

Modified Atmosphere Packaging of Fruits and Vegetables for Extending Shelf-Life: A Review

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ABSTRACT

Fresh fruits and vegetables being living require oxygen (O_2) for their metabolic processes especially for respiration. Modified-atmosphere packaging (MAP) of fresh produce refers to the technique of sealing actively respiring produce in polymeric film packages to modify the O_2 and CO_2 concentration levels within the package atmosphere necessary to maintain the freshness and extend shelf-life. It is often desirable to generate an atmosphere low in O_2 and high in CO_2 concentration to influence the metabolism of the produce being packaged, or the activity of decay-causing organisms to increase storage life. In addition to atmosphere modification, MAP vastly improves moisture retention, which can have a greater influence on preserving quality. Furthermore, packaging isolates the produce from the external environment and helps to ensure conditions that, if not sterile, at least reduce exposure to pathogens and contaminants and physiological injuries. MAP is a dynamic process during which respiration and permeation takes place simultaneously. Hence MAP design requires the determination of intrinsic properties of the produce, i.e. respiration rate, optimum O_2 and CO_2 gas concentrations, and film permeability characteristics. The objective of MAP design is to define conditions that will create the optimum atmosphere inside the package best suited for extending shelf-life of a given produce with shortest possible time period. This can be done by matching the respiration rate of the packaged produce with the film permeation rate for O_2 and CO_2 gases. The details of review on all these aspects of MAP have been done and presented in the present paper.

Keywords: carbon dioxide, controlled atmosphere, MAP, oxygen

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INTRODUCTION

The world production of fruits and vegetables has reached to the tune of 1.4 billion tons. Approximately 900 MT of vegetables and 500 MT of fruits were produced in the world (http://www.lol.org.ua/eng/showart.php). annually The vegetable production is persistently increasing and the same trend is observed for fruit production. The average yearly growth of vegetables (4.2% p.a.) was almost double than that of fruits (2.2% p.a.) during 1980-2004 (http://faostat. fao.org). About 10% of fruits grown in the world are the external trade items; this figure is quite smaller for vegetables, which is around 3-4%. Over the last quarter of a century (1980-2004), the fruit and vegetable market has been one of the fastest growing of all agricultural markets. Global fruit and vegetables consumption increased by an average of 4.5% per annum. This was higher than the world population growth rate, meaning that the global per capita consumption of fruit and vegetables has also increased. According to World Health Organization, for the prevention of chronic diseases such as heart diseases, cancer, diabetes and obesity, fruit and vegetable consumption should be at least 400 g per day per capita and around 50% of the coun-(http://www.who.int/ reached level tries this dietphysicalactivity/media/en/gsfs fv.pdf). However, the post harvest losses of fruits and vegetables are still considerably high. The estimated annual loss of fruits and vegetables due to inadequate facilities and improper technologies of handling, packaging and storage is in the range of 25-40% of the total production (Salunke and Kadam 1995).

Fruits and vegetables are an important source of carbohydrate, protein, organic acid, dietary fibers, vitamins and mineral for human nutrition and are considered as an integral part of the dietary system (Irtwange 2006). Hence fresh fruits and vegetables have always a good market demand. However, fruits and vegetables are perishable commodities, which generally have a short storage life, and they lose their freshness shortly after harvest. The high post harvest losses as well as the market demand of fresh fruits and vegetables even during lean periods necessitated the development of various storage technologies to preserve the commodity in pristine condition for extended period.

Protection of fruits and vegetables from mechanical damage and microbial infection keeps the fruits in sound condition; however it does not increase the shelf-life of the commodities beyond its normal season. This is because fresh fruits and vegetables are still living and their metabolic process continues even after harvest. However, their metabolism is not identical with that of the parent plant growing in its original environment and therefore, they are subjected to physiological and pathological deterioration and losses (Giusti *et al.* 2008; Martins *et al.* 2008). Loss means any change in the availability, edibility, wholesomeness or quality of the food that prevents it from being consumed by the people (Fallik and Aharoni 2004). Causes of losses could be biological, microbiological, chemical, biochemical reactions, mechanical, physical, physiological

and psychological. Microbiological, mechanical and physiological factors cause most of the losses in perishable crops (Kader 1992). Other causes of losses, according to Fallik and Aharoni (2004), may be related to: inadequate harvesting, packaging and handling skills; lack of adequate containers for the transport and handling of perishables; inadequate storage facilities to protect the food; inadequate transportation to move the food to the market before it spoils; inadequate refrigerated storage; inadequate drying equipment or poor drying season. Traditional processing and marketing systems can also be responsible for high losses, and legal standards can affect the retention or rejection of food for human use being lax or unduly strict. Losses may occur anywhere from the point where the food has been harvested or gathered up to the point of consumption, that is, harvest, preparation, preservation, processing, storage and transportation (Itwange 2006). In this respect respiration is considered to be the major catabolic process, which leads the natural ripening, senescence and subsequent deterioration (Saltveit 2005).

Quality is generally defined as all those characteristics of a food that lead a consumer to be satisfied with the product (Echeverria et al. 2008). Quality optimization and loss reduction in the post harvest chain of fresh fruits and vegetables are the main objective of post harvest technology. Temperature control and modified atmosphere (MA) are the two important factors in prolonging the shelf-life (Fonseca et al. 2002). The primary factors in maintaining quality and extending the post harvest life of fresh fruits and vegetables are harvesting at optimum maturity, minimizing mechanical injuries using proper sanitation procedures, and providing the optimum temperature and relative humidity during all marketing steps. Secondary factors include modification of oxygen (O2), carbon dioxide (CO2), and/or ethylene (C_2H_4) concentrations in the atmosphere surrounding the commodity to level different from those in air. This is referred to as the controlled atmosphere (CA) or MA storage systems. CA implies a greater degree of precision than MA in maintaining specific levels of O₂, CO₂ and other gases (Mahajan 2001).

MODIFIED ATMOSPHERE PACKAGING (MAP)

History of MAP

MAP was first recorded in 1927 as an extension of the shelf-life of apples by storing them in atmospheres with reduced O_2 and increased CO_2 concentrations. In the 1930's it was used as MA storage to transport fruit and beef carcasses in the holds of ships by increasing the CO_2 concentrations for long distance transport and it was observed to increase the shelf-life by up to 100% (Davies 1995). However, the technique was not introduced commercially for retail packs until the early 1970's in Europe. The primary limitation of MAP application in the early studies was technical in nature; specifically, the lack of consistent control of O_2 concentration levels in the package. Since then, the types

and properties of polymers have increased to provide a wider range of gas permeability, tensile strength, flexibility, printability, and clarity. As a result, successful MA packaging systems have been developed for a number of commodities. In the U.K. Marks and Spenser introduced MAP for meat in 1979; the success of this product lead to years later to the introduction of MAP for bacon, fish, sliced cooked meats and cooked shellfish. Other food manufacturers and super market chain followed the same, resulting in a sharply increased availability of MAP food product reflecting to the increase in consumer demand for food with longer shelf-life and less use of preservatives. MAP techniques are now used on a wide range of fresh or chilled foods, including raw and cooked meat, fish and poultry, fresh pasta, fresh and cut fruits and vegetables and more recently coffee, tea and bakery products (Church and Parson 1995).

Definition of MAP

MAP emerged in the 1960s as a new technology that extends storage life of perishable agricultural produce and reduces its spoilage and decay (Henig 1975). MAP is one of the food preservation methods that maintain the natural quality of food products in addition to extending the storage life. In other words MAP is a technique used for prolonging the shelf-life of fresh or minimally processed foods by changing the composition of the air surrounding the food in the package. The use of MAP reduces the respiration rate and activity of insects or microorganisms and provides control of fruit and vegetable ripening, retardation of senescence, or browning in cut produce, and ultimately prolongs the shelf-life (Stiles 1991; Kader 1995; Fonseca *et al.* 2002; Rennie *et al.* 2003).

In the literature, the terms MA and controlled atmosphere are used interchangeably. They both differ based on the degree of control exerted over the atmosphere composition. In MAP the modification of the atmosphere inside the package is achieved by the natural interplay between two processes, the respiration of the products and the permeation of gases through the packaging (Smith et al. 1987; Mahajan et al. 2007). Also, the gas composition is modified initially and it changes dynamically depending on the respiration rate of food product and permeability of the film surrounding the food product (Jayas and Jeyamkondan 2002). In CA storage the atmosphere is modified and its composition is precisely controlled according to the specific requirements of the food product through out the storage period (Ryall and Pentzer 1982; Raghavan and Gariepy 1985; Parry 1993; Mahajan 2001).

Principles of MAP

MAP of fresh produce relies on modification of the atmosphere inside the package, achieved by the natural interplay between two processes, the respiration of the product and the transfer of gases through the packaging, that leads to an atmosphere richer in CO_2 and poorer in O_2 ; and it depends on the characteristics of the commodity and the packaging film (Fonseca *et al.* 2002; Mahajan *et al.* 2007). This atmosphere can potentially reduce respiration rate, C₂H₄ sensitivity and production, ripening, softening and compositional changes, decay and physiological changes, namely, oxida-tion (Kader et al. 1989; Parry 1993; Kader 1995; Saltveit 1997; Gorris and Tauscher 1999). MAP involves the exposure of produce to the atmosphere generated in a package by the interaction of the produce, the package and the external atmosphere. The initial atmosphere may be either air or a gas mixture. Different additives that may affect the atmosphere may be introduced into the package before it is sealed.

Packaging fresh produce in polymeric films results a commodity generated MA. Atmosphere modification within the package depends on film permeability, commodity respiration rate and gas diffusion characteristics of the commodity, and weight of commodity, surface area, initial free volume and atmospheric composition within the package. Temperature, relative humidity and air movement around the package can influence the permeability of the film. Temperature also affects the metabolic activity of the commodity and consequently the rate of attaining the desired MA. All these factors must be considered in developing a mathematical model for selecting the most suitable film for each commodity (Parry 1993).

