers that separate food from the outside (Brody, Bugusu, Han, Koelsch and McHugh, 2008; Pradas and Moreno, 2016).

These traditional containers, by themselves, can hardly meet the needs of today effectively and adequately. However, the concept of conventional packaging has evolved over the years because of the advances in the packaging sector (Bodbodak and Rafiee, 2016). The new techniques developed are characterized by interacting with the product they contain and/or with the environment, that is, they act as active barriers that have an effect on the content (Majid et al., 2016).

Several sources examine the main packaging technologies that have been developed in recent times. Analysing some of them, it has been observed that there is controversy in which new packaging technologies are considered (Techpress, 2012; Majid et al., 2016; Yildirim et al., 2017). In this work it has been considered that the most appropriate classification is the following:

- active packaging (AP)
- smart packaging (SP)
- modified atmosphere packaging (MAP)
- and high-pressure packaging (HPP)

This decision is since some technologies that mention other sources, such as nanotechnology and bioactive packaging, are understood as an application to active and/or intelligent packaging, but not another alternative as such. In the case of nanotechnology, it would be the application of nanomaterials to said containers; and in the case of bioactive packaging, it would consist in the application of bioactive ingredients, enzymes and biodegradable packaging materials (Majid et al., 2016).

The **active packaging (AP)** release and/or absorb substances from the food or from the headspace of the container, understood as the free space between the food and the container. That is, they are packaging systems that actively participate in food preservation and deliberately incorporate an active substance that retains undesirable

substances or releases substances that are beneficial to the product (Wyrwa and Barska, 2017; Yildirim et al., 2017).

In general, there are two types, the absorber systems and the releasing systems. The most common of each of them are absorbers of oxygen, moisture, ethylene, carbon dioxide, odours and flavours; and emitters of antioxidant agents, antimicrobial agents, carbon dioxide, food additives and flavourings (EOI, 2015; Vikas, Anil, Anupam, Ashish, Sumit, Neeharika and Hada, 2017; Vilela, Kurek, Hayouka, Röcker, Yildirim, Antunes, Nilsen-Nygaard, Kvalvag and Freire, 2018).

Figure 1. Example of meat packaging

(02/06/19 vía Troy PAckaging: Packaging Supplies and Solutions Ireland & UK)

The **Intelligent packaging (or smart packaging, SP)** controls the state of the food or headspace throughout the supply chain and provides information to users about the quality of the packaged food. To do this, they monitor the conditions of the packaged product, recording the changes that occur inside and outside the container, and provide a signal that allows perceiving and evaluating the circumstances in which the content is (Majid et al., 2016; Pacman, 2013).

Figure 2. Example of ripeness indicator

(Ross Galbreath, 02/06/19 vía Te Ara – The Encyclopedia of New Zealand)

In short, intelligent packaging is responsible for analysing the system, processing the information they receive and presenting it to the consumer. They can be classified into two groups: indicators and carriers. The former warns, usually visually and through a change of colour, and the latter, transport data in a way that allows information to be transmitted without the need for direct visual contact (Catalá, Hernández-Muñoz and Gavara, 2012; Techpress, 2012).

There are several types of indicators such as time-temperature indicators (TTis), indicators/detectors of gas leaks, indicators of ripeness, freshness indicators, among others. On the other hand, the carriers are the radiofrequency identification (RFID) devices, which consist of a tag that contains a microchip that stores data, which are collected by a reader that emits radio waves and sent to a computer to analyse them. and make the right decisions (Majid et al., 2016; Techpress, 2012).

The **modified atmosphere packaging (MAP)** consists of adding or removing gases from the interior of the package, specifically of the headspace, with the aim of achieving a specific composition that favours the conservation of the packaged product. Generally, this composition is different from atmospheric or the composition that normally surrounds the food (AbcPack, 2016 – Website).

Figure 3. Example of MAP

(02/06/19 vía Modified Atmosphere Packaging)

Mainly, the gases that are used to replace the atmosphere inside the container are nitrogen, oxygen and carbon dioxide. Nitrogen is an inert gas that lacks microbial activity and is commonly used as a filler gas. In addition, it has low solubility in water and is used mainly to prevent the collapse of the container. Oxygen has beneficial or harmful effects depending on the food to which it is applied, given that, among other effects, it inhibits the growth of anaerobic microorganisms, but favours that of aerobic microorganisms. Finally, carbon dioxide has bacteriostatic properties, although it can cause the collapse of the container due to its solubility with the food. The gas mixture used in each case depends on the type of food to be packaged, the material of the container and the temperature at which it is to be stored (AbcPack, 2016 – Website; Techpress, 2012).

The **packaging at high pressures** or also known as hyperbaric pasteurization **(HPP)** is a technique that consists in subjecting the food, previously packaged in the flexible hermetic container that corresponds to it, to high levels of hydrostatic pressure (around 4000 - 6000 bars) during a few minutes. Generally, this pressurization process is carried out in cold or at room temperature and it is possible to inactivate the vegetative microorganisms (bacteria, yeast, fungi, etc.) that are present in the food (Carroll, Chen, Harnett and Harnett, 2004; Wasin and Shafiur, 2015).

Figure 4. Example of packaging at high pressure
(02/06/19 vía DVI German Packaging Institute EV)

1.2. JUSTIFICATION AND OBJECTIVES

Among these technologies, it has been decided to focus this project on active packaging given its innovative approach to food preservation and the progress it has been achieving in recent times. The application of active packaging provides several

benefits, such as the improvement of the sensory characteristics of food, greater microbiological safety, the reduction of food waste and the possibility of prolonging transport and storage times (Wyrwa and Barska, 2017).

This technology has been selected since it goes beyond the provision of information or control of the content (main function of the IP/SP) since the AP acts and exercises an action on the content of the container (product or environment thereof) that generates the adequate conditions for its preservation (Sardarodiyan and Mahdian, 2016). That is, while IP/SP can detect changes that occur in the food, the head space or the environment, AP can prolong the useful life of the product (Dávila, Solis, Rojas-Verde and Salas, 2015). In addition, another reason to select AP with respect to IP/SP is that the latter has a higher cost (Pradas and Moreno, 2016).

The AP is part of a new generation of packaging technologies that represents an evolution of traditional packaging functions, from acting as passive barriers to acting as functional barriers that exercise a specific function. Active packaging is a good alternative for a wide variety of applications in the food industry (Wyrwa and Barska, 2017).

The general objective of this project is the development of an active technology of food packaging that can extend its useful life by incorporating active ingredients that exert the appropriate effects on the product to be packaged.

To achieve the general objective, specific objectives must be specified, such as:

- Select the type of product to be packaged
- Select the active packaging system that will be incorporated in the container
- Select the active ingredients with the active function required by the product to be packaged
- Identify the packaging system, the form of incorporation of the active substances, the structure and formulation most suitable for the container to be developed
- Establish the basic engineering for a viable manufacturing process of the selected active packaging

2. SELECTION OF THE PRODUCT TO BE PACKAGED

The present work focuses on the new technologies of active packaging, as described in the introduction section. Once the technology on which the study is based is determined, the type of product that is required to be packaged must be selected to subsequently establish the package that best suits its properties. For this, the types of food must be known and, considering aspects such as their susceptibility to deterioration, possible storage problems, relationship with the different active packaging systems, among others, establish the sector of greatest interest for this work.

2.1. FOOD SECTORS

First, to address this chapter, it is necessary to determine how food is classified. Food can be classified in different ways according to the criterion used, but for this work it has been decided to classify them according to their functional characteristics. This classification is based on the model established in Spain by the EDALNU programm ("Educación en la Alimentación y Nutrición") it consists of 7 food groups (FIsterra, 2006 – Website):

- Group I: Milk and dairy products
- Group II: Meat, eggs and fish
- Group III: Tubers, legumes and nuts
- Group IV: Vegetables
- Group V: Fruits
- Group VI: Bread, pasta, cereals and sugar
- Group VII: Fats, oils and butters

It has been decided to focus the study on those foods that present the most problems for storage due to their rapid deterioration since they are the ones that are more interesting in prolonging their useful life. For this reason, the foods classified in group III and VII are discarded for the analysis.

Figure 5: Example of food pyramid

(21/06/19 vía Casco Bay CAN)

Foods have different ways of degrading itself, so to preserve them, it must be known which intrinsic properties or external factors influence the deterioration, such as which microorganisms affect the product, among others. The factors that cause the decomposition of food can be classified in internal (e. g., pH, water activity) or external (Rodríguez, 2016). The latter in turn are divided into (Rojas, 2009):

- Physical factors: physical injuries, such as bumps, pressures, bruises, …
- Chemical factors: rancidity, browning, pesticides
- Biological factors: enzymes, microorganisms, parasites
- Environmental factors: temperature, light, humidity, oxygen, weather, dryness

On the other hand, it is important to know what active system will be more suitable for each type of food since each one requires certain needs to combat its deterioration. The existing types of active packaging have been mentioned in general terms in *Chapter 1* and will be explained more extensively in the next one (*Chapter 3*). For it, by the collection of information from different sources, a table has been prepared which shows, in a general way, a classification on what type of packaging is suitable for each food sector (Table 1) (Pacman, 2013; Vilela et al., 2018). It has also been developed another table that indicates which are the most common bacteria that affect each one of them (Table 2) (Gimferrer, 2014; Rodríguez, 2016).

		Meat products	Dairy products	Fishing products	Vegetables	Bakery and baked products	Ready to eat products	Cut vegetables
Scavengers/ Absorbers	**Oxygen**	X	X	X	X	X	X	X
	Moisture and exudates	X		X	X	X	X	X
	Ethylene				X			X
	Carbon dioxide	X	X	X	X			
	Odours and flavours	X	X	X				
Emitters/ Liberators	**Antioxidant agents**	X		X	X	X		X
	Antimicrobial agents	X	X	X	X	X	X	X
	Carbon dioxide	X	X	X	X	X		
	Food additives and flavourings		X	X			X	X

Table 1: Application of active packaging systems in different food sectors (Own elaboration)

	Meat products	Dairy products	Fishing products	Vegetables	Bakery and baked products	Ready to eat products	Cut vegetables
Escherichia Coli	X	X		X			X
Staphylococcus Aureus	X	X			X		
Listeria Monocytogenes	X	X	X	X		X	
Salmonella	X	X	X	X	X		X
Campylobacter	X		X				
Clostridium botulinum	X		X	X			

Table 2: Affectation of the most common bacteria in food in different food sectors (Own elaboration)

As can be seen in *Table 1*, the application of AP in foods is varied. In the case of meat, fish, dairy and vegetable products, it has been found that the number of active containers that are usually or can be applied is usually greater than in other types of products. This may be because they are fresh, perishable and have a limited shelf life. In

addition, the influence of some conditions (such as light, oxygen, temperature and humidity) accelerate deterioration (Chavarrías, 2012).

In addition, *Table 2* shows that these four groups of products are affected by a greater number of the most common food bacteria. For this reason, more emphasis has been placed on the use of AP in this type of product, since they are the ones that are exposed to the greatest risk of degradation and waste.

2.2. SELECTION OF THE PRODUCT

After the analysis of the different food sectors, the most appropriate active system for each one and the microorganisms that affect them, the type of product which is more suitable to carry out the development of an AP has to be selected. For that, several aspects are considered, such as consumer demand, manufacturing volume, possible conservation problems, useful life or perishability, among others.

The selection focuses on perishable foods, those that begin to decompose quickly, since they pose a problem when it comes to preserving them and require more attention during storage. In addition, the large amount of existing perishable products is another aspect that makes it important to improve their preservation. Vegetables and products derived from animals are considered perishable, that is, fruits, vegetables, dairy products, meats and fish. Cooked foods are also considered perishable foods (Aytojaen, 2017 – Website).

Among them, vegetables and fruits (F&V) are selected as products for which to develop an AP. One of the main reasons is that they are foodstuffs with the highest degree of perishability, so they have storage, handling and transport limitations. In addition, in recent years the consumption of fruits and vegetables has increased due to the increasing preference of consumers for diets based on healthy and nutritious foods. That is, there are a great demand and acceptance towards them (Vikas et al., 2017). Fruits and vegetables are foods that are produced in large volume and have a short shelf life, of only a few days, because of their great tendency to decompose.

In addition, being fresh food, its freshness is a determining factor at the time of being purchased by the consumer, so the food industry must face the challenge of keeping

them fresh to offer products with the best quality. To get them to the users they must be stored and transported, which requires a longer lifetime. For this reason, it is necessary to pack them to prolong their useful life and keep them in the best condition until they are consumed, that is, offer the final consumers fresh and attractive products.

Another aspect that makes F&V a type of product very suitable for this study is the high level of possible contamination to which they are exposed, from their production process, in the agricultural environment, during storage, handling, transportation and until the moment of its consumption. Also, this aspect is aggravated because they are products that are minimally processed and therefore have virtually no treatments (Wasin and Shafiur, 2015).

Figure 6: Fruits and vegetables, among others
(Thinkstock, 06/05/19 vía RTVE)

2.3. CHARACTERISTICS OF THE SELECTED PRODUCTS

Both selected foods, fruits and vegetables, come from plants but there are several differences between them by the type of product. While the fruits are the ovaries that contain the seeds, the vegetables are from any other part of the plant. Next, each of the groups or varieties in which they can be differentiated is explained in a general way.

I. Fruits

Fruits are the part of the plant that springs from a flower and correspond to the fertilized ovaries of plants that, generally, surround the seed or seeds to protect them. There are different criteria to classify them, depending on the type, the form of

collection or the maturation process. For the development of this work, the classification that most interests is the last one. According to the type of ripening the fruits are divided into (Intagri, 2017 - Website; Knee, 2002):

- **Climacteric fruits:** Those in which there is a notable increase in the respiratory rate and ethylene production during maturation (to a maximum and then decreases). The ripening process continues after being harvested. For this reason, they are usually separated from the plant in a pre-climacteric state (immediately before maturing, in green-ripe state) to store them under controlled conditions and that the ripening takes place at the moment of being commercialized. In this type of fruit ripening is coordinated by ethylene, which regulates the changes in colour, flavour, texture and composition.
- **Non-climacteric fruits**: those in which there are no substantial variations in the respiration rate and maintain low levels of ethylene production during maturation. They should be collected once they reach maturity, since once separated from the plant they do not continue ripening and do not improve their flavour and aroma. Ethylene does not regulate its maturation nor the main organoleptic changes, but on the contrary it accelerates its deterioration.

CLIMACTERIC	apple, pear, peach, nectarine, fig, plum, melon, watermelon, cranberry, tomato, custard apple, avocado, banana, mango, papaya, kiwi, carrot, onion
NON-CLIMACTERIC	cherry, grape, raspberry, pomegranate, orange, grapefruit, lemon, lime, tangerine, strawberry, cucumber, pimento, pineapple,

Table 3: Examples of climacteric and non-climacteric fruits (Own elaboration)

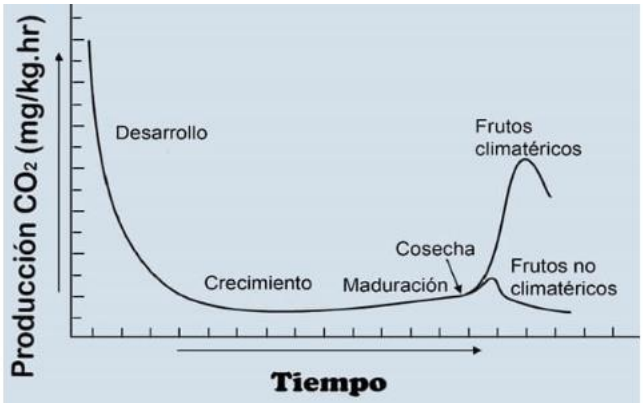

Figure 7: Behaviour of climacteric and non-climacteric products in relation to their respiration rate. (Yahía, E., 10/06/19 vía INTAGRI)

II. **Other vegetables that are not fruits**

The vegetables are considered all parts of the plant except the fruit. On several occasions, there are products that are classified as vegetables but correspond to the fruit of the plant, such as tomatoes, cucumbers, peppers, aubergines, pumpkins.

Vegetables come from herbaceous plants and are grouped according to the part of the plant from which they come (Stguitars, 2018 - Website). The groups that can be distinguished and some examples of each are (Animalgourmet, 2014 - Website):

- **Leaves:** spinach, lettuce, chard, chicory, cabbage, endive
- **Stems:** asparagus, leek, celery
- **Roots:** carrot, radish, turnip, cassava
- **Tubers:** potato, sweet potato, sweet potato
- **Bulbs:** onion, garlic
- **Flowers:** broccoli, artichoke, cauliflower

Some of the factors that affect the shelf life of F&V are respiration, maturation, the presence of ethylene, humidity and temperature. During maturation, changes in texture, flavour, colour, aroma and reduction of firmness occur. The loss of moisture leads to dehydration and causes fruits and vegetables to wrinkle and wilt (Decco, 2017 – Website; Nayik and Muzaffar, 2014).

Both fruits and vegetables are exposed to contamination and growth of microorganisms due to the appearance of fungi, bacteria and viruses, among others. In the case of fruits, they are more prone to the alteration by fungi due to their acidity. In contrast, vegetables are more prone to alteration by bacteria because of their lower acidity (Cinatur Group, 2016 – Website).

The aspects that most affect fruits are oxidation, enzymatic browning, loss of colour, of nutrients, of vitamins, softening, among others. In the case of most vegetables the main problem is the loss of moisture and subsequent drying. Generally, vegetables considered roots and tubers do not present special conservation problems. In the case of leafy vegetables, with the passage of time they deteriorate due to the loss of moisture and become limp.

The type of product selected to be package, F&V, has been thought to be a product of proximity for small businesses. It is intended that they themselves can store the merchandise they receive for later sale. Therefore, it will be small quantities and it is not expected to have it stored for very long periods of time. Therefore, it is intended to prolong the shelf life of F&V a few days more, to avoid waste and that small businesses can keep their fresh products for longer, with the most appropriate quality and the highest degree of acceptability by of the consumer.

To achieve this, it is sought to slow down the maturation process, decreasing the respiration rate, reducing the presence of ethylene, and decreasing deterioration, inhibiting or reducing the growth of microorganisms, avoiding oxidation, dehydration, enzymatic browning, among others.

Figure 8: Fruits and vegetables

(06/05/2019, OMENT)

3. SELECTION OF ACTIVE PACKAGING SYSTEM

3.1. TYPES OF ACTIVE PACKAGING

In this section, a review is made about the most important AP technologies. As explained in *Chapter 1*, AP interacts with its content or its environment. This interaction can be to absorb or eliminate unwanted substances that deteriorate the food or to incorporate beneficial substances that help its conservation (Limbo and Khaneghah, 2015; Pacman, 2013).

In the first case, they are active capture systems and are called absorbers or eliminators. In the second, they are active release systems called emitters. The most used active capture systems are oxygen absorbers, moisture absorbers and exudates, carbon dioxide, ethylene absorbers, odour and flavour absorbers. The active release ones are emitters of antioxidants, antimicrobial agents, carbon dioxide, food additives and flavouring agents (Brody, et al., 2008; Pacman, 2013; Vilela et al., 2018).

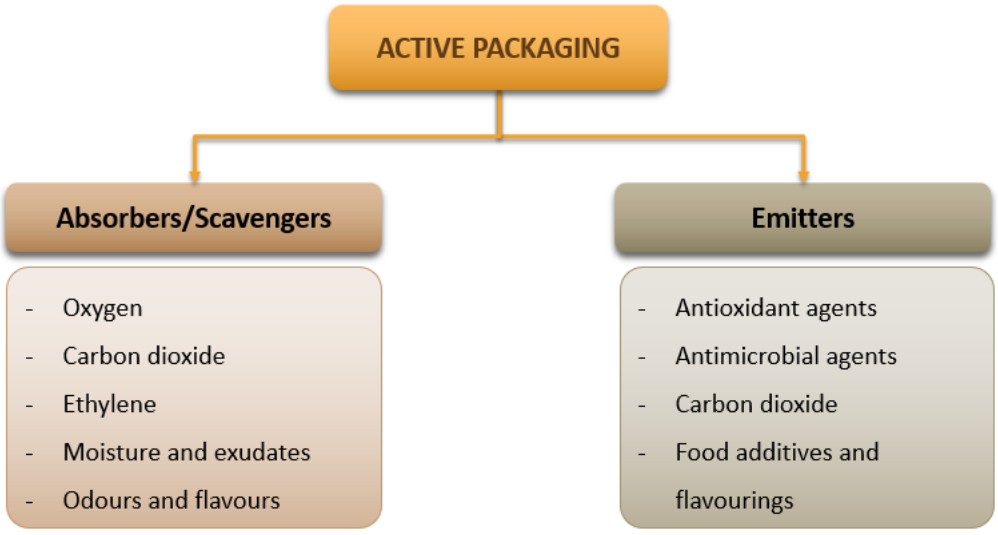

Figure 9. Classification of potential active packaging for food applications (Own elaboration)

As previously defined, the type of food to be packaged are F&V. Therefore, the study focuses on the active systems applicable to this type of food. By means of a bibliographic compilation of information from different sources, (Nayik and Muzaffar, 2014; Vikas et al., 2017) it has been concluded that the types of AP that are applicable to F&V are:

- Oxygen scavengers
- CO_2 absorbers
- Ethylene Absorbers
- Moisture and exudates scavengers
- Emitters of antimicrobial agents
- Emitters of antioxidant agents
- CO_2 emitters

In the case of F&V, their own smell and taste are indicators of the good condition of the product, therefore, generally absorbers of odours and flavours or food additives and flavourings are not applied to them, since, for example, they could fall the error of masking bad odours and the consequent bad state of the product. Although they are not applied to F&V, they are briefly described to provide an idea about them.

I. Absorb Systems: Scavengers

- **Oxygen scavengers**

The food industry seeks to eliminate or regulate the oxygen of the packaging because it negatively affects the quality and shelf life of many foods as it leads to the oxidation of the product and promotes the growth of aerobic microorganisms. The contact of food with oxygen causes multiple degradations such as discoloration, browning, appearance of unpleasant odours and tastes, mould growth, nutritional losses and rancidity. The development of these degradations can be limited by reducing the oxygen level in the packages (Catalá, 2010; Pacman, 2013).

To exclude oxygen in the packaging process, gas scrubbing or modified atmosphere processes are generally employed, but in many cases, the concentration of residual oxygen that is obtained in the container is not reduced as much as required and may increase during the storage. This can be due to insufficient evacuation during packaging, to the penetration of oxygen through the material of the package given its permeability, to a poor seal or to the dissolved oxygen contained in the food and that is released in the headspace. In such cases, where the usual processes are not enough to extend the

useful life of the product as much as desired, by the use of oxygen absorbers a greater reduction of the residual oxygen level can be achieved (Yildirim et al., 2017).

These oxygen absorbers can be presented in bags, envelopes or labels as independent systems placed inside the container, which are the most common, or incorporated in the packaging material itself, for example, in a polymer film (Brody, et al., 2008; Pacman, 2013).

By applying these scavengers, it is possible to slow down the deterioration of the food, therefore, the use of preservatives and antioxidants in the food itself can be reduced or eliminated. Specifically, in F&V, with the reduction of the amount of oxygen, the respiration of vegetables, the growth of aerobic microorganisms, the oxidation reactions, the browning processes are limited. A low oxygen level reduces the production of ethylene and keeps the product fresh for a longer time (Brody et al., 2008; Vikas et al., 2017).

- **Moisture and exudates scavengers**

The moisture content and water activity are factors that affect the quality and safety of many foods. An excess of moisture in some foods favours the development of microorganisms, the softening of dry and crunchy products, and the caking and hardening of powdered products. The presence of exudates liquids (water, blood or others) devalues the presentation of food and increases the risk of deterioration (Brody et al., 2008; Yildirim et al., 2017).

In fresh foods such as fish, meat products, F&V, the loss of moisture has negative effects on the quality of the product, so it is beneficial to maintain a high level of relative humidity in the package to prevent drying (Yildirim et al., 2017). In F&V, maintaining an adequate humidity reduces the darkening, dehydration, drying, or discoloration and, therefore, lengthens the shelf life. This type is used mainly in F&V of the IV range (packed already washed and cut) (Mehyar and Han, 2010).

The condensation or "sweating" that occurs due to the processes of respiration and transpiration is a problem, especially in fresh F&V, as it harms the appearance of the container and makes it less attractive to the consumer. Humidity absorbers are used to control humidity and reduce the condensation that forms on the inner surface of food

packaging. To do this, they retain the liquids that can be released by exudation or condensation without drying the packaged product (Vikas et al., 2017).

Active moisture control systems are divided into moisture controllers that remove moisture from the headspace (desiccant) and moisture removers that absorb liquids. The first, normally, are presented in envelopes, microporous bags or pads, although they can also be integrated with the packaging material. The seconds are mainly presented in absorbent pads or sheets placed under fresh products, but they can also be incorporated in the polymer films (Brody et al., 2008; Yildirim et al., 2017).

Figure 10. Example of packaging with moisture absorbent pads for cut vegetables (FreshWell, 15/06/19 vía Aptar - Maxwellchase)

- **Ethylene Absorbers**

Ethylene is a substance that acts as a plant hormone, known as maturation hormone, produced by plants and that stimulates the growth of these. This substance is released during the process of ripening or the breathing process of climacteric fruits (see *Chapter 2.3*), even after being harvested. Ethylene increases the respiration rate of fresh and minimally processed climacteric products, thus accelerating their maturation, inducing senescence and softening. In addition, it accelerates the degradation rates of chlorophyll, mainly in leafy vegetables. Therefore, it has a negative impact on the quality and shelf life of F&V, as it leads to deterioration during storage and distribution (EOI, 2015).

By controlling the ethylene content in the headspace of the containers, the product's useful life is extended, delaying ripening, aging and deterioration. Specifically, in F&V,

reducing or eliminating it reduces maturation and senescence, thus quality is improved, and the shelf life of the product can be extended (Brody et al., 2008).

The permanganate-based ethylene absorbers are placed in sachets or envelopes that are placed inside the container, the rest of the systems can be found in the form of envelopes, sachets, trays, pads disposed inside the container or incorporated in the polymer film. So that the amount of ethylene absorbed is adequate in each case, the absorber is designed according to the type of fruit to be packed (Balaguera-López, Gutiérrez, García and Herrera-Arévalo, 2014).

- **Carbon dioxide absorbers**

The presence of carbon dioxide has beneficial or harmful effects depending on the product you want to keep. When the effects are negative, the CO_2 absorbers are used.

Due to deterioration of food and respiration reactions, high levels of CO_2 are produced in the packages. This can cause changes in the flavour of the product, pressure build-up, swelling or even bursting of the package. Therefore, the waste of CO_2 has to be eliminated to avoid deterioration of the food or the container itself (Pacman, 2013). CO_2 is generated in fresh F&V due to its physiological activity. High levels of CO_2 can cause changes in the flavour of the products and cause the package to expand or even collapse (Prasad and Kochhar, 2014).

They can be found in the form of edible films or coatings that have selective permeability with respect to gases. For example, in some F&V, a high CO_2 permeability is needed to reduce spoilage (Prasad and Kochhar, 2014).

- **Odour and flavour absorbers**

The quality of the packaged products can be impaired by the absorption of aromatic compounds or the filtration of substances with foreign flavours to the food. Also, the food itself may contain substances that are the cause of unpleasant tastes. In these cases, the odour and flavour absorbers are used, which can selectively absorb odours or flavours that are harmful to the food.

Some undesirable substances would be naringin or limonin, which cause a bitter taste in citrus juices due to the pasteurization process and storage (Pacman, 2013). Some substances that cause a bad smell would be amines and aldehydes.

However, it is prohibited to eliminate substances that are indicative of the deterioration of the food, since they would be masking bad odours resulting from products of poor quality that could cause danger for consumers. Normally, the active substance is incorporated in the packaging material itself and is released to the food or headspace by diffusion (EOI, 2015).

II. Release Systems: Emitters

- **Antioxidant agents**

Oxidation of lipids is one of the causes of food spoilage. The effects it causes on the product are the reduction of shelf life, loss of nutritional quality and changes in taste, smell and/or texture. One way to prevent such oxidation from occurring in packaged foods is using oxygen absorbers and/ or antioxidant releasers. In this way, the oxidation reactions are avoided or delayed and, with it, the deterioration, the loss of quality and the diminution of the lifetime of the product. Also, residual oxygen is controlled, and oxidative stability is improved (Prasad and Kochhar, 2014).

These systems are usually applied as a coating or varnish on the inner layer of the packaging material, and act by direct contact with the food or by releasing the agents in the headspace of the package. Due to the use of these emitters, it is not necessary to add antioxidants to the food itself (Limbo and Khaneghah, 2015).