Objective/goal of MAP

The objective of MAP design is to define conditions that will create the atmosphere best suited for the extended storage of a given produce while minimizing the time required achieving this atmosphere. In other words, the goal of MAP is to achieve the equilibrium concentration of O_2 and CO_2 within the package within shortest possible time because of the interaction of the produce, the package and the external atmosphere; and these concentration lies within the desired level required for maximum possible storage life of the commodity. The equilibrium concentration of O_2 and CO_2 achieved within the package for a packaging system needs to be remained constant through out the period of storage to continue the respiration rate and rate of all metabolic process at a minimum possible rate for maintaining freshness and extending shelf-life of stored commodity (Kader et al. 1989; Das 1995; Mahajan et al. 2007). Matching the film permeation rate for O2 and CO2 with the respiration rate of the packaged produce can do this. As different products vary in their behavior and as MA-packages will be exposed to a dynamic environment, each package has to be optimized for specific demands (Saltveit 1993; Chau and Talasila 1994; Jacxsens et al. 2000; Mahajan et al. 2007). An improperly designed MAP system may be ineffective or even shorten the storage life of a commodity. If the desired atmosphere is not established rapidly, the package will have no benefit; if O₂ and/or CO₂ are not within the recommended range, the product may experience serious alterations and its storage life may thereby shortened.

Effect of MAP

The effects of MAP are based often on the observed slowing of plant respiration in low O₂ environment. As the concentration of O₂ inside the package falls below about 10-12%, respiration starts to slow (Saltveit 1993, 1997; Gorris and Tauscher 1999). This suppression of respiration continues until O_2 reaches about 2-5% for most of the produces. If O₂ gets lower then 2-5% (depending on product and temperature) fermentative metabolism replaces normal aerobic metabolism and off-flavors, off odours and undesirable volatiles are produced (Kader et al. 1989; Faber 1991). Similarly, as the concentration of CO₂ increases above the atmospheric level, a suppression of respiration rate, C₂H₂ production, and sensitivity to C2H4 and suppression of activities of microorganism, fungal/bacterial growth, results for some commodity (Daniels et al. 1985; Dixon and Kell 1989; Faber 1991). Reduced O₂ and elevated CO₂ concentrations together can reduce rate of respiration more than that done by either alone. The diminution of enzymatic activities by providing low temperature, low O₂ and high CO₂, in general reduces utilization rate of substrate (i.e. carbohydrate, organic acid and other reserves) and increase post harvest life of the fruits and vegetables beyond its normal span (Mahajan and Goswami 2001). Others consider that, elevated CO₂ might inhibit C₂H₂ production and/or suppresses plant tissue sensitivity to the effects of the ripening hormone C₂H₄ rather than having a direct effect on respiretion process (Kubo et al. 1989). For those products that tolerate high concentration of CO_2 , suppression of the growth of many bacteria and fungi results at greater than 10% CO₂ (Kader et al. 1989).

Utility of MAP

MAP is a multidisciplinary technology of maintaining freshness and extends shelf-life; that utilizes basic principles of chemistry, physics, plant physiology and pathology, microbiology, food science, engineering, and polymer chemistry. Better understanding of this wide scope will promote implementation of the technology. MAP technology has developed rapidly over the past decade (Lioutas 1988; Kader et al. 1989; Gorris and Peppelenbos 1992; Lu 2009). This rapid development is due to two contradictory trends affecting modern post harvest handling of fruits, vegetables, and other perishable produce, viz., 1) food distribution in developed countries now involves many perishable food items, some of which are minimally processed, such as shredded lettuce, carrot or celery sticks, and fresh salad mixes, that increases the perishable nature and susceptibility to decay and desiccation, and consequent greater need for quality and decay control measures; 2) there is growing anxiety among consumers about the use of synthetic chemicals to protect food from pathogens and pests to extend the life of perishable produce. One of the consequences of this public anxiety is that more and more synthetic food protectants such as certain fungicides and pesticides are being banned.

MAP technology, which utilizes only the natural components of air, has achieved public acceptance due to these two trends. MAP has the advantages that synthetic chemicals are not used, no toxic residue is left, and there is little environmental impact, particularly if the plastic films used can be recycled. Recent advances in the design and manufacture of polymeric films with a wide range of gasdiffusion characteristics have also stimulated interest in MAP of fresh produce. In addition, the increased availability of various absorbers of O₂, CO₂ (Kader et al. 1989), water vapour (Shirazi and Cameron 1992), and C_2H_4 (Ben Aries and Sonego 1985) provides possible additional tools for manipulating the microenvironment of MAP. There is extensive literature on the benefits of MAP and the dramatic extensions of shelf-life for various foods (Lioutas 1988; Kader et al. 1989). However, there are few papers dealing with the microbiological safety needed for successful MAP implementation (Genigeorgis 1985; Hintlian and Hotchkiss 1986). Future approaches must put consumer safety first and freshness second.

Applications of MAP

There are many advantages of MAP of fruits and vegetables, but the most obvious one must be the extension of shelf-life. By decreasing the amount of available O_2 to the produce, the respiration rate and the rate of all metabolic process are correspondingly decreased. This result in delayed ripening and senescence, which may be seen as chlorophyll retention, delayed softening and the prevention of discoloration (Gorris and Peppelenbos 1992). The extension of shelf-life is most noticeable with prepared products; this combined with ease of used for the consumer, makes a MAP pack an attractive form of product presentation (Church 1994). Additionally MAP packs reduce the quantity of water vapor lost from the produce (Church and Parson 1995).

Although fresh fruits and vegetables have been removed from the parent plant and from their normal nutrient supplies, they will continue to respire. Under normal aerobic conditions the rate of respiration of a product may be determined by either O_2 uptake rate or CO_2 production rate. A high respiration rate is usually associated with a short shelflife. When the rate of packaging film transmission of O_2 and CO_2 equals the rate of respiration of the products, an equilibrium concentration of both gases is established (Church and Parson 1995). The equilibrium value attends depend on: the respiration rate of the product, fill weight of the product and the film surface are which is available for gas exchange. The respiration rate of the product is influenced by: storage temperature, produce variety, growing area and condition, injury to the product (Parry 1993).

The current application of MAP technologies include long term storage of apple, pears, kiwi fruits, potato, sapota, orange, cabbage and Chinese cabbage; temporary storage and/or transport of strawberries, bush berries, cherries, bananas, litchi, guava, mushroom, tomato, etc. and other commodity and retailing of some cut or sliced (minimally processed) vegetables. MAP facilitates maintenance of the desired atmosphere during the entire post harvest handling time between harvest and consumption (Zagory and Kader 1988; Church 1994; Mahajan *et al.* 2007).

MAP gases

Various MAP systems have been developed and investigated for increasing the shelf-life of fresh commodity. Common gases used in MA are CO_2 , O_2 and N_2 . CO_2 is bacteriostatic. Nitrogen is an inert gas; it does not possess any bacteriostatic effect. It is used as a filler gas in the MA gas mixture. The inhibitory effect of CO_2 increases with a decrease in temperature (Mahajan and Goswami 2001).

Advantages and disadvantages of MAP

The beneficial and detrimental effects of MAP have been extensively reviewed (Isenberg 1979; Smock 1979; Kader 1980; Lioutas 1988; Kader *et al.* 1989; Dilley 1990; Parry 1993; Ben-Yehoshua 1994; Phillips 1996; Zagory 1998; Fonseca 2002; Irtwange 2006; Mahajan *et al.* 2007; Siva-kumar *et al.* 2007) and are summarized below:

Advantages

- 1. MAP maintains freshness and extends shelf-life from several days to several weeks, compared to conventional storage.
- 2. Reduction of O_2 and increment of CO_2 environment suppresses respiration rate of the commodity, there by slows vital processes and prolongs the maintenance of post harvest quality.
- 3. Reduction of respiration rate, loss of moisture, production of metabolic heat, yellowing, browning decay and C_2H_4 sensitivity and production occurs.
- 4. Delay of ripening takes place.
- 5. Reduction of weight loss, desiccation/water loss and shriveling takes place in MAP.
- 6. In MAP reduction of physiological injury, disorder and pathological deterioration takes place.
- 7. Quality advantages such as color, moisture, flavors and maturity retention occurs.
- 8. Reduction of fungal growth and diseases is common.
- 9. MAP retards softening and compositional changes.
- 10. Alleviation of chilling injury is common.
- 11. Increased shelf-life allowing less frequent loading of retail display in shelves occurs.
- 12. Improved presentation and clear visibility of product all around the package occurs.
- 13. In MAP little or no chemical preservatives is used.
- 14. Centralized/semi-centralized packaging option is possible.
- 15. Expanded distribution area and reduced transport costs due to less frequent deliveries is possible.
- 16. Reduction of labor and waste at the retail level occurs.
- 17. Excellent branding options.
- 18. Reduction of handling and distribution of unwanted or low grade produce.
- 19. Quality advantages transferred to the consumer.
- 20. Reduction in production and storage cost due to better utilization of labour, space and equipments.
- 21. MAP has great advantage in developing countries because it can economically be done by hand saving the high cost of new machinery. Additionally the need there for such a technique is much greater because of the dearth of refrigerated storage.

Disadvantages

- 1. Requirement of additional investment in machinery and labour in the packaging line.
- 2. Risks of spoilage of produce may occur due to improper packaging or temperature abuse.
- 3. Possible occurrence of new risks of microbiological safety due to possible development of anaerobic pathogenic flora.
- 4. Plastic films may be environmentally undesirable unless effective recycling is installed.
- 5. MAP technology is still unavailable for most produce.
- 6. No particular standard is available for MA packaging, because the intrinsic properties of the commodity varies greatly with cultivar, place of cultivation, maturity stage etc. and the permeability of the films varies with the manufacturing company and process, etc.

Physiological factors affecting shelf-life of fresh produce

Shelf-life may be defined as the time period from harvest to manufacture to consumption that a food product remains safe and maintains its desired/recommended harvest/production quality through out the storage period. Shelf-life is affected by intrinsic factors such as respiration rate, biological structure, C_2H_4 production and sensitivity, transpiration, compositional changes, developmental stages and physiological breakdown (Wills *et al.* 1981, 1989; Irtwange 2006; Martinez-Romeroa *et al.* 2007).

Respiration rate

The plant tissues in fresh-cut produce are still living and continue to respire even after harvest and deriving energy primarily through the process of respiration. Respiration is a catabolic process, which involves the consumption, using atmospheric O₂, of carbohydrates, fats, proteins and organic acids in the plant tissue to form various intermediate compounds and eventually CO₂, water and metabolic energy (Meyer *et al.* 1973; Kader 1987; Zagory 1998; Fonseca *et al.* 2002). The energy produced by the series of reactions comprising respiration can be captured as high energy bonds in compounds used by the cell in subsequent reactions and biochemical processes, or lost as heat. The energy and organic molecules produced during respiration are used by other metabolic processes to maintain the health of the commodity. Heat produced during respiration is called vital heat and contributes to the refrigeration load that must be considered in designing storage rooms. For a biochemist: respiration is the oxidative breakdown of complex substrate molecules normally present in the plant cells such as starch,

sugars and organic acids to simple molecules such as CO_2 and water (Saltveit 2005). Under normal atmospheric conditions, aerobic respiration consists of oxidative breakdown of organic reserves (carbohydrate) to simple molecules, including CO_2 as described by the simplified equation: $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + energy$ (heat). During the respiration process there is a loss of stored food reserved in the commodity. This leads to hastening of senescence because the reserves that provide energy are exhausted. Also, use of substrates in the respiration can result in loss of food reserves in the tissue and loss of quality (especially sweetness) and food value to the consumer.