- **Antimicrobial agents**

Packaged foods can be contaminated microbiologically due to improper processing or because the integrity of the package is compromised during storage (inefficient sealing, breaks, punctures, etc). In F&V, surface deterioration due to the growth of microorganisms is the main cause of the short shelf life of them (Mehyar and Han, 2010).

One of the methods to combat the deterioration caused by the growth of microorganisms in food is the use of emitters of antimicrobial agents. With them, it is

possible to inhibit or delay the growth of pathogenic microorganisms and of deterioration and, therefore, prolong the useful life of the product (Brody et al., 2008).

The application systems of these emitters are in sachets inside the container, bioactive agents dispersed in the container, coatings of bioactive agents on the surface of the packaging material or antimicrobial macromolecules that form films or edible matrices (Prasad and Kochhar, 2014).

- **Carbon dioxide emitters**

In cases where carbon dioxide is beneficial for the food conservation, CO_2 emitters are used to obtain adequate levels.

Carbon dioxide has an antimicrobial effect and it is introduced as fungistatic given its ability to suppress aerobic microbial activity. Therefore, the high levels of CO_2 in the headspace of the containers, inhibits microbial growth. In addition, it serves to decrease the breathing speed of fresh foods (Brody et al., 2008).

The carbon dioxide emitting systems are also used in addition to the oxygen absorbers, since they compensate for the partial vacuum that can be formed with the elimination of oxygen and, thus, avoids possible problems in the flexible containers. Due to the permeability of CO_2 (between 3 and 5 times greater than that of O_2) in many of the packaging materials, generally polymeric films, it is necessary to use said emitters to produce it continuously and maintain the required concentration in the container (EOI, 2015; Prasad and Kochhar, 2014).

- **Emitters of food additives and flavourings**

The sensory changes that can occur in food products can be corrected with the addition of food additive and flavouring emitters. With the addition of these emitters, you can increase consumer acceptance of the product, improve the aroma of the fresh product or enhance the flavour of the food (Prasad and Kochhar, 2014).

The release of these substances can occur slowly and uniformly during the time that the food is packaged, or it can occur during the opening of the package. Through the gradual release of odours and/or flavours, it is possible to compensate for the natural loss of aromas or flavours or to improve the natural aromas of packaged products that

have a prolonged shelf life. These emitters are usually substances that are used as additives for plastics and have a high thermal resistance (EOI, 2015).

3.2. SELECTION OF ACTIVE PACKAGING

An active container may consist of one or more active functions. It has been decided that the container to develop will consist of a combination of effects, that is, it will be a multi-function system. By combining active functions in the same package, a more effective effect can be obtained than using only one function (Mehyar and Han, 2010).

Considering all the systems and their contribution to the preservation of F&V, the ethylene absorbers and the emitters of antimicrobial agents are chosen as active systems for the container that is going to be developed. The combination of the reduction of the maturation and senescence of the product, together with the reduction or inhibition of the growth of microorganisms, can give rise to an increase in the useful life and conservation of the optimal conditions of quality enough for the purpose which the container will be destined.

The container to be developed is intended for small commerce so that they can package themselves the merchandise they receive for later sale. Given the characteristics of the material to be packaged, which is a product of proximity and that is not intended to be stored for long periods of time, it is considered reasonable to use two active systems, since, although more could be used, this would imply a considered increase in costs and it would end up not being profitable.

I. Ethylene absorber

Ethylene (C_2H_4) is a very volatile substance that occurs naturally in F&V during its metabolism (EOI, 2015). Since ethylene has physiological effects on F&V, this active system is selected to be incorporated into the container to be developed. As previously mentioned, ethylene is responsible for the fruit to start ripening, but once the ripening is complete it has negative effects since it leads to its deterioration (Mehyar and Han, 2010). To know more in detail the synthesis of ethylene in plants consult Appendix 1.

The application of ethylene absorbers is more common in the so-called climacteric fruits. The climacteric fruits are those that continue to mature after being harvested, however, the non-climacteric only mature in the plant, and once separated, they interrupt their maturation irreversibly (Sozzi, 2007).

In other words, the climacteric fruits produce and release ethylene to the environment, which regulates its maturation once harvested. Non-climacteric fruits only produce ethylene in response to physiological or pathological damage and it does not regulate its maturation, but it does accelerate its deterioration since, for example, it accelerates the degradation of chlorophylls, which are the pigments responsible for the green colour of the fruits (Contreras, 2014 - Website).

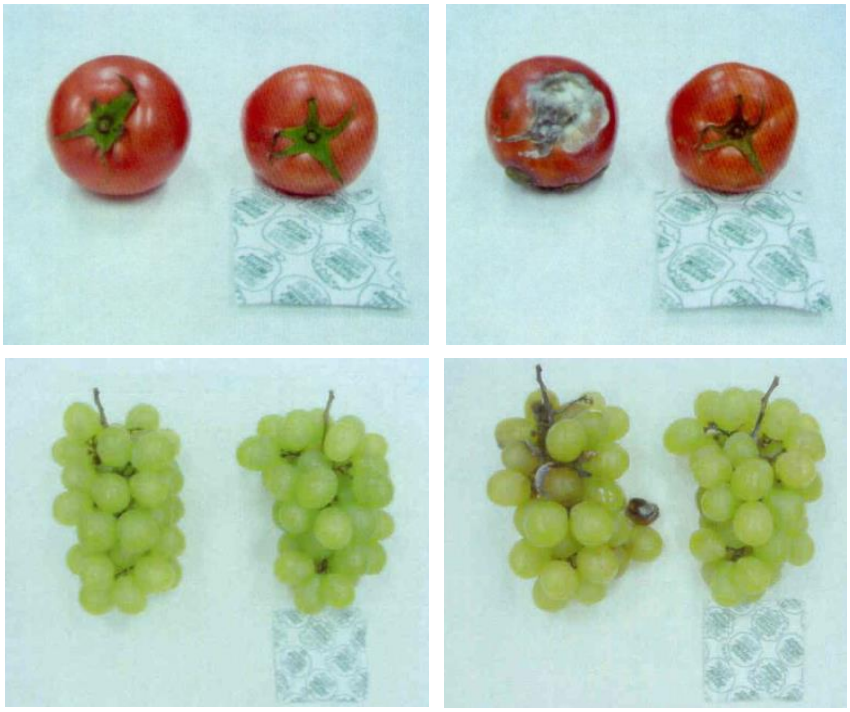

Figure 11. Comparison of ethylene absorber results in climacteric (tomato) and non-climacteric (grape) fruits. Right: before test. Left: After test

(San-Ai, 03/06/19 vía Ethylene Control)

II. Emitter of antimicrobial agents

Since the main cause of deterioration in F&V is the contamination and growth of microorganisms, it is considered of great importance to apply an emitter of antimicrobial agent in the container to be developed. In EOI (2015) there is a study on patents related

to this type of packaging in which it is appreciated that there are many patents related to them. Specifically, 175 records are located.

A breakdown is made per year (*Figure 12*) in which the evolution of publications can be observed up to 2015. Of the 175 patents located, 159 have been published in the last years, from 2005 to 2015. In the same article it is observed that the AP with antimicrobial agents is the second technology with the greatest number of published patents, only overcome by the AP of oxygen absorbers (EOI, 2015).

Hence, it is understood that it is one of the active systems that has generated more interest in recent years. One reason can be that developing antimicrobial packaging has been a challenge to reduce food waste and prolong the shelf life of perishable foods (Limbo and Khaneghah, 2015).

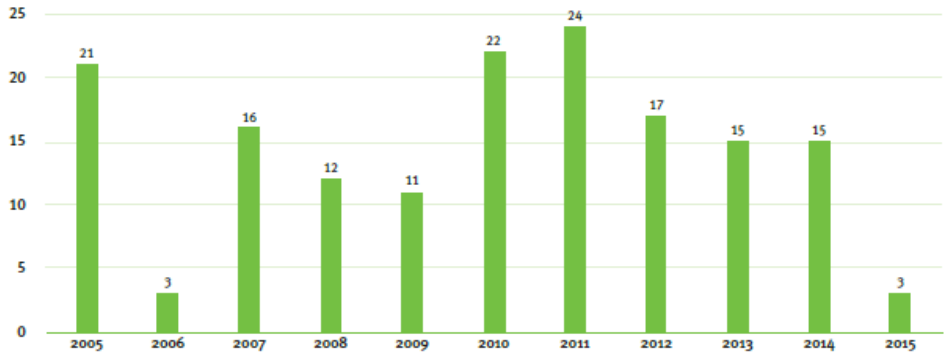

Figure 12: Number of patents on antimicrobials per year of publication

(Source: EOI– WIPO Patentscope)

4. SELECTION OF ACTIVE INGREDIENTS

In this chapter is defined the active ingredients that the container to be developed will incorporate. As seen in the previous chapter, there are several types of AP, and for each one of them different active ingredients are used. Once the active systems to be used have been determined, the active substances that will be part of each of them must be known and selected. For this, several bibliographic sources are consulted, and the active components used are analysed.

4.1. ACTIVE INGREDIENTS FOR ETHYLENE ABSORBER

Vilela et al. (2018) mentions that the most commonly used ethylene absorbers are based on potassium permanganate ($KMnO_4$) supported on inert matrices (e.g., silica gel or alumina). Other alternatives for ethylene removal indicated in the review are metal oxides, (e.g., silica gel and activated alumina), layer silicates and zeolites (e.g., clays, vermiculite and zeolite), nanoparticles and activated carbon. In the EOI report (2015) it is mentioned that other alternatives are based on adsorption on activated carbon, in which palladium or bromide catalysts are needed.

Since it is the most widely used and commercially studied option, aspect that other sources also highlight (Brody et al., 2008; EOI, 2015; Martínez-Tenorio and López-Malo, 2011, Pascal and Han, 2018; Pradas and Moreno, 2016), it has been decided to select as an active ingredient the $KMnO_4$ for the ethylene absorber system that will be implemented in the container to be developed.

When the $KMnO_4$ comes into contact with ethylene, it is oxidized to ethylene glycol, which is later decomposed into carbon dioxide and water (Balaguera-López et al., 2014; Nayik and Muzaffar, 2014). The carbon dioxide and water obtained have a complementary effect in the increase of the useful life, since the CO_2 reduces the rate of respiration of the fruit and blocks the synthesis of endogenous ethylene (autocatalytic), and the H_2O decreases the rate of perspiration (Mehyar and Han, 2010). The $KMnO_4$ that has a purple colour, when oxidizing the ethylene, passes to the reduced species of brown colour, and this change of colour indicates the saturation of the absorber (EOI, 2015).

4.2. ACTIVE INGREDIENTS FOR EMITTER OF ANTIMICROBIAL AGENTS

Vilela et al. (2018) made a review is on the latest advances in active ingredients that are used in the various AP systems. This review emphasizes on active functions such as antimicrobial and antioxidant activity, oxygen and ethylene scavenging, and carbon dioxide emitting. In this section, it focuses on the information provided on active antimicrobial agents, and for the later section, on the ethylene absorbers.

Figure 13: Active agents for active food packaging

(Source: Vilela et al., (2015))

The active ingredients that stand out for antimicrobial packaging are metal ions (e.g., silver, copper, gold and platinum), metal oxides (e.g., TiO_2, ZnO and MgO), essential oils (e.g., thyme, oregano, pepper, clove, citron, lemon verbena, lemon balm and cypress leaf), plant extracts (e.g., grape seed, green tea, pomegranate peel/rind, acerola, pine bark, bearberry, cinnamon bark, rosemary, garlic, oregano, ginger and sage), polysaccharides (e.g., chitosan), pure bioactive components (e.g., thymol and carvacrol), peptides (e.g., nisin and lactoferrin), enzymes (e.g., peroxidase and lysozyme) and synthetic antimicrobial agents (e.g., quaternary ammonium salts, ethylenediaminetetraacetic acid (EDTA) and propionic, benzoic and sorbic acids) (Vilela et al., 2018).

Limbo and Khaneghah (2015) show the following table with some examples of substances with microbial activity classified by class:

Class	Example of substances
Organic acids	Propionic acid, benzoic acid, sorbic acid, lactic acid
Polymers	Chitosan
Gas	CO_2, SO_2
Metals	Silver
Bacteriocins	Nisin, pediocin, lacticin
Enzymes	Lysozyme, glucose oxidase
Chelating agents	EDTA
Spices (extracts)	Horseradish, cinnamon
Essential oils/oleoresins	Carvacrol, cinnamaldehyde, eugenol

Table 4: Main class of antimicrobials applied to food packaging
(Source: Limbo and Khaneghah, 2015)

Based on all this information collected, the following table has been drawn up in which some of the main substances with antimicrobial activity that are applied in food packaging are collected and shown in a more schematic way.

Class	Example of substances
Organic acids	Propionic acid, benzoic acid, sorbic acid, lactic acid
Polymers/polysaccharides	Chitosan
Gas	CO_2, SO_2
Metals	Silver
Metal oxides	TiO_2, ZnO, MgO
Bacteriocins/peptides	Nisin, pediocin, lacticin
Enzymes	Lysozyme, glucose oxidase, peroxidase
Chelating agents	EDTA
Spices (extracts)	Horseradish, cinnamon, rosemary, oregano, ginger, green tea, tea tree
Essential oils/oleoresins	Thyme, oregano, pimento, clove, citron, lemon verbena, lemon balm,
Pure bioactive components	Carvacrol, cinnamaldehyde, eugenol, thymol

Table 5: Example of antimicrobial substances for antimicrobial active packaging (Own elaboration)

As it can see, the range of possible active substances is wide. Metals, especially silver and silver compounds, are one of the most widely used antimicrobial agents over the years, because they have an effective antimicrobial effect against a wide variety of microorganisms at low concentrations and have low toxicity (Vilela et al., 2018). In order to take a decision, several patents, scientific articles or reviews are analysed.

According EOI (2015) the containers with antimicrobial effects must fulfil a series of characteristics:

- Wide spectrum of action.

- Active at low concentrations of the microbial substance

- Not having adverse sensory effects

- Low cost and be approved for use in food

From this bibliographical study, it is observed that, at present, the tendency to use essential oils (EOs) and natural extracts as antimicrobial agents and to use them as substitutes for synthetic additives is growing (Wasin and Shafiur, 2015). EU Patent No. 1,657,181,A1 (2006) uses an active compound formed by a resin substrate, solvents, additives and an extract of natural essences such as cinnamon, ginger, rosemary, oregano, dill, basil or others. US Patent No. 0,273,276 (2018), is based on the combination of active ingredients with microbial activity, specifically citral, hexanal, and linalool.