The rate of deterioration of harvested commodities is proportional to the respiration rate (Fallik and Aharoni 2004). In general, the storage life of commodities varies inversely with the rate of respiration. This is because respiration supplies compounds that determine the rate of metabolic processes directly related to quality parameters, e.g. firmness, sugar content, aroma, flavors, etc. Commodities and cultivars with higher rates of respiration tend to have shorter storage-life than those with low rates of respiration. Storage life of asparagus, mushroom, broccoli, lettuce, peas, spinach, and sweet corn (all of which have high respiration rates) is short in comparison to that of apples, cranberries, limes, onions, and potatoes - all of which have low respiration rates. The commodities are classified according to their respiration rates (Church and Parsons 1995; Saltveit 2005; Irtwange 2006) and are given in Table 1. However, the summary of respiration and C2H4 production rates of fruits and vegetables at various temperatures are presented in Tables 2 and 3. Furthermore, when fruits and vegetables are cut, sliced, shredded or other wise processed, their respiration rates increases. This is probably due to the increased surface area exposed to the atmosphere after cutting that allows O₂ to diffuse into the interior cells more rapidly and to the increased metabolic activities of injured cells (Zagory 1998).

Respiratory quotient

The composition of the commodity frequently determines which substrates are utilized in respiration, the nature of the respiratory process and consequently the value of the respiratory quotient (RQ). RQ is defined as the ratio of CO₂ produced to O₂ consumed during respiration (Kader *et al.* 1989; Fonseca *et al.* 2002). The RQ value is normally assumed to be one if the metabolic substrates are carbohydrates. The total oxidation of 1 mol of hexose consumes 6 mol of O₂ and produces 6 mol of CO₂. If the substrate is a lipid, the RQ is always lower than unity, because lipid/fat are poor in O₂ and hence require greater amount of O₂ from atmosphere for respiration. Also the ratio between C and O

Table 1 Classification of horticultural commodities according to respiration and ethylene production rates.

| Class | | Respiration rates | Ethylene production rates | | | |
|-------------------|-----------------------------|--|---|--|--|--|
| | Ranges at 5°C | Commodities | Ranges at 20°C | Commodities | | |
| | (mg CO ₂ /kg-hr) | | (µl C ₂ H ₄ /kg-hr) | | | |
| Very low | < 5 | Dates, nuts, dried fruits and vegetables | < 0.1 | Artichoke, asparagus, cauliflower, cherry, citrus, grape, jujube, strawberry, pomegranate, leafy vegetables, root vegetables, potato, most cut flowers | | |
| Low | 5-10 | Apple, celery, citrus fruits, garlic, grape, kiwifruit, onion, persimmon, pineapple, potato, sweet potato, watermelon | 0.1-1.00 | Blueberry, cranberry, cucumber, eggplant, okra, olive, pepper, persimmon, pineapple, pumpkin, raspberry, tamarillo, watermelon | | |
| Moderate | 10-20 | Apricot, banana, cabbage, cantaloupe, carrot, cherry, cucumber, pig, gooseberry, lettuce, nectarine, olive, peach, pear, pepper, plum, tomato, guava, mango, sapota | 1.0-10.00 | Banana, fig, guava, honeydew, melon, mango, plantain, tomato | | |
| High | 20-40 | Strawberry, litchi, blackberry, raspberry avocado, cauliflower, lima bean | 10.00-100.00 | Apple, apricot, avocado, cantaloupe, feijoa, kiwifruit (ripe), nectarine, papaya, peach, pear, plum | | |
| Very high | 40-60 | Artichoke, bean sprouts, broccoli, brussels sprouts, cut flower, green onion, snap beans | >100 < 200 | Cherimoya, mammee apple, passion fruit, sapota | | |
| Extremely high | >60 | Asparagus, broccoli, raspberry, mushroom, parsley, peas, spinach, sweet corn | >200 | | | |

Sources: Church and Parsons 1995; Saltveit 2005; Irtwange 2006

Table 2 Summary of respiration and ethylene production rates of some fruits at different temperatures.

| Commodity | | Respiration rate (mg CO ₂ /kg-hr) temperature of | | | | | | C ₂ H ₄ production |
|-------------|-------------|---|-----|------|-----------|------|------|---|
| | | 0°C | 5°C | 10°C | 15°C | 20°C | 25°C | (μl C ₂ H ₄ /kg-hr) |
| Apple | Fall | 3 | 6 | 9 | 15 | 30 | na | Varies greatly |
| | Summer | 5 | 8 | 17 | 25 | 31 | na | Varies greatly |
| Apricot | | 6 | na | 16 | na | 40 | na | < 0.1 (0°C) |
| Artichoke | | 30 | 43 | 71 | 110 | 193 | na | <0.1 |
| Asian pear | r | 5 | na | na | na | 25 | na | Varies greatly |
| Avocado | | na | 35 | 105 | na | 190 | na | > 100 (ripe; 20°C) |
| Banana (ri | ipe) | na | na | 80 | 140^{3} | 280 | na | 5.0 (15°C) |
| Beets | | 5 | 11 | 18 | 31 | 60 | na | < 0.1 (0°C) |
| Blackberry | y | 19 | 36 | 62 | 75 | 115 | na | Varies; 0.1-2.0 |
| Blueberry | | 6 | 11 | 29 | 48 | 70 | 101 | Varies; 0.5-10.0 |
| Cherry | | 8 | 22 | 28 | 46 | 65 | na | < 0.1 (0°C) |
| Grape, An | nerican | 3 | 5 | 8 | 16 | 33 | 39 | < 0.1 (20°C) |
| Grape, Mu | iscadine | 10^{6} | 13 | na | na | 51 | na | < 0.1 (20°C) |
| Grape, Tal | ble | 3 | 7 | 13 | na | 27 | na | < 0.1 (20°C) |
| Grapefruit | | na | na | na | < 10 | na | na | < 0.1 (20°C) |
| Guava | | na | na | 34 | na | 74 | na | 10 (20°C) |
| Kiwifruit (| (ripe) | 3 | 6 | 12 | na | 19 | na | 75 |
| Litchi | | na | 13 | 24 | na | 60 | 102 | Very low |
| Mamey ap | ple | na | na | na | na | na | 35 | 400.0 (27°C) |
| Mandarin | (tangerine) | na | 6 | 8 | 16 | 25 | na | < 0.1 (20°C) |
| Mango | | na | 16 | 35 | 58 | 113 | na | 1.5 (20°C) |
| Nectarine | (ripe) | 5 | na | 20 | na | 87 | na | 5.0 (0°C) |
| Orange | | 4 | 6 | 8 | 18 | 28 | na | < 0.1 (20°C) |
| Papaya (rij | pe) | na | 5 | na | 19 | 80 | na | 8.0 |
| Passion fru | uit | na | 44 | 59 | 141 | 262 | na | 280.0 (20°C) |
| Peach (ripe | e) | 5 | na | 20 | na | 87 | na | 5.0 (0°C) |
| Pineapple | | na | 2 | 6 | 13 | 24 | na | < 1.0 (20°C) |
| Plum (ripe | e) | 3 | nd | 10 | na | 20 | na | < 5.0 (0°C) |
| Pomegrana | ate | na | 6 | 12 | na | 24 | 39 | < 0.1 (10°C) |
| Raspberry | | 17^{6} | 23 | 35 | 42 | 125 | na | ≤ 12.0 (20°C) |
| Sapote | | na | na | na | na | na | na | < 100 (20°C) |
| Strawberry | y | 16 | na | 75 | na | 150 | na | < 0.1 (20°C) |
| Tomato | | na | na | 15 | 22 | 35 | 43 | 10.0 (20°C) |

Note: na = Data not available, very low is considered to be $< 0.05 \mu l C_2H_4$ /kg-hr Sources: Biale and Young 1981; Blanke 1991; Abeles 1992; Saltveit 2005

in lipids is lower than the ratio in carbohydrates. If the substrate is an organic acid, the RQ is greater than unity because organic acids are richer in O_2 , and hence require less O_2 for respiration. Depending upon the extent of oxidation of the substrate, the RQ value for fresh commodity ranges from 0.7 to 1.3 for aerobic respiration (Kader 1987; Beaudry *et al.* 1992; Renault *et al.* 1994).

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

Glucose: RQ = 1

- $C_{18}H_{36}O_2$ +26 O_2 → 18 CO_2 +18 H_2O Stearic acid: RQ = 0.7
- $\begin{array}{c} C_4H_6O_5 + 3O_2 \rightarrow 4CO_2 + 6H_2O \\ \text{Malic acid: } RQ = 1.33 \end{array}$

RQ is affected by CO_2 fixation, incomplete oxidation and storage conditions. RQ of apples increased with time from 1.02 to 1.25 at climacteric peak and subsequently to 1.4 (Phan et al. 1975). Within the biological range of temperature, RQ falls with an increase in temperature. However, towards lower temperatures, low temperature breakdown (LTB) increases RQ while towards higher temperatures, denaturing of oxidative metabolism affects O₂ consumption more than the CO₂ evolution, which in turn, decreases RQ (Forward 1960). Very high RQ values usually indicate anaerobic respiration in those tissues that produce ethanol. In such tissues, a rapid change in the RQ can be used as an indication of the shift from aerobic to anaerobic respiration. The RQ is much greater than 1.0 when anaerobic respiration takes place. In fermentative metabolism, ethanol production involves decarboxylation of pyruvate to CO2 without O₂ uptake. The influence of CO₂ concentration on RQ

was not observed for apple (Jurin and Karel 1963) although Beaundry (1993) observed an RQ increase in high CO₂ concentrations for blue berries. The RQ values depend on both O₂ concentration and temperature (Beaudry *et al.* 1992; Lakakul *et al.* 1999). The RQ value of blueberries fruit increased as O₂ concentrations approached zero and the RQ breakpoint (the lowest O₂ concentration that does not induce anaerobic respiration) increased with temperature (Fonseca *et al.* 2002). Beaundry *et al.* (1992) explained this latter observation as being due to the fruit skin's permeability not rising as rapidly as O₂ consumption for a given temperature change. Thus the risk of anaerobiosis increases with temperature.

Various MAP studies have reported values of RQ indicative of anaerobic respiration (Carlin et al. 1990; Beaudry et al. 1992; Joles et al. 1994). The RQ value for apples at 20°C remained relatively constant up to 3.5% O₂, and when the O_2 concentration was decreased to less than 3.5% O₂ the RQ increased rapidly (Jurin and Karel 1963). Beit-Halachmy and Mannheim (1992) found an RQ of approximately 1 for mushrooms at 20°C and at O2 levels greater than 1.5-2%; below this O₂ level, RQ increased rapidly to a value higher than 6. Kader et al. (1989) reported that the RQ might be affected by ambient gas concentration. That is as the O₂ and CO₂ concentrations are changing in a package, the ratio of CO₂ produced to O₂ consumed may itself be changing. Henig and Gilbert (1975) used the regression analysis of gas concentration changes for tomato in PVC film packages to calculate O₂ consumption and CO₂ evolution rates under different O₂ and CO₂ concentrations. They found that RQ values remained constant at about 0.9 in the range of 0-9% CO₂, then a drop to 0.4 was observed with a later increase to 1.4 as CO₂ concentration increased.

Table 3 Summary of respiration and ethylene production rates of some vegetables at different temperatures.

| Commodity | | Respiration rate (mg CO ₂ /kg-hr) temperature of | | | | | C ₂ H ₄ production | |
|------------------|-------------------|---|-----|------|------|----------------|--|---|
| - | | 0°C | 5°C | 10°C | 15°C | 20°C | 25°C | (μl C ₂ H ₄ /kg-hr) |
| Asparagus | | 60 | 105 | 215 | 235 | 270 | na | 2.6 (20°C) |
| Beans | Snap | 20 | 34 | 58 | 92 | 130 | na | < 0.05 (5°C) |
| | Long | 40 | 46 | 92 | 202 | 220 | na | < 0.05 (5°C) |
| Beets | | 5 | 11 | 18 | 31 | 60 | na | < 0.1 (0°C) |
| Broccoli | | 21 | 34 | 81 | 170 | 300 | na | < 0.1 (20°C) |
| Brussels sprouts | | 40 | 70 | 147 | 200 | 276 | na | < 0.25 (7.5°C) |
| Cabbage | | 5 | 11 | 18 | 28 | 42 | 62 | < 0.1 (20°C) |
| Carrot | | 15 | 20 | 31 | 40 | 25 | na | < 0.1 (20°C) |
| Cauliflower | | 17 | 21 | 34 | 46 | 79 | 92 | < 1.0 (20°C) |
| Coriander | | 22 | 30 | na | na | na | na | Very low |
| Cucumber | | na | na | 26 | 29 | 31 | 37 | 0.6 (20°C) |
| Garlic | Bulbs | 8 | 16 | 24 | 22 | 20 | na | Very low |
| | Fresh peeled | 24 | 35 | 85 | na | na | na | Very low |
| Ginger | * | na | na | na | na | 6 ³ | na | Very low |
| Lettuce | Head | 12 | 17 | 31 | 39 | 56 | 82 | Very low |
| | Leaf | 23 | 30 | 39 | 63 | 101 | 147 | Very low |
| Okra | | 215 | 40 | 91 | 146 | 261 | 345 | 0.5 |
| Olive | | na | 15 | 28 | na | 60 | na | < 0.5 (20°C) |
| Onion | | 3 | 5 | 7 | 7 | 8 | na | < 0.1 (20°C) |
| Pea | Garden | 38 | 64 | 86 | 175 | 271 | 313 | < 0.1 (20°C) |
| | Edible pod | 39 | 64 | 89 | 176 | 273 | na | < 0.1 (20°C) |
| Pepper | - | na | 7 | 12 | 27 | 34 | na | < 0.2 (20°C) |
| Potato (cured) | | na | 12 | 16 | 17 | 22 | na | < 0.1 (20°C) |
| Radicchio | | 8 | 13 | 23 | na | na | 45 | 0.3 (6°C) |
| Radish | Topped | 16 | 20 | 34 | 74 | 130 | 172 | Very low |
| | Bunched with tops | 6 | 10 | 16 | 32 | 51 | 75 | Very low |
| Salad green | Rocked salad | 42 | 113 | na | na | na | na | Very low |
| - | Lamb's lettuce | 12 | 67 | 81 | na | 139 | na | Very low |
| Southern pea | Whole pods | 24 | 25 | na | na | 148 | na | na |
| - | Shelled peas | 29 | na | na | na | 126 | na | na |
| Spinach | * | 21 | 45 | 110 | 179 | 230 | na | Very low |
| Sprout (mung be | an) | 23 | 42 | 96 | na | na | na | < 0.1 (10°C) |
| Sweet corn | • | 41 | 63 | 105 | 159 | 261 | 359 | Very low |
| Turnip | | 8 | 10 | 16 | 23 | 25 | na | Very low |

Note: na = Data not available, very low is considered to be $\leq 0.05 \text{ µl } C_2 H_2/kg$ -hr

Sources: Abeles 1992; Gorny 1997; Saltveit 2005

Factors affecting respiration rate

Factors affecting respiration are broadly classified as external or environmental factors and internal or commodity factors. Respiration is affected by a wide range of environmental factors that include light, chemical stress (fumigants), radiation stress, temperature, atmospheric composition, physical stress, water stress, growth regulators, and pathogen attack. The internal factors affecting rate of respiration are genetic make-up, type and maturity stage of the commodity. The most important factors affecting respiration are temperature, atmospheric composition, physical stress and stages of development (Kader 1987; Pal et al. 1993; Saltveit 2005; Irtwange 2006).

Temperature

Without doubt the most important external factor affecting respiration is temperature. This is because temperature has a profound affect on the rates of biological reactions, e.g., metabolism and respiration (Fonseca et al. 2002; Saltveit 2005). Over the physiological range of most crops, i.e., 0 to 30°C (32 to 86°F), increased temperatures cause an exponential rise in respiration. The Van't Hoff Rule states that the velocity of a biological reaction increases 2- to 3-fold for every 10°C rise in temperature within the range of temperature normally encountered in the distribution and marketing chain (Burzo 1980; Zagory and Kader 1988). At higher temperatures, enzymatic denaturation may occur and reduce respiration rates. If temperatures are too low, physiological injury may occur, which may lead to an increase in respiration rate (Fidler and North 1967). For distribution and retail temperature (0-30°C) at which MAP is suitable, the effect of low temperature in lowering biochemical reaction rate is positive. The influence of temperature on respiration rate was first quantified with the $\hat{Q}_{10}^{\ R}$ (temperature quotient for respiration) values, which is the respiration rate increase for a 10°C rise in temperature. It can be expressed as:

$$\mathbf{Q}_{10}^{\mathbf{R}} = \left(\frac{\mathbf{R}_{2}}{\mathbf{R}_{1}}\right)^{10/(T_{2}-T_{1})}$$

where R_2 is the respiration rate at temperature T_2 and R_1 is the respiration rate at temperature T_1 . The temperature quotient is useful because it allows us to calculate the respiration rates at one temperature from a known rate at another temperature. However, the respiration rate does not follow ideal behavior, and the Q_{10}^{R} can vary considerably with temperature. For various products Q_{10}^{R} value may ranges from 1 to 4 depending on the temperature range (Kader 1987; Emond *et al.* 1993; Exama *et al.* 1993). At higher temperatures, the Q_{10}^{R} is usually smaller than at lower temperatures. Typical figures for Q_{10}^{R} are presented in **Table 4**. These typical Q_{10}^{R} values allow us to construct a table showing the effect of different temperatures on the rates of

respiration or deterioration and relative shelf-life of a typi-

Table 4 Variation of Q_{10}^{R} with a 10°C rise in temperature.

| Temperature (°C) | Q_{10}^{R} | |
|-----------------------------------|--------------|--|
| 0 to 10 | 2.5 to 4.0 | |
| 10 to 20 | 2.0 to 2.5 | |
| 20 to 30 | 1.5 to 2.0 | |
| 30 to 40 | 1.0 to 1.5 | |
| Sources: Wills 1981; Saltveit 199 | 6, 2005 | |

7

| Table 5 Effect of temperature on rate of deterioration. | |
|---|--|
|---|--|

| Temperature | Assumed Q ₁₀ ^R | Relative velocity | Relative shelf |
|----------------|--------------------------------------|--------------------------|-----------------------|
| (°C) | | of deterioration | life |
| 0 | - | 1.0 | 100 |
| 10 | 3.0 | 3.0 | 33 |
| 20 | 2.5 | 7.5 | 13 |
| 30 | 2.0 | 15.0 | 7 |
| 40 | 1.5 | 22.5 | 4 |
| Sources: Wills | 1981; Saltveit 1996, 2 | 005 | |

cal perishable commodity (**Table 5**). This table shows that if a commodity has a mean shelf-life of 13 days at 20°C it can be stored for as long as 100 days at 0°C, but will last no more than 4 days at 40°C (Saltveit 2005).

Atmospheric composition

The other external factor that affects respiration are atmospheric composition, particularly O₂ and CO₂ concentrations. Respiration is widely assumed to be slowed down by decreasing available O₂ as a consequence of reduction of overall metabolic activity (Isenberg 1979; Smock 1979; Kader 1987; Solomos and Kanellis 1989). Reduced O₂ level will decrease respiration rates, (Burton 1975; Isenberg 1979) and C₂H₄ biosynthesis (Konze et al. 1980; Yang 1985) as well as decrease sensitivity to C_2H_4 (Burg and Burg 1965; Kader 1986; Kader et al. 1989). The reduction of respiration rate in response to low O₂ levels is due to a decrease in the activities of other oxidases, such as polyphenoloxidase, ascorbic acid oxidase and glycolic acid oxidase activities whose affinity is much lower (Kader 1986; Jayas and Jeyamkondan 2002). Adequate O₂ levels are required to maintain aerobic respiration. However, excessive depletion of O₂ inside the package can lead to anaerobiosis accompanied by undesirable metabolic reactions such as tissue breakdown, odour and off-flavour production (Hulme 1971; Lipton 1975; Kader et al. 1989; Church 1994). At extremely low O₂ levels, toxin production by anaerobic pathogen organism can occur (Faber 1991). The exact level of O₂ that reduces respiration while still permitting aerobic respiration varies with commodity. In most crops, O₂ level around 2 to 3% produces a beneficial reduction in the rate of respiration and other metabolic reactions. Levels as low as 1% improve the storage life of some crops, e.g., apples, but only when the storage temperature is optimal. At higher storage temperatures, the demand for ATP may outstrip the supply and promote anaerobic respiration (Saltveit 2005).