Society is increasingly rejecting synthetic chemical preservatives because they can be harmful to human health. Thence, researchers face the challenge of applying oils and essential extracts in food products and food packaging (Zanetti, Carniel, Dalcanton, Silva dos Anjos, Riella, de Araújo, de Oliveira and Fiori, 2018). Many studies show that essential oils (EOs), plant extracts and their isolated components have a great capacity to inhibit the growth of microorganisms (Vilela et al., 2018). In addition, natural extracts have the advantage that they are all classified as GRAS materials (Generally Recognized as Safe) (Garcés, 2006). Therefore, given its great potential as antimicrobial agents in food packaging, its low toxicity for humans and the growing acceptance by society, EOs are selected as antimicrobial active ingredients for the packaging to be developed.

López et al. (2005) studied the effect of EOs vapours of cinnamon, clove, basil, dill, rosemary and ginger on Gram-positive bacteria (Staphylococcus aureus, Bacillus cereus, Enterococcus faecalis and Listeria monocytogenes), Gram-negative bacteria (Escherichia coli, Yersinia enterocolitica, Salmonella choleraesuis and Pseudomonas aeruginosa) and three fungi (Candida albicans, Penicillium islandicum and Aspergillus flavus); obtaining that the cinnamon and clove EOs showed the highest antimicrobial activity. Lopéz et al. (2007) demonstrated the antibacterial and antifungal activity of cinnamon, thyme and oregano EO. Inouye et al. (2001) studied the efficacy of vapours from different EOs, obtaining that the cinnamon and thyme EOs showed the highest antimicrobial activity since their major components are phenols and aldehydes. In addition, Inouye et al. (2006) investigated the antifungal activity of different EOs, obtaining that those EOs that have as main components the phenols were the ones with the highest antifungal

activity, such as, for example, thyme EO, followed by cloves according to Tullio et al. (2007) (Reyes-Jurado, Palou and López-Malo, 2012).

Hence, from these studies, it is considered that the EOs that could be used for this project are cinnamon, clove, oregano and thyme EO. Even so, it would be necessary to carry out tests to verify that with these EOs, in the application required in F&V, the expected effects are achieved without altering the organoleptic properties of the product. Research should also be done to determine with which, or with which combination, a more adequate effect is achieved.

These EOs present a series of drawbacks that must be considered. The main one is that high concentrations are required to achieve the same effectiveness in food products as with other antimicrobials, so care must be taken not to affect the organoleptic characteristics of food (Vilela et al. 2018). To solve this drawback, the container to be developed will consist of the amount necessary so that it does not affect the aroma or flavour of the food, although this implies a lower microbicidal effect.

5. SELECTION OF THE APPLICATION SYSTEM

After defining the type of product to be packaged, the AP systems used and the active ingredients, the application system must be defined. For this, it is necessary to know the different forms that can be presented and determine which one will be the most suitable for selected the AP systems and ingredients.

Actuation mechanisms:

To establish the packaging system, the mechanisms of action or principles of action of the active packages must be known. These can be presented in two ways depending on where the active component is (EOI, 2015; Galindo-Galiana and Gonzalez-Leyba, 2012; Pascall and Han, 2018; Pradas and Moreno, 2016):

- **Inside the package**: it consists of the introduction of an external element that contains the active substance inside the package together with the product to be packaged, being the most common forms in sachets, envelopes, pads, adhesives, sheets or labels.
- **In the packaging material**: it consists of incorporating the active substance directly into the packaging material itself, either integrated with the material or applied as a coating. It is released in a controlled way to the headspace, or absorbs, also in a controlled form, some undesirable substance from inside the package.

The *Image 14* obtained from Limbo and Khaneghah (2015) shows the different ways of applying antimicrobial release systems, but it can be extrapolated to other active systems, so it serves to give a general idea. Systems in which the active component is in the packaging material would correspond to *14a* (incorporated in the material itself), *14b* (incorporated in the material itself, as coating and by transfer from the headspace) and *14c* (incorporated into the material itself and by diffusion by direct contact with the food). Examples of systems in which the active component is inside the package would be *14d* (pad in direct contact) and *14e* (envelope with transfer from the head space). *14f* would correspond to a coating of edible film on the food itself.

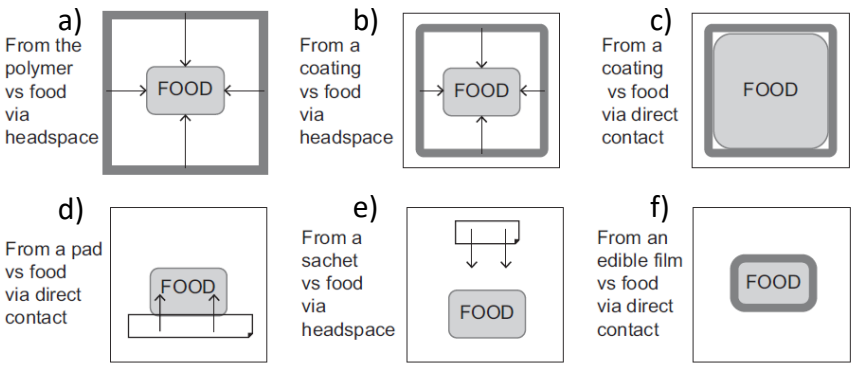

Figure 14: Possible forms of antimicrobial release systems for food packaging applications (Source: Limbo and Khaneghah (2015))

The migration of the active ingredients can be achieved by direct contact between the food and the active material, or by diffusion of the active substance in the headspace from the packaging material to the surface of the food. If the active ingredient is not volatile, direct contact with the food is required for diffusion migration of the active compound or absorption of the unwanted compound, as in *14c* and *14d* or *14f*. If it is volatile, direct contact is not required and migration can be achieved by transfer through the headspace, as in *14a*, *14b* and *14e* (Limbo and Khaneghah, 2015).

5.1. ETHYLENE ABSORBER APPLICATION SYSTEM

$KMnO_4$ is a substance with high oxidizing power and toxicity, so it cannot be used in direct contact with food products. In consequence, the ethylene absorber based on $KMnO_4$ is used absorbed in a carrier, which is incorporated into elements that prevent contact with the stored product, such as envelopes, sachets, films or filters (Mehyar and Han, 2010). For that, in most of the consulted sources, ethylene absorbers are applied in external devices that are placed inside the container, generally in sachets or envelopes with high permeability to ethylene but impervious to $KMnO_4$ (Brody et al., 2008; EOI, 2015; Nayik and Muzaffar, 2014; Vikas et al., 2017).

Generally, for $KMnO_4$ to be effective, it must be applied adsorbed on an inert support (carrier) with a large surface area (Pascall and Han, 2018). In this way a solid absorbent is formed that increases the contact area, because the only forces that produce

ethylene-absorbent contact are the diffusion and natural convection of the air in the atmosphere (Balaguera-López et al., 2014).

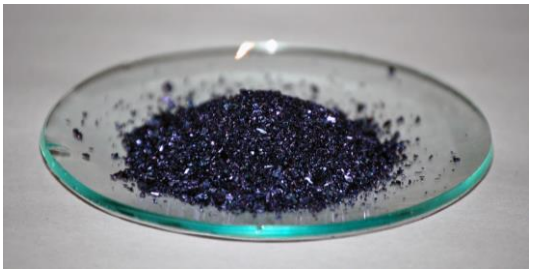

Figure 15: Potassium permanganate

(12/08/2019, Wikimedia)

Balaguera-López et al. (2014) indicates that some of the most used carriers are vermiculite, alumina, perlite, zeolite, among others. For its part, Pascall and Han (2018) mentions silica gel, celite, vermiculite, alumina pellets, glass, or activated carbon as the most common inert supports. Nayik and Muzaffar (2014) mentions that it is frequently embedded in silica and that metal catalysts, such as palladium or light-activated titanium dioxide, can be used to accelerate the oxidation reaction of $KMnO_4$, and may increase adsorption capacity even 6 times. EOI (2015) mentions that $KMnO_4$ is immobilized in alumina, silica gel or graphite.

The ethylene absorber to be developed has been decided to be applied in sachets or envelopes since it is the most common form of application for this ingredient in the sources consulted. Besides, many of the AP technologies for F&V are based on sachet technology (Mehyar and Han, 2010).

Figure 16: Example of sachets for F&V of $KMnO_4$

(20/08/2019, Chengde Hongya Activated Carbon Co. Ltd)

The adsorbent chosen is activated alumina, a decision that has been taken based on the article by Wills and Warton (2004) in which the efficacy of $KMnO_4$ impregnated in alumina beads is studied. Alumina is a material with high adsorption capacity and large surface area, which as mentioned, many other sources mention it for the described application.

Therefore, the ethylene absorber to be developed consists of $KMnO_4$ adsorbed in activated alumina spheres and incorporated into sachets. The principle of action of the ethylene eliminator is the absorption and subsequent oxidation of ethylene (Martínez-Tenorio and López-Malo, 2011; Nayik and Muzaffar, 2014). The oxidation reaction of ethylene (C_2H_4) by $KMnO_4$ that takes place is as follows:

$$4\ KMnO_4 + C_2H_4 \rightarrow 4\ MnO_2 + 2\ CO_2 + 4KOH$$

5.1.1. Design of potassium permanganate sachets impregnated in alumina

First, the size of the alumina spheres in which the $KMnO_4$ is to be impregnated must be determined. There are alumina spheres of various sizes, one size or another being more appropriate depending on the application (Perry and Green, 1999). Wills and Warton (2004) used 0.5 cm diameter alumina beads for the study. The diameter to be used in this project is 0.6 cm, to obtain a larger surface area, in which to be able to adsorb a greater amount of $KMnO_4$, and therefore, require a smaller number of spheres for the same amount of ethylene to be removed. This size is considered adequate as it is visible to the consumer.

Figure 17: Example of sizes of alumina spheres.

(20/08/2019, Pingxiang Xingfeng Chemical Pckaging Co., Ltd)

- **Determination of the number of spheres per package**

The number of impregnated spheres required for a package will depend on the amount of $KMnO_4$ needed to remove ethylene from the container. The dose of $KMnO_4$ depends on several factors such as the product, the carrier, the characteristics of the container, the storage conditions, among others. Although there are several studies on ethylene absorbers based on $KMnO_4$, they do not define the $KMnO_4$ content of such absorbers or the amount of ethylene that can be eliminated (Wills and Warton, 2004). In order to estimate the required $KMnO_4$, first, the quantity of product that the containers will store is established to know how much ethylene that can be produced in a container.

It must be considered that the quantity of product contained in the package is not the only factor that determines the amount of ethylene present in the package, since it also depends on the rate of ethylene production of each fruit. There are fruits that are of greater volume and greater weight than others, so in some cases the containers must be larger so that they contain an adequate number of pieces. But this does not imply that, the larger the size of the fruit, the greater the production of ethylene. In those cases, an amount of absorber proportional to the amount of ethylene produced by the amount of product to be packaged should be added.

Consequently, we can face different situations depending on the dose of ethylene produced by the packaged fruit and the quantity of product packaged. Therefore, to achieve greater effectiveness, each case should be analysed, and a more specific design adapted to each product. Since this would entail a very high cost, it has been decided to establish a convenient amount of packaging and consider an average ethylene production rate.

In order to make a reality-adjusted decision, the quantities contained in the containers in several stores have been examined, and generally, the most common packages are 0.25, 0.5 or 1 kg. The quantity chosen as the basis for the design of the packages is 0,25 kg, so each envelope of absorber will be suitable for that quantity. It is considered adequate since it is an amount that is on the market and, in addition, that they are small quantities of product will cause consumers to consume them shortly after opening the container, so that it is not necessary to keep it for a long time once opened.

On the other hand, that they are sachets destined to small quantities, it has the advantage that, if larger packages are required, more sachets can be added. That is, in the case of 0.5 kg containers, two envelopes will be added, and in the case of 1 kg, three.

The amount of ethylene produced is different depending on the fruit. No reliable sources have been found that indicate the specific ethylene production rate for each fruit. Despite having no values, if it has been possible to determine which ones have a higher or lower production rate, which can give an idea of how they are classified (*Table 6*). Wills and Warton (2004) state that "the rate of production of ethylene by horticultural produces varies widely with non-climacteric produces generally generating ethylene at <1 µL/(kg·h), at 20 °C while preclimacteric climacteric fruit often generate ethylene at 1-10 µL/(kg·h)," (p.437). The ethylene production rate to be considered for the development of this project is 10 µL/(kg·h), since it is the upper limit for climacteric fruits, those that have more difficulties to delay ripening.

Class of ethylene production	Product
Very low	Strawberry, pomegranate, lime, tangerine, orange, grapes
Low	Raspberry, melon, honey dew, blackberry, mango, pineapple, watermelon, tomato
Moderate	Banana, avocado, guava, papaya,
High	Apricot, plum, peach, apple, pear, cape gooseberry,
Very high	Custard apple, sapodilla, passion fruit

Table 6: Class of ethylene production in fruits (Own elaboration)

Once the quantity of product to be packaged and the average production rate have been determined, the amount of ethylene produced in said container can be determined. Then, it is necessary to determine what is the amount of $KMnO_4$, or consequently of absorbent, necessary to eliminate said amount of ethylene.

The absorbed permanganate-ethylene ratio is determined by the study conducted by Wills and Warton (2004). In this study, activated alumina beads impregnated with $KMnO_4$ at a concentration of 4 g/100 g are used. Under conditions of packaging of horticultural products of 20 °C and 90% RH, and for an ethylene production of 1 µL/(kg·h), 6 g of absorbent is required per kg of product to reduce to 90% of ethylene

for 14 days From these conditions, it is obtained that to eliminate 302.4 µL of ethylene, 0.24 g of $KMnO_4$ is needed (*Appendix 2*).

In this project, it is considered enough to delay the maturation of the packaged product by 4 days. With this, the seller will manage to keep the fresh product longer at the appropriate point of consumption, so that it will extend its useful life and may increase the term to be acquired by the consumer.

The range of $KMnO_4$ concentrations found in commercial alumina-based absorbents according to Wills and Warton (2004) is 2.7 to 6.0 g/100g. In the product to be developed, it is decided to use a concentration of $KMnO_4$ of 6 g/100 g, so that the spheres obtained have a high concentration of $KMnO_4$ and thus less numbers of spheres are needed per envelope, so that they occupy the minimum possible space.