The influence of CO₂ depends on type and developmental stage of the commodity, CO_2 concentration and exposure time. The idea of respiratory inhibition by CO₂ was first supported by simple explanations, i.e., that CO₂ was a product of the respiration process and, caused simple feedback inhibition (Wolfe 1980; Herner 1987). Kader (1989) considered that elevated CO₂ might affect the Krebs cycle intermediates and enzymes. Others considered that CO₂ inhibits C₂H₄ production rather than having a direct effect on the respiration process (Kubo et al. 1989). However, increasing the CO₂ level around some commodities reduces respiration, reduces C₂H₄ sensitivity and production, delays ripening and senescence, retards bacterial and fungal growth and lowers the pH (Wolfe 1980; Kader 1986; Harner 1987; Kader et al. 1989; Kubo et al. 1989; Paul and Buescher 1993; Prasad 1995; Peppelenbos and Levon 1996; Mahajan and Goswami 2001). The respiration rate increase due to the increase in CO₂ concentration may be explained in terms of CO_2 injury of tissues with a concomitant increase in C_2H_4 production. Some varieties of lettuce are very sensitive to CO₂, and brown stain (browning of the epidermal tissue near the midrib) is a common CO_2 injury when the product is exposed to levels above its tolerance limit (Kader et al. 1989; Ke and Saltveit 1989).

Physical stress

Even mild physical abuse can cause a substantial rise in respiration that is often associated with increased C_2H_4 evolution. The signal produced by physical stress migrates from the site of injury and induces a wide range of physiological changes in adjacent, non-wounded tissue. Some of the more important changes include enhanced respiration, C_2H_4 production, phenolic metabolism and wound healing. Woundinduced respiration is often transitory, lasting a few hours or days. However, in some tissues wounding stimulates developmental changes, e.g. to promote ripening, that result in a prolonged increase in respiration. C_2H_4 stimulates respiration and stress-induced C_2H_4 may have many physiological effects and induced detrimental effects on commodities besides stimulating respiration (Ryall and Lipton 1979; Kays 1991; Martinez-Romeroa *et al.* 2007, 2009).

Stage of development/maturity stage of the commodity

Respiration rates vary among and within commodities. Tissues with vegetative or floral meristems such as asparagus and broccoli have very high respiration rates. Vegetables include a great diversity of plant organs (roots, tubers, seeds, bulbs, fruits, sprouts, stems and leaves) that have different metabolic activities and consequently different respiration rates. Even different varieties of the same product can exhibit different respiration rates (Fidler and North 1967; Gran and Beaudry 1992; Song et al. 1992). As plant organs mature, their rate of respiration typically declines. This means that commodities harvested during active growth, such as many vegetables and immature fruits, have high respiration rates. Mature fruits, dormant buds and storage organs have relatively low rates. After harvest, the respiration rate typically declines; slowly in non-climacteric fruits and storage organs, rapidly in vegetative tissues and immature fruits (Fernández-Trujillo et al. 2008). The rapid decline presumably reflects depletion of respirable substrates that are typically low in such tissues. An important exception to the general decline in respiration following harvest is the rapid and sometimes dramatic rise in respiration during the ripening of climacteric fruit (Fig. 1). This rise, which has been the subject of intense study for many years, normally consists of four distinct phases: 1) pre-climacteric minimum, 2) climacteric rise, 3) climacteric peak, and 4) post-climacteric decline. In general, non-climacteric commodities have higher respiration rates in the early stages of development that steadily decline during maturation (Lopez-Galvez et al. 1997). Respiration rates of climacteric commodities also are high early in development and decline until a rise occurs that coincides with ripening or senescence (Fig. 1). Climacteric products exhibit a peak of respiration and C₂H₄ production associated with senescence or



Fig. 1 The climacteric pattern of respiration in ripening fruit.

| Table 6 | Fruits | classified | according | to respiratory | / behavio | or during | ripening. |
|---------|--------|------------|-----------|----------------|-----------|-----------|-----------|
| | | | | | | | |

| Climac | teric fruits | Non-climacteric fruits | | | |
|------------|---------------|------------------------|--------------|--|--|
| Apple | Papaya | Blackberry | Loquat | | |
| Apricot | Passion fruit | Blueberry | Lychee | | |
| Avocado | Peas | Cacao | Okra | | |
| Banana | Pear | Caju | Olive | | |
| Blueberry | Persimmon | Carambola | Orange | | |
| Breadfruit | Plantain | Cashew apple | Peas | | |
| Biriba | Plum | Cherry | Pepper | | |
| Cherimoya | Quince | Cucumber | Pineapple | | |
| Fig | Rambutain | Date | Pomegranate | | |
| Guava | Sapodilla | Eggplant | Prickly pear | | |
| Jackfruit | Sapota | Grape | Raspberry | | |
| Kiwifruit | Soursop | Grapefruit | Strawberry | | |
| Mango | Tomato | Jujube | Summer | | |
| Muskmelon | Watermelon | Lemon | squash | | |
| Nectarine | | Lime | Tamarillo | | |
| | | Longan | Tangerine | | |

Sources: Kays 1991; Salunke and Kadam 1995; Mahajan 2001; Saltveit 2005; Irtwange 2006

ripening. However, this does not imply that the respiratory response to MA/CA necessarily changes during the climacteric period. For example, Cameron *et al.* (1989) observed no influence of maturity or ripeness stage of tomatoes on O_2 uptake as a function of O_2 concentration.

The division of fruits into climacteric and non-climacteric types has been very useful for post harvest physiologists. However, some fruits, for example kiwifruit and cucumber, appear to blur the distinction between the groups. Respiratory rises also occur during stress and other developmental stages, but a true climacteric only occurs coincident with fruit ripening. **Table 6** shows general classification of fruits according to their respiratory behavior during ripening.

Care is necessary when packing in MAP due to alterations of respiration rate over time that are not normally considered in MAP design. The storage time period after harvest may influence the respiration curve due to: the normal deterioration of the product with ageing, ripening of climacteric products and wound metabolism in fresh-cut products. In the senescent stage of climacteric plant organ development there is a rise in respiration, presumably in order to obtain more energy for metabolic processes. In non-climacteric tissues and climacteric tissues in the post climacteric stage, increased respiration after some period of time in storage may be caused by the onset of decay by microorganisms (Rediers et al. 2009). Products in MAP are usually in short-term storage (distribution and retailing), thus, the influence of storage time due to senescence may be considered negligible. Normally, climacteric changes are considered important only in long term and not relevant to MAP (Fishman et al. 1996). MA conditions may control the timing of the climacteric rise as well as the magnitude of the peak. Young et al. (1962) observed a delay in the climacteric rise in avocados and bananas due to elevated CO₂ levels, but only a reduction of O₂ uptake at the climacteric peak in avocados. Fidler and North (1967) observed a delay in the onset of the climacteric rise in apples due to reduced O₂ levels. Wounding plant cells and tissues causes the respiration rate to increase. Wounding induces elevated C₂H₄ production rates, which may stimulate respiration and consequently accelerate deterioration and senescence in vegetative tissues and promote ripening of climacteric fruit (Brecht 1995). The wounding may be due to mechanical damage or cutting of the product. The respiration rate may gradually increase over time until a maximum value is reached and then start decreasing again to either the value before the wounding or to a higher value (Lopez-Galvez et al. 1996). For example, the respiratory rate of apple slices was about 2-3 times that of the whole fruit (Lakakul et al. 1999).

Biological structure

The resistance of fruits and vegetables to diffusion of O_2 , CO_2 , C_2H_4 and water vapour is dependent on the biological structure of individual commodity. Resistance to gas diffusion varies depending on the type of commodity, cultivar, part of the plant, surface area and stage of maturity, but appears to be little affected by temperature (Fallik and Aharoni 2004).

Ethylene production and sensitivity

 C_2H_4 is the natural product of plant metabolism and is produced by all tissues of higher plants and by some microorganisms. It is the simplest of all the organic compounds and considerably affecting the physiological processes of plants and the commodity after harvest (Abeles et al. 1992). Being a plant hormone, C₂H₄ regulates many aspects of growth, development, and senescence and is physiologically active in trace amounts (less than 0.1 ppm). It also plays a major role in the abscission of plant organs (Tomas-Barberan *et al.* 1997). C_2H_4 production rates increase with maturity at harvest, physical injuries, disease incidence, increased temperatures up to 30°C and water stress (Fidler and North 1976; Kader 1987; Kays 1991; Ables et al. 1992; Saltveit 1996). On the other hand, C_2H_4 production rates by fresh horticultural commodities are reduced by storage at low temperature, by reduced O_2 levels, and elevated O_2 levels around the commodity (Isenberg 1979; Kader 1986, 1987; Solomos and Kanellis 1989; Saltveit 1997). Exposure of climacteric fruits to C2H4 advanced the onset of an irreversible rise in respiration rate and rapid ripening. Various packages can delay the onset of climacteric and prolong shelf-life of fruits by reducing C₂H₄ production and sensitivity (Peleg 1985; Ables et al. 1992). Even non-climacteric fruits and vegetables can benefit from reduced C₂H₄ sensitivity and lower respiration rate under various conditions.

Transpiration

Transpiration is the process of evaporation of water from fruits and vegetables. Water loss is a very important cause of produce deterioration like wilting/shivering with severe consequences (Ryall and Pentzer 1974; Rizzini et al. 2009). In fact water loss is, first, a loss of marketable weight and then adversely affects appearance (wilting and shriveling). Also, the textural quality is reduced by enhanced softening, loss of crispness and juiciness, and reduction in nutritional quality (Irtwange 2006). Transpiration is a result of morphological and anatomical characteristics, surface-to-volume ratio, surface injuries and maturity stage on the one hand, and relative humidity (RH), air movement and atmospheric pressure on the other. The transpiration can be controlled by applying waxes and packaging in plastic films to act as barriers between the produce and the environment, by manipulating RH, temperature and air circulation (Kader et al. 1989; Church and Parson 1995; Irtwange 2006).

Compositional changes

Some changes in pigments of the commodity may continue after, or start only at harvest. These changes can occur as loss of chlorophyll, development of carotenoids (yellow orange and red colors) and development of anthocyanins and other phenolic compounds (Tomas-Barberan *et al.* 1997; Bureau *et al.* 2009; Quevedo *et al.* 2009). Changes in carbohydrates are generally desirable in fruits but are quite important in all commodities. In fruits starch is converted to sugars. In most commodities starch is used as a substrate for respiration. In ripening process, softening occurs and polysaccharides such as pectins, cellulose and hemicellulose are degraded (Ayers *et al.* 1960). There are changes in proteins, amino acids and lipids, which may affect the flavour of the commodity. Development of flavour and aroma volatiles is very important for the eating quality. Loss of vitamins, particularly ascorbic acid (vitamin C), takes place during storage and thus adversely affects nutritional quality (Ryall and Pentzer 1974; Kays 1991; Irtwange 2006).

Developmental processes

Sprouting, seed germination and rooting of commodities during storage are undesirable processes and greatly reduces their commercial value (Kays 1991). Asparagus spears continue to elongate during storage and bend when held horizontally during transportation. Seed germination occurring inside fruit during storage is undesirable in tomato, pepper, avocado and lemon (Wills 1981; Irtwange 2006).

Physiological breakdown

Exposure of a commodity to undesirable conditions such as freezing results in the collapse of tissues (Kays 1991). Chilling injury occurs in some tropical and subtropical commodities, which are store at temperatures above their freezing point but still cause injury (below 15°C or lower, depending on the commodity) (Adusule and Kadam 1995; Salunke and Kadam 1995). Chilling injuries are expressed as internal discoloration (browning), pitting, water-soaked areas, uneven ripening or failure to ripen, off-flavour development and accelerated incidence of decay (Adsule and Kadam 1995). Some physiological disorders originate from preharvest factors such as heat or chilling injuries in the field, which appear as bleaching, surface burning or scalding or nutritional imbalances. Very low O₂ or too-high CO₂ and the presence of excessive C₂H₄ concentrations, may exacerbate the severity of physiological disorders related to storage conditions (Wills et al. 1981; Kader et al. 1989; Saltveit 1996).

Postharvest pathology of fruit and vegetables

Vegetables have more available water. less carbohydrates (sugars) and high pH (near to neutral) than fruits (Shakuntala Manay and Shadakshraswami 2006). Due to more available water and having pH near to neutral, bacteria is the predominant microflora in vegetables. The common spoilage bacterium is Erwina spp., which causes bacterial rots in vegetables. The pH of the fruits is below the level to support bacterial growth. Moulds and yeasts (fungi) are major spoilage microorganisms in fruits. Fungi and bacteria are the two main sources of infection that may occur during growing and post harvest handling of produce (Hotchkiss 1989; Saltveit 1996; Rediers et al. 2009). Bacteria gain entry through wounds or natural opening (such as stomata, lenticels, or hydathodes) and multiply in the spaces between plant cells (Tomas-Barberan et al. 1997; Lu 2009)). Entry via wounds or natural openings is also characteristic of many fungi. Certain species of fungi, however, are capable of direct penetration of intact food commodity (Irtwange 2006).

Fruits are resistant to fungal attack until unripe; the infection process at this stage is halted; however the fungus remains alive, entering an inactive or dormant phase. The process of ripening is accompanied by weakening of cell walls and a decline in ability to synthesize anti-fungal substances, and during ripening phase it is no longer able to resist the advance of the fungus (Biale and Young 1981; Will et al. 1981; Miller et al. 1986). The decay reduction and disease control can be done through sanitation, careful handling, storing at low temperature, use of approved chemicals (fungicides which prevent or delay the development of molds and rots in the products, chemicals that delay ripening or senescence, growth retardants that inhibit sprouting and growth, metabolic inhibitors that block certain biochemical reactions that normally occur, C₂H₄ absorbents and fumigants to control insects or molds), physical treatments (heat, gamma-ray, UV irradiation), biological control and controlled and MA (Biale and Young 1981; Faber 1991; Kader 1995; Ahvenainen 2003; Irtwange 2006).

Response of fresh produce to MAP

MAP is the modification or replacement of air (N₂ content 78%, O₂ content 21%, CO₂ content 0.035%, together with water vapor and traces of inert gases) in a pack with a mixture of gases achieved by the natural interplay between two process, the respiration of the product and the transfer of gases through the packaging that leads to a atmosphere richer in CO₂ and poorer in O₂ or introduction of fixed proportion of gas mixture in to the package before being sealed (Mahajan et al. 2007). No further control is exerted over the initial composition, and the gas composition is likely to change with time owing to the diffusion of gases into and out of the product, the permeation of gases into and out of the pack, and the effects of product and microbial metabolism. Storage in plastic films in all kinds of combinations (different materials, perforation, inclusions, individual seal packing – shrunken and non-shrunken) is ad-ditional types of MA storage. Most perishable commodities require a R.H. of 90 to 95% in order to avoid excessive moisture loss during storage. Cooling slows down the changes in the produce during ripening and subsequent deterioration, reduces water loss, and slows or stops the growth and spread of rots. Wilting, re-growth, ripening, senescence and decay can be postponed through good temperature and relative humidity management (Ayers et al. 1960; Aradhya et al. 1993; Andriach et al. 1998).

A MA is created as a result of the produce respiratory activity; consumption of O_2 and emanation of CO_2 , occurring within a sealed plastic package. Special film packages, with suitable permeability to CO_2 and O_2 are used to ensure an optimal equilibrium of these gases during storage and shipment. The goal of MAP of fresh produce is to create an equilibrium package atmosphere or steady state condition with O₂% low enough and CO₂% high enough to be beneficial to the produce and not injuries. Steady state level depends on rate of produce respiration, produce weight and package permeability (Exama et al. 1993; Del Nobile et al. 2007). The benefits of film packaging include easy to handle (consumer package); protection from injuries; reduction of water loss, shrinkage, wilting; reduction of decay by MA; reduction of physiological disorders (chilling injury); retardation of ripening and senescence processes; retardation of regrowth and sprouting (green-onion radishes) and control of insect in some commodities (Kawada and Kitagawa 1988; Moyls et al. 1988; Kader et al. 1989; Prasad and Singh 1994; Phillips 1996; Kim et al. 2006; Sivakumar and Korsten 2006). Harmful effects of film packaging include enhancement of decay due to excess humidity; initiation and/or aggravation of physiological disorders; internal browning, irregular ripening in improper concentrations of CO₂/O₂; off-flavors and off-odours and increased susceptibility to decay (Hotchkiss 1989; Phillips 1996; Koide and Shi 2007)

The MA/CA potential benefit for fruits and vegetables at various storage temperature and air composition are presented in **Tables 7** and **8**, respectively (Parry 1993; Saltveit 1993; Kader 1997; Saltveit 1997; Mahajan 2001; Irtwange 2006).

Generally speaking, CA has its most beneficial effects on climacteric fruits at the pre-climacteric stage by prolonging this stage (Kader 1980; Raghavan et al. 1984; Mahajan 2001). The effects are less marked in climacteric fruits at its ripening stage, and in non-climacteric fruits at any stage. Most importantly the product to be stored must be of very good quality. CA storage can at best maintain quality, but cannot improve initially inferior quality of products. Also the crop to be stored must have been harvested at the correct stage of maturity. It must be free of disease and should have only minimal physical damage due to harvest and handling procedure (Ryall et al. 1974; Wills 1981). Recommended optimum condition for CA/MA and refrigerated storage for climacteric and non-climacteric fruits are summarized in Table 9 (Saltveit 1993; Saltveit 1997; Kader 1997; Mahajan 2001). Optimum levels of O₂ are the

Table 7 Potential benefits of MA/CA for fresh fruits.

| Commodity | Temperature | MA/CA | | Potential |
|-----------------------|-------------|------------------|-------|-------------|
| | (°C) | % O ₂ | % CO2 | for benefit |
| Apple | 0-3 | 1-3 | 1-5 | Excellent |
| Apricot | 0-5 | 2-3 | 2-3 | Fair |
| Avocado | 5-13 | 2-5 | 3-10 | Good |
| Banana | 12-15 | 2-5 | 2-5 | Excellent |
| Fig | 0-5 | 5-10 | 15-20 | Good |
| Grape | 0-2 | 2-5 | 1-3 | Fair |
| Guava | 10-15 | 2-5 | 2-5 | Good |
| Kiwifruit | 0-5 | 1-2 | 3-5 | Excellent |
| Lemon | 10-15 | 5-10 | 0-10 | Good |
| Lime | 10-15 | 5-10 | 0-10 | Good |
| Litchi | 0-2 | 2-3 | 2-5 | Good |
| Nectarine | 0-5 | 1-2 | 3-5 | Good |
| Olive | 5-10 | 2-3 | 0-1 | Fair |
| Orange | 5-10 | 5-10 | 0-5 | Fair |
| Mango | 10-15 | 3-5 | 5-10 | Fair |
| Papaya | 10-15 | 3-5 | 5-10 | Fair |
| Peas | 0-5 | 1-2 | 3-5 | Good |
| Pear, Asian | 0-5 | 2-4 | 0-1 | Good |
| Pear, European | 0-5 | 1-3 | 0-3 | Excellent |
| Persimmon | 0-5 | 3-5 | 5-8 | Good |
| Pineapple | 8-13 | 2-5 | 5-10 | Fair |
| Plum and prune | 0-5 | 1-2 | 0-5 | Good |
| Raspberry | 0-3 | 5-10 | 15-20 | Excellent |
| Strawberry | 0-2 | 5-10 | 15-20 | Excellent |
| Sweet cherry | 0-2 | 3-10 | 10-15 | Good |
| Nuts and dried fruits | 0-25 | 0-1 | 0-100 | Excellent |

| Commodity | Temperature | N | IA/CA | Potential for |
|------------------|-------------|------------------|-------------------|---------------|
| - | (°C) | % O ₂ | % CO ₂ | benefit |
| Artichokes | 0-5 | 2-3 | 2-3 | Good |
| Asparagus | 0-5 | 15-20 | 5-10 | Excellent |
| Beans | 5-10 | 2-3 | 4-7 | Fair |
| Beets | 0-5 | 2-5 | 2-5 | Fair |
| Broccoli | 0-3 | 1-2 | 5-10 | Excellent |
| Brussels sprouts | 0-5 | 1-2 | 5-7 | Good |
| Cabbage | 0-5 | 2-3 | 3-7 | Excellent |
| Cantaloupes | 3-7 | 3-5 | 10-15 | Good |
| Carrots | 0-5 | 3-5 | 2-5 | Fair |
| Cauliflower | 0-2 | 2-3 | 2-5 | Fair |
| Celery | 0-5 | 1-1 | 0-5 | Good |
| Corn, sweet | 0-5 | 2-4 | 5-10 | Good |
| Cucumbers | 8-12 | 3-5 | 0-2 | Fair |
| Honeydews | 10-12 | 3-5 | 0-2 | Fair |
| Leeks | 0-5 | 1-2 | 3-5 | Good |
| Lettuce | 0-5 | 1-3 | 0-3 | Good |
| Mushroom | 0-3 | Air | 10-15 | Fair |
| Okra | 8-12 | 3-5 | 0-2 | Fair |
| Onions, dry | 0-5 | 1-2 | 0-5 | Good |
| Onions, green | 0-5 | 1-2 | 10-20 | Fair |
| Peppers, bell | 8-12 | 3-5 | 0-2 | Fair |
| Peppers, chili | 8-12 | 3-5 | 0-3 | Fair |
| Potatoes | 4-10 | 2-3 | 2-5 | Fair |
| Radish | 0-5 | 1-5 | 2-3 | Fair |
| Spinach | 0-5 | 18-21 | 10-20 | Good |
| Tomato | 15-20 | 3-5 | 0-3 | Good |