In summary, for the absorber to be developed we have to:

Parameter	Value
Sphere diameter	0.6 cm
Time	4 days
Quantity of packaged product	250 g
Ethylene production	10 µL/(kg·h)
$KMnO_4$ concentration	6g/100g
Ethylene removed	90%

Table 7: Properties of ethylene absorber (Own elaboration)

Under these conditions it is obtained that:

- Amount of ethylene produced per container:

$$\frac{10\mu L}{kg \cdot h} \cdot 0{,}25\ kg \cdot 4\ d \cdot \frac{24h}{1d} = 240\ \mu L\ ethylene$$

- Amount of ethylene to be removed:

$$240\ \mu L\ ethylene \cdot 0{,}9 = 216\ \mu L\ ethylene$$

- Amount of absorbent (impregnated spheres):

$$0{,}171\ g\ KMnO_4 \cdot \frac{100\ g\ absorbent}{6\ g\ KMnO_4} = 2{,}86\ g\ absorbent$$

The amount of spheres per sachet will be set at 3 grams, since different suppliers of impregnated alumina spheres have been analyzed and it is the minimum amount that they have been found to provide. Generally, the commercial product can be found in envelopes of 3, 5, 10 or 20 grams. In this way, 3g per envelope is an amount that is consistent with commercial products. To determine what number of spheres, represent 3g of absorbent it is necessary to know their density. To this end, a search has been made for different suppliers that provide beads of the required characteristics and specify their density. It has been found to be 0.85 g/mL. Thus:

- Sphere volume:

$$Vsphere = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(\frac{0{,}6}{2})^3 = 0.113\ cm^3 = 0.113\ mL$$

- Sphere mass:

$$msphere = 0.1131\ mL \cdot \frac{0{,}85\ g}{mL} = 0{,}0961\ g\ sphere$$

- Number of spheres impregnated in $KMnO_4$ per package:

$$\frac{3\ g\ absorbent}{0{,}0961\ g\ sphere} = 31.2\ spheres\ \approx 31\ spheres\ per\ package$$

- Amount of $KMnO_4$ per sphere:

$$3\ g\ absorbent \cdot \frac{0.171\ g\ KMnO_4}{2.86\ g\ absorbent} = 0.179\ g\ KMnO_4$$

$$\frac{0.179\ g\ KMnO_4}{31\ spheres} = 0.00577\ g\ KMnO_4\ per\ sphere$$

Figure 18: Example of $KMnO_4$ impregnated spheres

(30/08/2019, eSalud)

These spheres will be arranged in sachets as explained above. The size of these sachets must be adequate to contain the necessary spheres. Suppliers offer sachets of different sizes depending on the amount of absorbent they contain, with some options being 4x5 cm, 4.5x5 cm, 4.5x6 cm, 6x6 cm, 6.5x7 cm, among others. Since the quantity in weight is the minimum quantity that they offer, it is decided to present it in the envelopes of smaller size, that is, in envelopes of 4x5 cm.

Figure 18: Example of $KMnO_4$-based ethylene absorber sachets
(14/08/2019, Dongguan Dingxing Industry Co., Ltd)

- **Sachet material**

As mentioned, this absorbent cannot be in contact with food due to the toxicity of $KMnO_4$. Therefore, it must be bagged in a material that is permeable to ethylene but impervious to $KMnO_4$, so that it is achieved that the oxidizing material can act while being contained in a safe support. That is, ethylene diffuses through the envelope material and is absorbed by potassium permanganate (Mehyar and Han, 2010).

Several patents indicate that the material that is usually used to contain the ethylene absorber is a material of unstructured fibers of high-density polyethylene, which is characterized by having a high resistance, gas permeability and water impermeability (Astigarraga and Wang, 2015). Hence, it is decided that this will be the material of which the sachets will be. With this material a resistant barrier is achieved that separates the active compound from the packaged product. A commercialized example of this material would be DuPont TYVEK bags (DuPont, n.d. – Website).

- **External sachet material**

It is important that during the time that the absorber is stored waiting to be used it is properly isolated from the environment since, the absorber can deteriorate and lose its properties if it meets air or certain substances. Therefore, each absorber sachet will be stored in a second bag that is completely impervious (SpGroup, n.d. – Website).

5.2. ANTIMICROBIAL EMITTER APPLICATION SYSTEM

Essential oils (EOs) are liquid substances consisting of volatile aromatic mixtures of low molecular weight compounds, with lipophilic character and strong aromatic properties (Vilela et al., 2018). The main components of EOs are volatile, such as, e. g., phenolic compounds, aldehydes, alcohols, ketones, hydrocarbons, esters, ethers and oxides. It is these compounds that have antimicrobial and, in some cases, antifungal effects. The antimicrobial activity of EOs depends mainly on their chemical components and the type of microorganism to which they must attack (Reyes-Jurado, Palou and López-Malo, 2012). The hydrophobicity of the EO allows them to penetrate the lipids of the cell membranes, altering the cell structures and making them permeable, which leads to leaks of the cell content and can lead to cell death (Burt, 2004).

Figure 20: Essential oils.

(22/08/2019, EcologíaVerde)

There are numerous studies on the antimicrobial effects of EOs against various microorganisms, but they do not quantify or explain its mechanism of action (Hernández, 2011). In addition, generally, the application of EOs in real foods is limited by the alterations that they can cause in their organoleptic characteristics given the high concentrations that are required to have an effective action. Unwanted organoleptics

effects can be limited or corrected by selecting the EOs carefully according to the type of food to which they are to be applied (Burt, 2004).

Normally, EOs with high antimicrobial capacity contain a high level of phenolic compounds such as carvacrol, eugenol and thymol (Hernández, 2011). Some research indicates that EOs vapours have a superior antimicrobial effect than they have in liquid form through direct contact. Through the application by vapor phase and not by direct contact, it is achieved that the aromatic active ingredients do not affect the organoleptic characteristics of the final product (Reyes-Jurado, Palou and López-Malo, 2012).

Most of these compounds are thermolabile substances, that is, they are easily altered by the action of heat, so they are incompatible with some manufacturing processes. For the manufacture of the packaging material, extrusion is generally applied, and the active agents that are incorporated in said packaging material are subjected to that process and, therefore, at relatively high temperatures. Given the sensitivity of EOs to high temperatures due to their volatility, in order to avoid evaporation losses due to heat during the extrusion process, it is decided that the EOs will be applied externally within the container, instead of being incorporated into the own material.

Specifically, it is decided to use the same method as for ethylene absorbent sachets, and the EOs will also be impregnated in activated alumina. In this way, you save on raw materials since the same carrier is used for both processes and the manufacturing process is facilitated by using the same method for both.

5.2.1. Design of EOs sachets impregnated in alumina

In the absence of information on the process of impregnating EOs in alumina spheres, a process similar to that of $KMnO_4$ is considered, but prior tests would be necessary to verify that the values obtained conform to reality.

The same alumina spheres as for the $KMnO_4$ process will be used, so the size of the spheres will be 0.6 cm, and the volume of each sphere 0.113 mL. Estimating the density of the spheres impregnated in EOs, a value of 0.76 g/mL is obtained (knowing that the average density of the selected EOs is 0.92 g/mL, concentration of EOs in spheres is 6 g/100 g and that the density of alumina spheres without impregnating is 0.75 g/mL)

(*Appendix 2*). Thus, it is obtained that the mass of each sphere impregnated in EOs is 0.0859 g.

We assume that the weight of absorbent in each sachet will be the same as for $KMnO_4$ sachets, that is, 3 g. Using a concentration of EOs in the spheres of 6 g/100 g, it is obtained that the amount of EOs in each envelope of 3 g is 0.18 g. With this data it gets that:

- Number of spheres impregnated in EOs per envelope:

$$\frac{3\ g\ absorbent}{0{,}0859\ g\ sphere} = 34.9\ spheres\ \approx 35\ spheres\ per\ sachet$$

- Amount of EO per sphere:

$$\frac{0.18\ g\ EO}{35\ spheres} = 0.00515\ g\ EO\ per\ sphere$$

These spheres are to be introduced in the same sachets described in *chapter 5.1.2* for the spheres impregnated in $KMnO_4$. The external envelope to protect the emitter's properties will also be the same.

6. MANUFACTURING PROCESS OF THE DEVELOPED PRODUCTS

6.1. RAW MATERIALS

I. Alumina spheres

First, it is necessary to define in which state the alumina is going to be obtained. Activated alumina is marketed in different forms such as dust, granules, spheres, fibrous scales (Perry and Green, 1999). Activated alumina spheres are required for the product to be developed. There are several possibilities to obtain the alumina in the required state, such as buying it in powder form and subsequently agglomerating, but to facilitate the manufacturing process it is considered more appropriate to buy the alumina directly in spheres of the desired size to subsequently impregnate them.

There are various suppliers of alumina spheres of different sizes. Next, a compilation of some of them is made

Company	Country	Spheres
Pingxiang Funeng Chemical Industry Co., Ltd	China	1-3mm, 2-4mm, 3-5mm, 4-6mm, 5-7mm, 6-8mm, 8-10mm
Xieta International, SL	Spain	3-5mm, 5-7m, 7-9mm, 9-11mm, 12mm, 14mm, 16mm, 18mm, 20mm, 25mm
Zibo Xiangrun Environment Engineering Co., Ltd	China	3.5mm, 4-6mm, 5-8mm, 8-10mm
GoodFellow	UK	0,5mm, 1mm, 3mm, 4mm, 5mm, 6mm, 7,5mm, 8mm, 10mm, 18mm, 20mm,

Table 8: Some alumina spheres suppliers (Own elaboration)

II. Potassium permanganate

To permeate the ethylene absorbing spheres, a solution of high concentration of potassium permanganate is needed. Potassium permanganate is to be purchased in a solid state and the $KMnO_4$ solution is prepared at the desired concentration prior to impregnation.

III. Essential oils

EOs can be extracted from different parts of plants, such as flowers, leaves, roots, from the resin they exude, from the shell of the fruits. The processes that are mainly used to obtain them are steam distillation and extraction (Reyes-Jurado, Palou and López-Malo, 2012). The EOs that are going to be used in the production process to be described will be acquired in a liquid state already extracted.

6.2. PRODUCTION DETERMINATION

- **Ethylene absorber sachets**

To determine the production of ethylene absorbent spheres, a number of stores to supply, a quantity of containers per store and day, and a supply time are established. It is considered reasonable to supply 250 stores, with 30 sachets per day and for 12 months. With this data, the number of ethylene absorber envelopes to be produced is 2,700,000 and, knowing the number of spheres above that obtained in *Chapter 5.1*, a total production of 83,700,000 spheres is obtained of ethylene absorber.

Parameter	Value
Number of stores	250
Number of sachets per store and day	30
Supply time	12
Number of sachets to produce	2,700,000
Number of spheres to produce	83,700,000

Table 9: Ethylene absorber sachets production (Own elaboration)

- **Antimicrobial emitter sachets**

Since this project has been proposed in such a way that the two active systems are applied in the same package, an ethylene absorber sachet and an antimicrobial agent emitting sachet will be introduced in each container (two of each if the package is of 0.5 kg, and three in the case of 1 kg). Therefore, the spheres emitting antimicrobial agents must cover the same number of containers as the ethylene absorbent spheres, so the same number of envelopes must be manufactured for both: 2,700,000 envelopes. That is, the production of antimicrobial emitting envelopes must supply the same number of stores, with the same envelopes per store and day, and during the same period.

Since the number of spheres that each antimicrobial agent emitting envelope contains (estimated in *Chapter 5.2*) is greater than that contained in ethylene absorbing envelopes, the production in number of spheres, to produce the same number of envelopes, is also greater than for ethylene absorbers.

Parameter	Value
Number of stores	250
Number of sachets per store and day	30
Supply time	12
Number of sachets to produce	2,700,000
Number of spheres to produce	94,500,000

Table 10: Antimicrobial emitter sachets production (Own elaboration)

6.3. DESCRIPTION OF THE MANUFACTURING PROCESS

The production process of the spheres is practically the same for both types of active sachets to be manufactured but will be explained individually for each of them in order to clarify the differences that may arise. In general, the following stages could be distinguished in both processes: dissolution, impregnation, solid-liquid separation and drying. Once the spheres were produced, the number of appropriate spheres in each sachet would be dosed, then these sachets would be suitably bagged in a second envelope that would protect their properties and eventually be stored pending distribution.

6.3.1. Manufacturing process of ethylene absorber sachets

I. Dissolution

The process starts from the preparation of the solution of $KMnO_4$ in water at the desired concentration. Wills and Warton (2004) conduct a study on the efficacy of alumina spheres impregnated in $KMnO_4$ according to different preparation methods. In this study, using a solution of 10 g/100 mL they obtain spheres with a $KMnO_4$ concentration of 4 g/100 g of absorbent.

In this project, the concentration required to obtain $KMnO_4$ in the spheres is 6 g/100 g, as defined in *Chapter 5.1*. Considering the results obtained in the study of Wills and Warton (2004), it follows that with a solution of 20 g/100 mL, spheres with a concentration of $KMnO_4$ that approximates 8 g/100 mL could be obtained. Assuming there was a linear proportion, to obtain 6 g/100 mL, $KMnO_4$ solutions of 15 g/100 mL

would be required. In any case, to determine the concentration of solution necessary to obtain them at 6 g/100 mL, tests with $KMnO_4$ solutions at concentrations higher than 10 g/100 mL would have to be made until reaching 6 g/100 mL.

Therefore, the concentration of the solution chosen is 15 g/100 mL. Since the solubility of $KMnO_4$ in water is 2.83 g/100 mL at 0 °C (Perry and Green, 1999), it is decided that the solution will be carried out by increasing the temperature to achieve greater solubility. This temperature will be 65 °C, since, as explained in the following section, it will be the temperature at which the impregnation will be carried out. In this way, energy is harnessed by having the solution at the temperature necessary for impregnation.

Figure 21: Example of $KMnO_4$ dissolution
(30/08/2019, Quimicasthai)

II. Impregnation

The impregnation stage is based on the adsorption of $KMnO_4$ in the alumina spheres. It is carried out by immersion of the spheres in the solution of $KMnO_4$. It can be done in different ways: a single impregnation, or more than one can be performed, leaving between them a drying time. In addition, it can be performed at room temperature or by increasing the temperature.

Wills and Warton (2004) employ a $KMnO_4$ solution of 6.4 g/100 mL at 20 °C, making a single impregnation at different times, from 3 min to 4 h, and on the other hand, making several impregnations and leaving 30 min between them to dry. On the other hand, they use a $KMnO_4$ solution of 10 g/100 mL at different temperatures, 20 °C, 65 °C and 90 °C, and impregnate for 1, 3 and 5 h for each (Appendix 3).

In the results obtained, in the same impregnation, the time does not greatly increase the amount of permanganate absorbed and even surface crystals are obtained or the oxidation of $KMnO_4$ occurs. In addition, it is observed that greater absorption is achieved when the temperature is increased during the dipping than when several dives are carried out with intermediate drying. That is, at a higher temperature a higher concentration of $KMnO_4$ is obtained in the spheres, but care must be taken since, when the temperature is increased too much, the oxidation of $KMnO_4$ also occurs, as happens at 90 °C. The concentration of $KMnO_4$ in alumina spheres obtained by immersion in saturated solutions is 2 g/100 g after 2 h at 20 °C and 4 g/100 g after 1 h at 65 °C.

Therefore, the concentration of $KMnO_4$ obtained in the spheres depends on how the preparation process is done. In this work, to obtain spheres with a concentration of 6 g/100 g, it is decided to make a single immersion, raising the temperature to speed up the impregnation process and achieve greater impregnation in less time. Specifically, at 65 °C and for 1 h. Wills and Warton (2004) affirm that commercial products are prepared mainly by immersion in solutions at high temperatures, so that the decision made fits reality. In any case, it would be necessary to carry out previous tests to verify that the established conditions conform to the expected, since the same conditions as in the article will not be used.

III. Solid-liquid separation

After impregnation, the alumina spheres impregnated in $KMnO_4$ must be separated from the remaining solution. Since it is a mixture of solids and liquid, in which the solid is insoluble in the liquid, it is considered that the most suitable unit operation is filtration. Filtration is based on passing the mixture through a porous barrier that retains the solid particles and lets the fluid pass (Perry and Green, 1999).

This separation does not have great difficulty since it is a heterogeneous mixture, in which the solid phase is insoluble particles with a sufficiently large size and the liquid phase is an aqueous solution. Filtration can be done by gravity, being this the force that drives the liquid through the pores of the filter, or under vacuum, if it wants to increase the filtration rate with respect to gravity filtration (Quercusblog, 2014 -Website).

IV. Drying

Once the spheres are filtered, drying is necessary to eliminate the moisture that the solid may contain. In the process described by Wills and Warton (2004), the spheres are allowed to air dry for 30 min between immersion and immersion, and the final drying of the impregnated spheres is carried out by means of ambient air at 20 °C for 16 h.

The type of drying to be used in this project is direct or convection drying, just as they do in the article by Wills and Warton (2004). That is, the heat necessary for the evaporation of the liquid is transmitted by a gaseous agent or a vapor that passes through the solid or passes through it. The gaseous agent that is decided to use is nitrogen. In addition, to accelerate the drying process, and as in this case what is going to evaporate is water, the N_2 will be heated to about 80 °C, since increasing the temperature favours drying. In this way, while there is water to evaporate, the product will be at a much lower temperature than N_2, at approximately 26 °C (See Appendix 4).

The speed of drying also depends a lot on how the gaseous agent circulates through the solid to be dried. That is, if nitrogen passes transversely to the spheres or if it circulates through them. In this second case, drying would be faster. Hence, it is thought to pass the nitrogen at counterflow. With all these conditions, it is assumed that a drying time of about 2 h can be obtained. To verify that this is so, prior tests must be done.

6.3.2. Manufacturing process of antimicrobial agents emitting sachets

No bibliographic articles or reviews were found detailing the impregnation process of EOs in alumina or other carrier spheres. Therefore, having no information, it would be necessary to perform tests in order to determine appropriate conditions. But despite this, a process similar to that used for alumina spheres impregnated with $KMnO_4$ is considered, since there are no reasons why it cannot be applied, but with the variations that are appropriate for the characteristics of EOs.

I. Dissolution

The first part of the process, consisting in the elaboration of a solution, is the same as for the ethylene absorber, with the difference that water cannot be used as a solvent since the essential oils are insoluble in it. Therefore, a suitable solvent must be selected.

For the impregnation of the antimicrobial emitting spheres, a dissolution of EOs in a solvent in which they are miscible is necessary. The characteristic that makes EOs related to the solvent is its polarity. That is, since EOs are nonpolar, said solvent must be non-polar so that EOs are soluble in it. In addition, since the containers in question are intended for food products, it must be a solvent that is allowed for the manufacture of food products. As Directive 2009/32/CE indicates, some of the apolar solvents that can be used are propane, butane, ethyl acetate or acetone.

The solvent chosen for said solution is ethyl acetate, since it is one of those allowed for this use and, in addition, it is mentioned as an EOs solvent in some source (Reyes-Jurado, Palou and López-Malo, 2012), having a lower boiling point than the EOs, evaporation will be achieved and that these remain impregnated in the spheres.

Compound	Boiling point
Essential oils	150 - 300
Ethyl acetate	77.11

Table 11: Boiling points (Own elaboration)

Ethyl acetate ($C_4H_8O_2$) is a highly flammable volatile liquid with a fruity aroma. It is widely used as a solvent in different industries, such as cosmetic, textile, food or pharmaceutical (INSST, 2018 – Website).

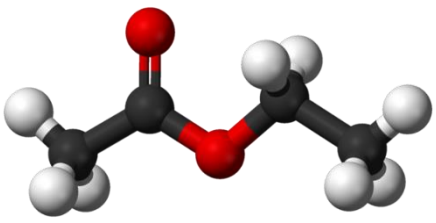

Figure 22: Model of spheres and bars for ethyl acetate

(30/08/2019, Lifeder - Benjah-bmm27)

Regarding the concentration of said solution, prior tests should be performed to determine an effective concentration. But, in principle, it is thought to use solutions of 15 g/100 mL of oil in ethyl acetate. Given the volatility of both EOs and allyl acetate, said solution will be prepared at room temperature to avoid evaporation losses.

II. Impregnation

The impregnation step of the EOs impregnated spheres, like the $KMnO_4$ impregnated spheres, is based on the immersion of the alumina spheres in the solution of EO-Ethyl acetate at the specified concentration.

For the same reasons as for the impregnation of the spheres in $KMnO_4$, it is decided to perform a single impregnation of 1 h. But in this case, due to the volatility of the EOs, such impregnation will be carried out at room temperature. It is expected to obtain spheres impregnated in EOs with an approximate concentration of $KMnO_4$ spheres, of 6 g/100 g of absorbent. As in the rest of the stages, prior tests should be carried out in order to determine whether these conditions meet what is expected.

At this stage, since a volatile organic solvent is being used, it will be recovered for reuse. Its recovery to reuse it is essential to reduce production costs. This recovery will be carried out by conducting the vapours produced to a condenser.

III. Solid-liquid separation

In the separation stage of the impregnated spheres and the EOs-ethyl acetate solution, in the same way as in the process of ethylene absorbers, the unit operation used is filtration. In both processes the phase of interest is the solid phase (impregnated spheres). The filtration mode in this case, in the absence of performing previous tests, is also by gravity.

IV. Drying

In the same way as with the spheres impregnated in $KMnO_4$, the drying of the spheres impregnated in EOs will be carried out using nitrogen. In this case, high temperatures are not wanted to minimize evaporation of EOs. Hence, the nitrogen is not going to be heated and it is decided to dry these spheres under vacuum, since this mode of operation allows to reduce the temperature at which the solvent evaporates, thereby reducing the drying temperature. Therefore, in this case nitrogen will be used at room temperature and vacuum dried.

As the boiling point of ethyl acetate is lower than of water, during drying, the spheres will be at a lower temperature, probably reaching temperatures close to 0-5 °C (See Appendix 4). Hence, despite not increasing the temperature, circulating nitrogen

through the spheres and using vacuum, drying could be fast enough to occur in a time of 2 h.

6.3.3. Equipment selection

Once described the stages of the process and the respective conditions in which they will be developed, the equipment in which each one of them will be carried out are selected. Since the process is very similar for the two types of active envelopes to be manufactured, the equipment to be used in the different stages will serve both. In addition, the mode of operation will be in batches, as explained in *chapter 6.4.1*.

I. Dissolution equipment

This stage consists in putting in contact two phases that are soluble. In the case of the ethylene absorber, it is a solid phase, $KMnO_4$, and another liquid phase, water. In the case of the antimicrobial emitter, these are two liquid phases, one the EOs, and the other the ethyl acetate. It is desired to obtain a homogeneous solution of both phases, for which agitation is necessary. In the case of $KMnO_4$ the temperature will be increased to favour solubility, but in the case of EOs it will be at room temperature.

The most recommended equipment for the application of mixing liquids and preparing solutions is a stirred tank, which consists of a mixing vessel with a stirring system (Sinnot, 2005). The agitated tank can be closed or opened. The choice of one or the other depends on the characteristics of the fluid being handled and the reaction. On the one hand, due to the toxicity and strong oxidizing power of $KMnO_4$, and on the other, the volatility of EOs and ethyl acetate, the agitated tank to be used must be closed.

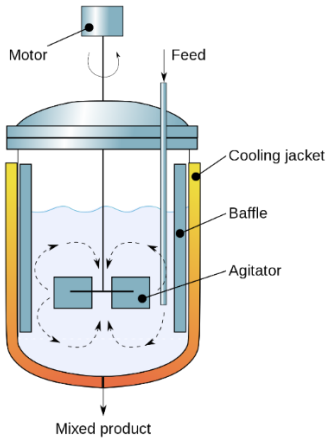

Figure 23: Closed stirred and jacketed tank.

(30/08/2019, Wikipedia)

Since the temperature is to be increased in the case of $KMnO_4$, the tank must have a heating system. An option that is considered adequate is a jacketed jacket. The agitator must be appropriate for homogenization. The bottom of the tank will be ellipsoidal, since it is the most appropriate geometry when the resulting solution is in a liquid state.

II. Impregnation equipment

At this stage, a solid is to be contacted with a liquid: the alumina spheres with the appropriate solution in each case. In this way, it is desired to achieve the impregnation of the spheres by immersion in the corresponding solution. In the case of $KMnO_4$ it will be necessary to increase the temperature, so the equipment must have a heating system.

The appropriate equipment for this operation is also a stirred tank, as in the dissolution stage. In this case, it must be of greater capacity since it must house the volume of the solution and that of the spheres. Like the dissolution tank, it will also be closed. For this stage, the agitator must be suitable for solids-liquid suspensions, since it is important that, while the impregnation lasts, the particles remain suspended throughout the solution and do not deposit in the bottom of the tank.

III. Solid-liquid separation equipment

As specified, for the stage of separation of the spheres and the excess liquid after impregnation, the operation used is filtration. Therefore, the type of equipment to be selected is a filter. Of the two existing phases, the one that interests us is the solid phase that corresponds to the impregnated alumina spheres. Therefore, the filter to be selected belongs to the group of cake filters, those that separate large amounts of solids (McCabe, Smith and Harriott, 1991).

Regarding the liquid phase, in the case of the $KMnO_4$ process it will be stored for future solutions since it still contains $KMnO_4$. On the other hand, ethyl acetate will be recovered from the liquid phase of the EO process.

The most important factor at selecting the filtering equipment are the filtration characteristics of the cake. That is, if it is a cake with a low specific resistance (fast filtering) or if, on the contrary, it is a cake with a high specific resistance (slow filtering).

In this case, it is a cake with small specific resistance, since they are relatively large solids and not pasty or sticky.

Of all the possible options, it is considered that the appropriate equipment to perform this filtration is a Nutsche filter. A Nutsche is the simplest type of batch filter. It consists of a tank with a false bottom, perforated or porous, which can act as a filter medium or support said medium. This equipment is very versatile since it can be used for some types of slurry that can occur. Filtration in this equipment can occur by gravity, by pressure, vacuum or a combination of them (Perry and Green, 1999). They can also perform, in addition to filtration, other tasks in the same unit, such as cake washing or thermal drying (SolidLiquid-separation, n.d. – Website).

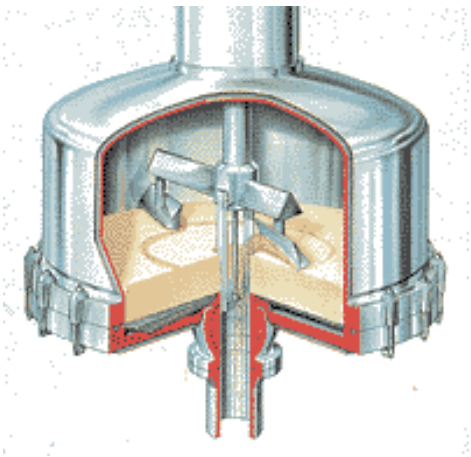

Figure 24: Nutsche filter.
(25/08/2019, Solidliquid-separation)

This aspect supposes a great advantage since it allows to realize the drying stage in this same equipment, so that save costs of machinery and time. Then, once the filtration and washing of the cake is finished, it will be dried by pressurized nitrogen at counterflow in the same filter. As previously mentioned, nitrogen will be used at 80 °C for the $KMnO_4$ process, and for the EO process, at room temperature and under vacuum.

6.4. EQUIPMENT SIZING

To be able to size the equipment, first, the load to be treated must be determined.

6.4.1. Determination of batch size and mode of operation

- **Batch size:**

The production process of active sachets is going to be in batch, due to its great flexibility. Since the equipment will be used to produce different products, it will be a multi-product plant (Flowshop batch plant). Both products will follow the same sequence of operations. Initially, it is proposed that the same equipment be used in both production processes at all stages of the process. Depending on the production needs, the equipment could be doubled, and one used for each process, if more production were necessary.

Of the stages that are part of the process, the one that limits the load is the drying, since, in order to be effective, it is convenient that the amount of spheres to be dried at one time is not very high. In other words, that the cake to dry is not very thick. Since drying takes place in the Nutsche filter, the amount of spheres that will have to be dried in each batch depends on the filter surface of said filter.

In the literature search it has been found that the filter surfaces of the Nutsche filters are from 0.07 m^2 and can reach up to 15 m^2. For the process to be developed, a filter area of 3 m^2 is established. With the diameter that has been established for the spheres (0.6 cm), assuming each sphere as a square with a side equal to the diameter, and setting 6 rows of spheres, it is obtained that the number of spheres that the filter would contain, and therefore, each lot is 500,000 spheres.