Sources: Parry 1993; Kader 1997; Mahajan 2001; Irtwange 2006

Sources: Parry 1993; Saltveit 1993, 1997; Irtwange 2006

Table 9 Optimum conditions of MA/CA for some fruits and their shelf-life.

| Commodity | Storage | Optimum MA/CA | | Injuries atmosphere | | Marketable life, days | | Major benefit under MA/CA | Commercial |
|------------|-------------|----------------------|-------|---------------------|-------|-----------------------|---------|-------------------------------------|------------|
| | temperature | % O2 | % CO2 | % O ₂ | % CO2 | RA | СА | storage | potential |
| | (°C) | | | | | storage | storage | | |
| Apple | 0-3 | 3 | 3 | 2 | 10 | 200 | 300 | Maintains firmness and acidity | Excellent |
| Avocado | 7 | 2-5 | 3-10 | 1 | 15 | 12 | 56 | Delays softening | Good |
| Banana | 12-15 | 2 | 5 | 1 | 8 | 21 | 60 | Suppression of climacteric pattern | Excellent |
| Grapes | 0-2 | 3-5 | 1-3 | 1 | 10 | 40 | 90-100 | Disease control | Fair |
| Guava | 12-15 | 2-5 | 2-5 | 2 | 12 | 15-20 | 45 | Delays ripening and chilling injury | Good |
| Lemon | 15 | 3-5 | 0-5 | 1 | 6 | 130 | 220 | Green color retention | Good |
| litchi | 0-5 | 3-5 | 3-5 | 2 | 14 | 20-30 | 2230 | Delay in ripening | Good |
| Mango | 13 | 3-5 | 5-8 | 2 | 8 | 14-28 | 21-45 | Delay ripening | Good |
| Orange | 5-10 | 10 | 5 | 5 | 5 | 42 | 84 | Maintenance of firmness | Fair |
| Papaya | 13 | 3-5 | 5-8 | 2 | 8 | 14-28 | 21-35 | Less decay | Fair |
| Pears | 0-1 | 2-3 | 0-1 | 1 | 2 | 200 | 300 | Delays the flesh and core browning | Excellent |
| Pineapple | 10-15 | 2-5 | 10 | 2 | 10 | 12 | 10-15 | Reduces chilling injury | Fair |
| Strawberry | 0 | 4-10 | 15-20 | 1 | 12 | 7 | 7-15 | Less decay | Excellent |

Sources: Saltveit 1993, 1997; Kader 1997; Mahajan 2001; Irtwange 2006

levels below which it causes injuries and above which it is ineffective in extending storage life. However, different studies have shown great variations in the effective combination and ranges used in CA storage for both fruits and vegetables.

MA: favorable and injurious effects on fresh commodity

Several authors have reviewed the beneficial and detrimental effects of MA on fruits and vegetables (Kader 1980; Wolfe 1980; Dewey 1983; Zagory and Kader 1988; Kader *et al.* 1989; Ben-Yehoshua 1994; Church 1994; Church and Parson 1995; Irtwange 2006; Mahajan *et al.* 2007). Prevention of ripening and associated changes in foods is one of the main benefits of MA O₂ concentration has to be lowered below 10% to have a significant effect on fruit ripening and the lower the O₂ concentration the greater the effect (Kader *et al.* 1989; Davies 1995). Elevated CO₂ levels (>1%) also retard fruit ripening and their effects are additive to those of reduced O₂ atmosphere (Daniels *et al.* 1985; Dixon and Kell 1989; Kader *et al.* 1989). The effects of MA/CA on delay or inhibition of ripening are greater at higher temperature (Saltveit 2005). Thus use of MA may allow handling of ripening (climacteric-type) fruits at temperature higher than their optimum temperature. This is especially beneficial for chilling/sensitive fruits such as tomatoes, melon, avocado, banana and mangoes to avoid their exposure to chilling temperature (Zagory and Kader 1988). MA condition reduced respiration rates as long as the levels of O₂ and CO_2 are within those tolerated by the commodities. These combined with the decreased C_2H_4 production and reduced sensitivity to C_2H_4 action, results in delayed senescence and extending shelf-life as indicated by retention of chlorophyll (green color), textural quality (decreased lignifications), and sensory quality of fruits vegetables (Makhlouf *et al.* 1989; Pal and Buescher 1993; Saltveit 2005; Lu 2009).

Exposure of fresh fruits and vegetables to O_2 levels below their tolerance limits or to CO_2 levels above their tolerance limits (**Tables 10** and **11**) may increase anaerobic respiration and the consequent accumulation of ethanol and acetaldehyde causing off-flavour (Bohling and Hansen 1984; Kader *et al.* 1989; Kays 1991; Kader 1997; Kays 1997; Kupferman 1997; Richardson and Kupferman 1997; Table 10 $O_2\%$ limits below which injury can occur for some commodities.

| Minimum O ₂ | Commodities |
|------------------------|---|
| concentration | |
| tolerated (%) | |
| 0.5 or less | Chopped greenleaf, redleaf, Romaine and iceberg |
| | lettuce, spinach, sliced pear, broccoli, mushroom |
| 1 | Broccoli florets, chopped butterhead lettuce, sliced |
| | apple, Brussels sprouts, cantaloupe, cucumber, |
| | crisphead lettuce, onion bulbs, apricot, avocado, |
| | banana, cherimoya, atemoya, sweet cherry, cranberry, |
| | grape, kiwifruit, litchi, nectarine, peach, plum, |
| | rambutan, sweetsop |
| 1.5 | Most apples, most pears |
| 2 | Shredded and cut carrots, artichoke, cabbage, |
| | cauliflower, celery, bell and chili pepper, sweet corn, |
| | tomato, blackberry, durian, fig, mango, olive, papaya, |
| | pineapple, pomegranate, raspberry, strawberry |
| 2.5 | Shredded cabbage, blueberry |
| 3 | Cubed or sliced cantaloupe, low permeability apples |
| | and pears, grapefruit, persimmon |
| 4 | Sliced mushrooms |
| 5 | Green snap beans, lemon, lime, orange |
| 10 | Asparagus |
| 14 | Orange sections |
| a | |

Sources: Bohling and Hansen 1984; Kader *et al.* 1989; Kays 1991; Gorny 1997; Kader 1997; Kays 1997; Kupferman 1997; Richardson and Kupferman 1997; Saltveit 1997; Beaudry 2000; Nazir and Beaundry 2006

Table 11 CO₂% above which injury can occur for some commodities.

| Maximum CO ₂ | Commodities |
|-------------------------|---|
| concentration | |
| tolerated (%) | |
| 2 | Lettuce (crisphead), pear |
| 3 | Artichoke, tomato |
| 5 | Apple (most cultivars), apricot, cauliflower, cucumber, |
| | grape, nashi, olive, orange, peach (clingstone), potato, |
| | pepper (bell) |
| 7 | Banana, bean (green snap), kiwi fruit |
| 8 | Рарауа |
| 10 | Asparagus, brussels sprouts, cabbage, celery, grapefruit, |
| | lemon, lime, mango, nectarine, peach (freestone), |
| | persimmon, pineapple, sweet corn |
| 15 | Avocado, broccoli, lychee, plum, pomegranate, sweetsop |
| 20 | Cantaloupe (muskmelon), durian, mushroom, rambutan |
| 25 | Blackberry, blueberry, fig, raspberry, strawberry |
| 30 | Cherimoya |
| C 11 | 1007 C 1007 K 1 1007 K 1007 K C 1007 |

Sources: Herner 1987; Gorny 1997; Kader 1997; Kays 1997; Kupferman 1997; Richardson and Kupferman 1997; Saltveit 1997; Nazir and Beaundry 2006

Saltveit 1997; Beaudry 2000; Nazir and Beaundry 2006). Low O₂ and/or high CO₂ concentrations can reduce the incidents and severity of certain physiological disorders such as those induced by C2H4 (scald of apple and pear) and chilling injury of some commodity (Kader 1997; Kupferman 1997; Richardson and Kupferman 1997; Saltveit 1997; Irt-wange 2006). Besides, O_2 and CO_2 levels beyond those tolerated by the commodity can induce physiological disorder such as brown stain on lettuce, internal browning and surface pitting of pome fruits, and black heart of potato. CA/MA combinations have direct and indirect effects on post harvest pathogens. EI-Goorani and Sommer (1981) pointed out that the delaying senescence, including fruit ripening, by MA/CA reduced susceptibility of fruits and vegetables to pathogen. On the other hand MA condition unfavorable to a given commodity can induce its physiological breakdown and render it more susceptible to pathogen. The elevated CO₂ concentrations inhibit the growth of some type of microorganism, bacteria and fungi during storage. O₂ level below 1% and/or CO₂ levels above 10% are needed to significantly suppress the fungal growth (Faber 1991; Kader et al. 1989). Elevated CO₂ levels (10-15%) can be used to provide fungistatic effects on commodities that

tolerate such CO_2 levels (Daniel *et al.* 1985; Dixon and Kell 1989).