- **Production planning:**

With a batch size of 500,000 spheres and with the productions obtained in *Chapter 6.2* for each active sachet, it is obtained that the number of lots to produce for each active sachet is:

Parameter	KMnO4 process	EOs process
Number of spheres to produce	83,700,000	94,500,000
Number of spheres per batch	500,000	
Batch to produce theoretical	168	189
Batch to produce established	200	200

Table 12: Boiling points (Own elaboration)

It is decided to increase the number of lots above the obtained theoretically, so that it is pretend to produce 200 lots per active sachet. Thus, a higher production than the one set would be obtained, which would ensure that, in case of any problem or incidence that may arise, even so, the desired production will be achieved. In addition, this margin offers a flexible production capacity, in which, once underway there may be variations according to the demand of the product, being able to work more or less days.

To produce these batches, it can work by alternating lots of one product and another (mixed product campaign), or, in campaigns of the same product (single product campaign). In the case of operating alternating batches, it would be necessary to clean thoroughly between each batch. Therefore, it is considered more appropriate to operate in campaigns of the same active sachet since this way, it will not be necessary to clean both lot and lot and the processing time of each batch will be reduced. If it will be necessary to clean thoroughly when changing products.

To determine the number of batches that could be made daily, an estimate of the production time of a batch of each of the active sachet is made. The results obtained are shown in the following tables:

$KMnO_4$ PROCESS		
STAGE 1: Dissolution		
Operation	**t (min)**	**Total (h)**
Load $KMnO_4$ and water	30	2
Mix and heat	60	
Pump to the impregnation tank	30	
Total time (min)	120	
STAGE 2: Impregnation		
Operation	**t (min)**	**Total (h)**
Load spheres	15	2.5
Receive solution from the previous stage	15	
Heat and stir	30	
Keep a 65°C	60	
Pump to the filter	30	
Total time (min)	150	
STAGE 3: Filtration and drying		
Operation	**t (min)**	**Total (h)**
Receive suspension from the previous stage and filter	30	4
Wash	30	
Drain	30	
Dry	120	
Download	30	
Total time (min)	240	
Total batch time	**510**	**8.5**

EOs PROCESS		
STAGE 1: Dissolution		
Operation	**t (min)**	**Total (h)**
Load EOs and ethyl acetate	30	1.5
Mix	30	
Pump to the impregnation tank	30	
Total time (min)	90	
STAGE 2: Impregnation		
Operation	**t (min)**	**Total (h)**
Load spheres	15	2
Receive solution from the previous stage	15	
Stir	60	
Pump to the filter	30	
Total time (min)	120	
STAGE 3: Filtration and drying		
Operation	**t (min)**	**Total (h)**
Receive suspension from the previous stage and filter	30	4
Wash	30	
Drain	30	
Dry	120	
Download	30	
Total time (min)	240	
Total batch time	**450**	**7.5**

Table 13 and 14: Batch time for $KMnO_4$ and EOs process (Own elaboration)

With these times it is observed that the limiting stage is Stage 3 in both processes. Working with overlap between batches to reduce the time in which the equipment is not being used and the production time of each campaign, it is obtained that four complete batches of the ethylene absorbent envelopes and five completed batches of the antimicrobials emitting envelopes can be produced. The time required to produce N lots is the Makespan (Mt_N), and is calculated as follows (Vicente, 2018):

$$Mt_N = Bt + (N-1)Ct$$

Parameter	KMnO4 process	EOs process
Batch time (h)	8.5	7.5
Cycle time (h)	4	4
Full batches per day	4	5
Full batch time per day (h)	20.5	23.5

Table 15: Full batch time per day (Own elaboration)

With this number of daily batches, it is obtained that 50 days are required to produce the 200 batches of the sachets of spheres impregnated in $KMnO_4$, and 40 days for the 200 batches of the sachets of spheres impregnated in EOs. In summary, it is decided to operate in campaigns of 40 batches for $KMnO_4$ sachets (5 campaigns will be carried out), and for Eos sachets, it would be operated in campaigns of 50 batches (4 campaigns will be carried out). In this way, the cleaning is minimizing.

6.4.2. Equipment

I. Closed stirred and jacketed tank for dissolution

Knowing that the batch size is 500,000 spheres, the amount of solution that is required in each process for that load is determined. For this, it is necessary to know the amount of $KMnO_4$ and EOs that is required in each case. This is determined by the amount of $KMnO_4$ and EOs per sphere that has been calculated in *Chapter 5.1.1* and *5.2.1* respectively.

Supposing the adsorbed amount of $KMnO_4$ and EOs is 60% of what is in solution, it is estimated how much $KMnO_4$ and EOs should have in total the respective solutions (in g). From here, knowing the concentrations required for each solution (15 g/100 mL for both), the volume of solution needed in each case is determined.

Parameter	KMnO4 process	EOs process
Batch size (nº spheres)	500,000	
Amount adsorbed per sphere (g)	0.00577	0.00515
Amount adsorbed per batch (g)	2,883.98	2,577.05
Total amount in solution (g)	4,806.64	4,295.90
Volume of dissolution per batch (L)	32.04	28.63

Table 16: Volume of dissolution per batch (Own elaboration)

Knowing the volume to be contain by the dissolution tank in each process, it is established that a tank of 50 L of capacity will be used for the dissolution stage.

Figure 25: Example of closed stirred and jacketed tank for dissolution (25/08/2019, Tecnodac)

II. Closed stirred and jacketed tank for impregnation

The impregnation tank must contain the corresponding solution and spheres. Therefore, to determine what capacity is required, the volume occupied by each batch of spheres must be determined. Knowing that the diameter that has been established is 0.6 cm for both processes, it is obtained that the volume of a sphere is 0.113 mL. Therefore, the total volume of spheres is 56.55 L. So, the capacities required in each process for this tank are:

Parameter	$KMnO_4$ process	EOs process
Dissolution volume (L)	32.04	28.63
Spheres per batch	500,000	
Sphere volume (mL)	0.113	
Volume of spheres per batch (L)	56.55	
Volume of impregnation per batch (L)	88.59	85.18

Table 17: Volume of impregnation per batch (Own elaboration)

With the volumes obtained, a tank of 120 L capacity is selected for the impregnation stage.

Figure 26: Example of closed stirred and jacketed tank for impregnation (25/08/2019, Shanghai Farfly Energy Technology Co., Ltd)

III. Nutsche filter

As determined in *chapter 6.4.1*, the filter surface of the Nutsche filter has been set at 3 m^2. Since each load is 500,000 spheres, the volume and weight of the cake to be produced in each process can be determined. The thickness of the cake will be 3.6 cm for both processes, since it has been established that in each batch 6 rows of spheres will be filled in the filter. The filter medium chosen for this filtration, considering the characteristics of the solid, is a metal screen.

Figure 27: Example of Nutsche filter

(30/08/2019, DeDietrich Process Systems)

6.4.3. Process Flow Diagram

The general flowchart that would describe both processes would be:

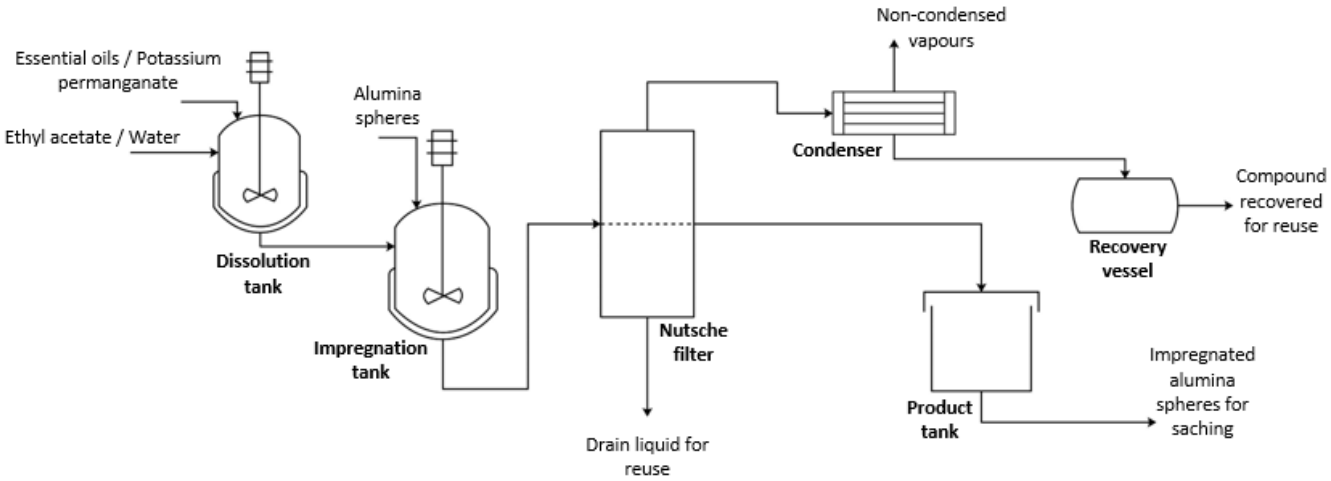

Figure 28: Process Flow Diagram for the process developed.

7. CONCLUSIONS

Several conclusions have been obtained from the development of this project:

Active packaging are packaging systems that interact with the product and generate conditions that favour the preservation of food by releasing beneficial substances or absorbing undesirable substances. Said containers allow the preservation of the food reducing the need to add preservatives or additives to the food itself.

From the study carried out on the different types of AP that exist and their application in different food sectors, it is concluded that the AP is used more frequently in fresh products, such as meats, fish, fruits and vegetables, and dairy products.

For an effective AP application, it is necessary to perform an analysis on the characteristics of the product to be packaged, as well as the packaging conditions, so that the most appropriate AP can be established (type of AP system, active ingredients, system of application, among others) for the effects to be obtained and the needs of the food to be packaged.

Some of the active systems applicable to fruits and vegetables, type of food selected in this project, are ethylene absorbers and emitters of antimicrobial agents. For ethylene absorbers, the most widely used is that based on $KMnO_4$. For the emitters of antimicrobial agents, interest in the use of natural substances (EOs or plant extracts, among others) as active ingredients is increasing, which is intended to be used as substitutes for synthetic antimicrobial substances. Even so, although there are many studies on EOs, it is necessary to investigate to quantify and define its mechanism of action as a commercial product.

From this study, it is concluded that, in the absence of previous tests, ethylene absorbers (based on $KMnO_4$) and emitters of antimicrobial agents (based on EOs) could be applied absorbed in activated alumina and in sachets inside the package. This project presents a manufacturing process that could be common for both. This process, in the absence of previous tests, could consist of the following stages: preparation of prior dissolution, impregnation, filtration, drying, dosing in sachets and storage.

In addition, it is considered that the most suitable equipment to carry out this productive process would be: closed stirred and jacketed tank, to prepare the previous dissolution; closed stirred and jacketed tank (of greater capacity than the previous one), for impregnation; and Nutsche filter, to separate the impregnated spheres and dry them.

- **Aspects outside the scope of this project:**

There are several aspects that have remained outside the scope of this project and in which this work is not deepened. Still it is important to mention them as they are issues to consider:

Solvent recovery: the design of the recovery process and the equipment for the recovery of the solvent used, in this case ethyl acetate, has not been carried out in this project, but would be indispensable for the viability of the plant. Therefore, before a real application, this process should be studied and designed in depth.

Application in department stores: this project focuses on the application of AP in packaging for small businesses, but it could also be extrapolated to department stores. A study should be carried out, since, in the department stores, open containers are usually used for what would be different conditions. The AP could solve possible problems of companies exporting high-end horticultural products, which are collected green so that they can reach the end of the distribution chain in the right conditions. But, sometimes, they still come green and entails their return. Products with a more appropriate maturity point could be collected and, using AP, control ripening so that it reaches its destination at the appropriate ripening point.

Reusing of drain liquid: The liquid streams resulting from the filtration are dissolutions more dilutes of KMnO4 or EOs. These can be reused for the impregnation of following batches to save costs. In each case, the amount of active ingredient or solvent needed to obtain the concentration required to impregnate should be added. In the case of EO, said stream would be mixed with condensed ethyl acetate and the amount of EO needed to compensate for what has been adsorbed.

11. NOTATION

AP	Active Packaging.
Bt	Batch time, h.
C_2H_4	Ethylene.
Ct	Cycle time, h.
EO	Essential oils.
F&V	Fruits and Vegetables.
GRAS	Generally recognized as safe.
HPP	High-pressure packaging.
IP	Intelligent Packaging.
$KMnO_4$	Potassium permanganate.
MAP	Modified atmosphere packaging.
Mt_N	Makespan, h.
N	nº of batches.
RH	Relative humidity, %.
SP	Smart Packaging.

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APPENDIX 1: BYOSHYNTHESIS OF ETHYLENE IN PLANTS

The biosynthesis of ethylene in plants begins with the conversion of the amino acid methionine to S-adenosyl-L-methionine (SAM) by the enzyme S-adenosyl-L-methionine synthetase (SAM synthetase). The SAM, then, is converted to 1-aminociclopropane-1-carboxylic acid (ACC) and 5'-methylthioadenosine by 1-aminociclopropane-1-carboxylic acid synthase (ACC synthase). The activity of ACC synthase is regulating in the production of ethylene; therefore, the regulation of this enzyme is crucial. The 5'-methylthioadenosine will be used to regenerate the initial methionine in a series of reactions and the ACC to form ethylene. The final step to form ethylene requires oxygen and involves the action of 1-aminociclopropane-1-carboxylic acid oxidase (ACC oxidase), formerly known as the ethylene forming enzyme (EFE) (Buchanan, Gruissem and Jones, 2000).

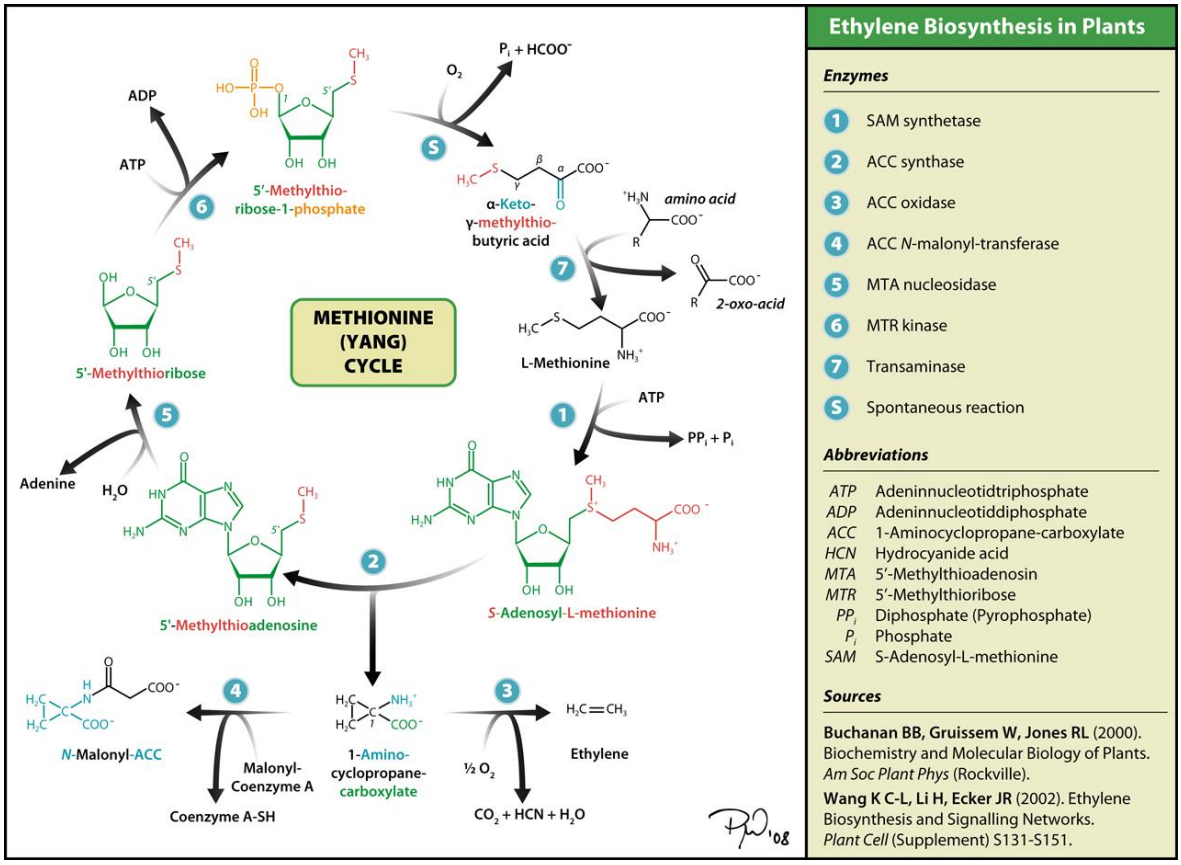


Figure 29: Ethylene Biosynthesis in Plants
De Crenim, 22/05/2019 vía Wikipedia)

APPENDIX 2: CALCULATIONS

Calculation of the amount of permanganate used in the article and ethylene removed:

- Concentration of permanganate in the spheres: In the article they use 4 g/100 g
- Conservation time: 14 days
- Ethylene production in products: 1 µL/kg/h
- The article says that 6 g of absorbent is needed per kg of product

$$6\ g\ absorbent \cdot \frac{4\ g\ KMnO_4}{100\ g\ absorbent\ (spheres)} = 0.24\ g\ KMnO_4$$

- The amount of ethylene produced per 1 kg of product would be:

$$\frac{1\mu L}{kg \cdot h} \cdot 1\ kg \cdot 14\ d \cdot \frac{24h}{1d} = 336\ \mu L\ ethylene$$

It is possible to eliminate 90% of ethylene so: 336 µL · 0.90 = 302.4 µL ethylene

To eliminate 302.4 µL ethylene, 0.24 g of $KMnO_4$ is required.

Estimate of the density of spheres impregnated in EOs:

- Density of EOs

  Cinnamon: 1.03 g/mL

  Clove: 0.89 g/mL

  Oregano: 0.94 g/mL

  Thyme: 0.8 g/mL

- Average density of EOs: 0.92 g/mL
- Density of alumina spheres without impregnating: 0.75 g/mL
- EOs concentration in spheres: 6 g/100 g

$$0.92\frac{g}{mL} \cdot \frac{6\ g\ EOs}{106\ g\ alumina\ and\ EOs} + 0.75\frac{g}{mL} \cdot \frac{100\ g\ alumina}{106\ g\ alumina\ and\ EOs}$$

$$= 0.76\frac{g}{mL}\ EOs\ impregnated\ spheres$$

APPENDIX 3: RESULTS OBTAINED IN A CONSULTED SOURCE

Tables of results obtained by Wills and Warton (2004):

Table 1. Potassium permanganate uptake and color of alumina beads dipped in saturated potassium permanganate solution at 20 °C for various times. Values are the mean of three replications.

Dip time	$KMnO_4$ uptake (g/100 g)	Bead color			
			Hunterlab		
		Visual	L	a	b
0	0 a[z]	White	59 a	5 a	18 a
3 min	0.5 b	Pale pink	45 b	26 b	4 b
1 h	1.5 c	Dark pink	38 c	30 b	–5 c
2 h	1.9 d	Purple	35 d	30 b	–5 c
3 h	2.0 d	Purple	35 d	30 b	–10 d
4 h	2.0 d	Purple	34 d	28 b	–8 d

[z]Mean separation by $LSD_{0.05}$.

Table 2. Potassium permanganate uptake and color of alumina beads following repeated dipping for 3 min in saturated potassium permanganate solution at 20 °C and 30 min between dips. Values are the mean of three replications.

Dip no.	$KMnO_4$ uptake (g/100 g)	Bead color			
			Hunterlab		
		Visual	L	a	b
0	0 a[z]	White	59 a	5 a	18 a
1	0.5 b	Pale pink	45 b	26 b	4 b
2	1.3 c	Dark pink	40 bc	29 c	–0 c
3	1.8 d	Purple	35 c	26 b	–1 c
4	2.1 d	Purple	33 c	26 b	–1 d

[z]Mean separation by $LSD_{0.05}$.

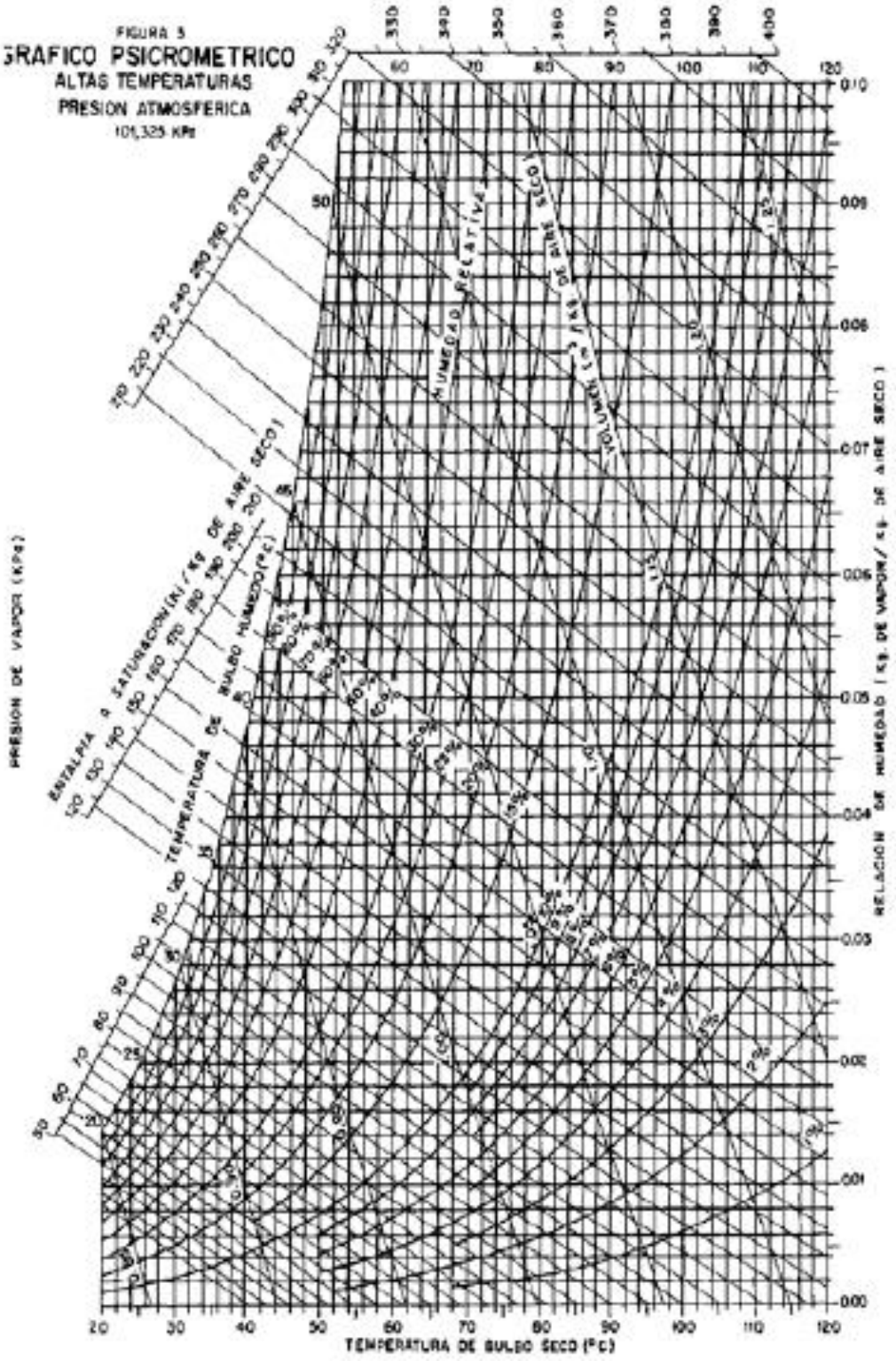
Table 3. Potassium permanganate uptake and color of alumina beads following dipping in 10 g/100 mL potassium permanganate solution at different temperatures for various times. Values are the mean of three replications.

Temp (°C)	Dip time (h)	$KMnO_4$ uptake (g/100 g)	Bead color			
				Hunterlab		
			Visual	L	a	b
20	1	2.3 a[z]	Purple	33 a	29 a	–10 a
	3	2.5 a	Purple, few surface crystals	29 b	27 b	–10 a
	5	2.7 a	Purple, few surface crystals	33 a	29 a	–11 a
65	1	4.0 b	Dark purple	30 b	25 c	–9 a
	3	4.8 c	Dark purple, surface crystals	32 a	25 c	–9 a
	5	4.7 c	Dark purple, surface crystals	26 c	20 d	–6 b
90	1	6.2 e	Many surface crystals	27 bc	16 e	–3 c
	3	5.4 d	Brown	24 d	7 f	8 d
	5	3.4 b	Brown	25 cd	7 f	10 e

[z]Mean separation by $LSD_{0.05}$.

APPENDIX 4: PSYCHOMETRIC DIAGRAM

Since the properties of air and nitrogen do not vary much, the psychometric air diagram can be used to determine the wet bulb temperature with nitrogen. As long as there is free moisture in the spheres, this will be the surface temperature. The N_2, when passing through the spheres, would be saturated at that temperature.



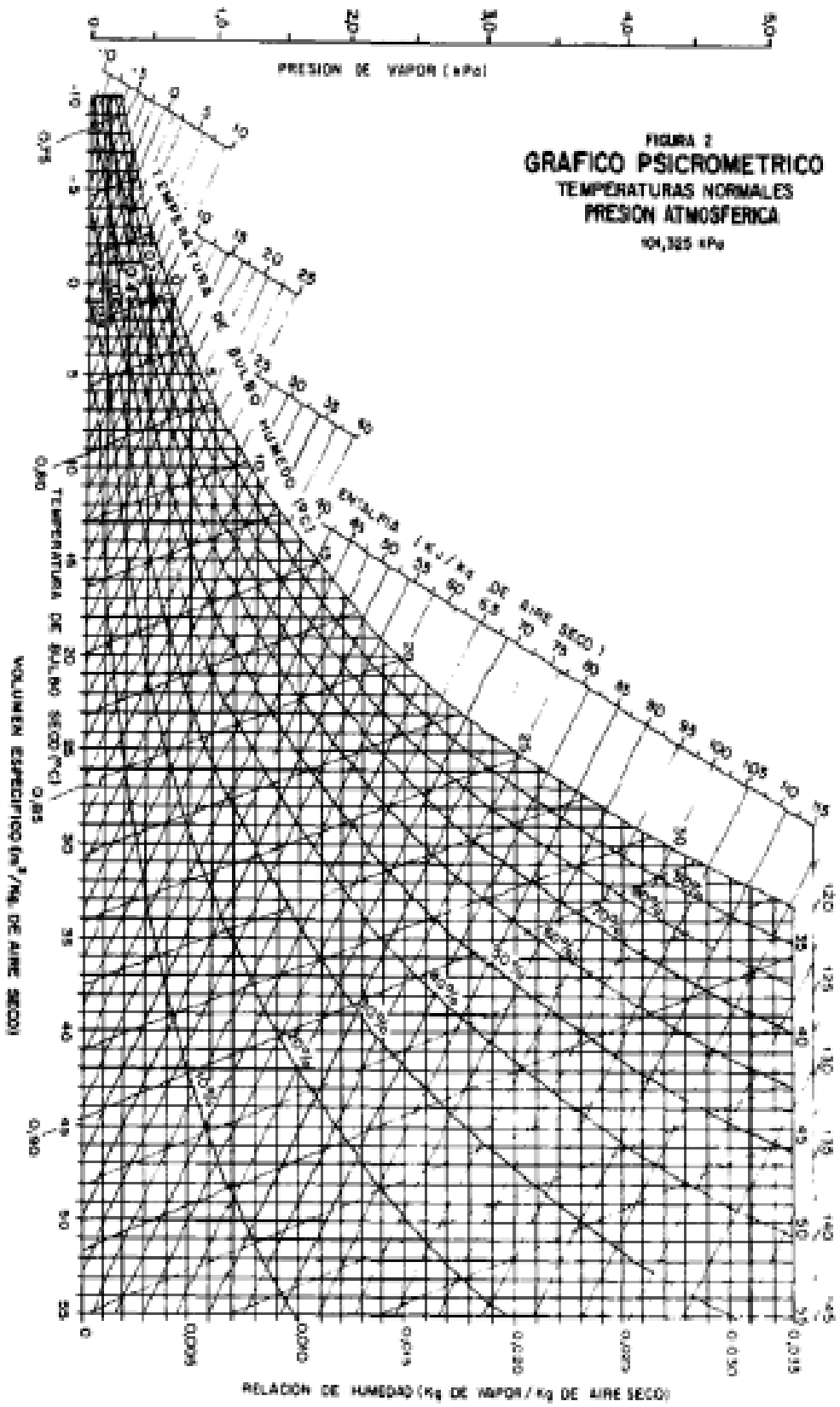


FIGURA 2
GRAFICO PSICROMETRICO
TEMPERATURAS NORMALES
PRESION ATMOSFERICA
101,325 kPa