Tolerance limit of commodities to MA

The extent of benefits from the use of MA depends upon the commodity, cultivar, physiological age (maturity stage), initial quality, concentration of O₂ and CO₂, temperature and duration of exposer to such condition. Subjecting a cultivar of a given commodity to O_2 level below and/or O_2 level above its tolerance limit at a specific temperature-time combination will result in stress to the living plant tissue, which is manifested as various symptoms, such as irregular ripening, initiation and/or aggravation of certain physiological disorder, development of off-flavors and increased susceptibility to decay and fungal growth (Marcelein 1974; Lipton 1975; Isenberg 1979; Smock 1979; Kader et al. 1989; Ke and Salteit 1989; Varoquaux et al. 1996; Beaundry 2000; Watkins 2000). Fruits and vegetables are classified according to their relative tolerances to low O2 or elevated CO₂ concentration (Kader *et al.* 1989; Kader 1997; Kupferman 1997; Richardson and Kupferman 1997; Saltveit 1997; Beaudry 1999, 2000; Watkin 2000) when kept at their optimum storage temperature and relative humidity and presented in Tables 10 and 11. The limits of tolerance to low O₂ level would be higher than those as indicated in Table 10; to maintain aerobic respiration if storage temperature and/or duration are increased. For some commodities, susceptibility to low O2 and/or high CO2 stress is influenced by maturity stage. For example ripe fruits often tolerate higher levels of CO₂ than mature green fruits. Minimally processed fruits and vegetables have fewer barriers to gas diffusion, and consequently they tolerate higher concentration of CO_2 and lower O_2 levels than intact commodities. The effects of stress resulting from exposure to undesirable MA/CA conditions (i.e. level of O2 and/or CO2) can be additive to other stresses (such as chilling injury, wounding, or ionizing radiation) in accelerating the deterioration of fresh produce. Successful MAP must maintain near optimum O_2 and CO_2 levels to attain the beneficial effects of MA without exceeding the limits of tolerance which may increase the risk of physiological disorders and other detrimental effects (Watkins 1998; Kader et al. 1989; Beundry 2000; Watkins 2000).

Physiological and biochemical effects of MAP

The respiration rate is considerably reduced by low O_2 and high CO_2 atmosphere in MAP. Low respiration rate reduces the overall metabolic and biochemical activities (C_2H_4 production and sensitivity to C_2H_4 , rapid acid catabolism, changes of pectic substances in the cell wall leading to softening, etc.) in the cell, thereby reducing the rate of utilization of food reserves (Kader 1986; Kader *et al.* 1989). By reducing the respiration rates, MA also lowers the production of heat due to respiration. CO_2 has an antagonistic effect on enzymes involved in C_2H_4 biosynthesis. As O_2 is required in the production of C_2H_4 , low O_2 concentrations suppresses the C_2H_4 production. During MAP, a compound precursor to C_2H_4 is accumulated in the products. Therefore, when the products are transferred to air, C_2H_4 is rapidly produced and the products ripen faster (Wang 1990).

MAs delay the onset of ripening process and increase the firmness in fruits. By inhibiting an enzyme polyphenol oxidase in litchi, strawberry, lettuce and mushrooms, MA prevents browning of these tissues (Wang 1990; Renault *et al.* 1994; Stewart *et al.* 2003; Sivakumar and Korsten 2006; Del Nobile *et al.* 2008). When O_2 is not available, fruits and vegetables degrade glucose anaerobically by glycolysis to generate energy. In the glycolysis pathway, aldehydes, alcohols and lactates are produced (Kader 1986). Accumulation of these anaerobic byproducts produces off-flavors associated with physiological disorders, leading to an unacceptable eating quality (Meyer *et al.* 1973; Harner 1987; Kader *et al.* 1989; Ke and Saltveit 1989; Varoquaux *et al.* 1996). Therefore, a minimum of 2-3% levels of O_2 must be maintained in the MAP to prevent anaerobic respiration (Wang 1990; Jayas and Jeyamkondan 2002). Hence, the objective of MAP design is to define the conditions so as to achieve the optimum concentration of O_2 and CO_2 in side the package with a shortest possible time to preserve the quality and extend shelf-life.

Packaging of fresh produce in polymeric films

The beneficial and detrimental effects of packaging fruits and vegetables in plastic film are many (Hardenburg 1971; Henig 1975; Ben-Yehoshua 1985; Kader *et al.* 1989; Ben-Yehoshua *et al.* 1994; Abdel-Bary 2003; Irtwange 2006). The benefits of film packaging, other than creation of MA condition includes: (i) reduction of surface abrasions by avoiding contact between the commodity and the material of the shipping container (ii) improved sanitation by reducing possibilities of contamination of the commodity during handling (iii) possible exclusion of exposure to light (iv) maintenance of high relative humidity and reduction of water loss and extension of shelf-life (v) provision of a barrier to the spread of decay from one unit to another (vi) possible carriers of fungicides and scald inhibitors and (vii) facilitation of brand identification.

Plastic films influence the rate of cooling and warming of the commodity and must be considered in selecting the appropriate temperature management procedure for a packaged commodity. Plastic film wrapped produce usually requires longer cooling time than unwrapped produce and the difference can be reduced by perforating the film. Another potential disadvantage of film wrapping is the possible water condensation within the package, which may encourage fungal growth and increase decay problems. Such condensation is likely to occur when the commodity is removed from low storage temperature to high ambient temperature during post harvest handling. The anoxic MA condition can favor the growth of facultative anaerobes and/or obligate anaerobes over aerobic spoilage organism, packaging of fruits in O2 excluded MAs could results in a dangerous absence of noxious odours produced by aerobic spoilage organism (Hintlian and Hotch 1986; Kader et al. 1989). Fresh fruits and vegetables, as living tissue, ferment and develop undesirable off-flavour due to the accumulation of ethanol, acetaldehyde and other volatiles under anaerobic conditions. Hence fresh produce should never be packaged in a way that may result in anoxic condition. This combined with maintenance of the optimum temperature range through out post harvest handling, should ensure safety (absence of harmful bacteria) of fresh produce in MAP (Ben-Yohoshua et al. 1985).

The polymeric films namely LDPE, HDPE, PP, polybutylene, plasticized PVC, polyvinylidene chloride and specially design film laminates of different thickness are used to provide barrier to water vapor with out effecting the gas diffusion properties of gases (Karel *et al.* 1975; Sacharow and Griffin 1980; Kader *et al.* 1989; Exama *et al.* 1993; Abdel-Bary 2003; Massey 2003). The water saturated atmosphere alleviates water stress, encourages wound healing and helps maintain the skin's resistance to pathogens (Ben-Yohoshua *et al.* 1983; Ben-Yohoshua *et al.* 1987; Barkai-Golan 1990; Cambrink *et al.* 1990).

Effects of MAP on disease control

The growth and activity of microorganisms can be retarded by elevated CO_2 and reduced O_2 concentrations. Fungi are aerobic organisms and their growth is reduced by storing fruits in low- O_2 atmospheres. At ambient temperatures, levels of up to 20% CO_2 extend both the lag and logarithmic growth phases of common spoilage organisms by as much as double (Daniels *et al.* 1985). Levels of below 1% O_2 and/or above 10% CO_2 are needed to significantly, suppress fungal growth (El-Goorani and Sommer 1981; Dixon and Kell 1989). Elevated CO_2 , levels (10-15%) can be used to retard the activities of microorganisms and provide fungistatic on commodities that tolerate such CO_2 levels (Daniels *et al.* 1985; Dixon and Kell 1989; Faber 1991). The growth of almost all aerobic microorganisms, particularly the psychrophilic (which are the main cause of deterioration of commodities), can be retarded by elevated CO_2 and reduced O_2 (Daniels *et al.* 1985; Hotchkiss 1989; Barkai-Golan 1990; Feber 1991). The inhibitory effect of CO_2 increases with a decrease in temperature.

MA suppresses the postharvest diseases in fruits and vegetables by increasing the host resistance and by affecting the pathogens (Barkai-Golan 1990). It is a well-known fact that the host resistance to pathogens decreases with ripeness. As fruits ripen, the pectic substances of the middle lamella of the plant cell membrane become more soluble and tissues become softer (Biale and Young 1981; Saltveit 2005). The pathogens secrete pectolytic enzymes for which soft tissues are more vulnerable. MA storage reduces the respiration rate and the production of C_2H_4 , thereby delaying the onset of ripening and reducing the rate of ripening. Thus, MA increases the host resistance by delaying fruit softening and maintains the firmness or integrity of fruits, which are then less prone to spoilage (Faber 1991). Growth of common postharvest pathogens is greatly inhibited only when the O2 is reduced below 1% (Philips 1996). Usually, all the fruits and vegetables are stored at 2-5% O₂ to prevent O₂ injury and off-odours. At these concentrations, the growth rate of pathogen is merely reduced and therefore the suppression of decay/diseases in fruits and vegetables can be largely attributed to the increase in natural host resistance (Barkai-Golan 1990). It is important to note that the fruits and vegetables are very sensitive to environmental conditions. If there is a low concentration of O₂ or high concentration of CO₂, or chilling injury, tissue integrity is affected and the tissues are more susceptible to pathogen attack (Hotchkiss 1989)

Individual seal-packaging reduced fruit decay by prevention of secondary rot infection, which is an important factor for fruits, particularly those destined for long-term storage or shipment (Daniels et al. 1985). An individual fruit infected by Botrytis, Geotrichum, or Phytophthora will rapidly induce decay in the other fruit in the same carton (El-Goorani et al. 1992). Seal packaging or MAP also changed the distribution of pathogens in commodity. Sealed fruit generally had slightly more stem-end rots and fewer moulds than those unsealed. The pathogens, particularly quiescent ones, generally start to develop rapidly in the humid atmosphere. Consequently, the balance between host and pathogens may at times, favour the pathogen, and decay percentage rises. For this reason, adequate decay control of sealed fruit may be of paramount importance (Hintlian and Hotchliss 1986; Ben-Yehoshua 1991).

MAP by itself may sometimes be ineffective in controlling decay. Thus, additional methods to combat diseases in packages should be sought. Combination of seal packaging and curing (36°C, 3 days) reduced decay and sensitivity to chilling injury, healed injury, and extended the life of fruits. The mode of action of curing was shown to be through: i) thermal inhibition of the pathogen; ii) induced synthesis of lignin-like materials which form a mechanical barrier to the invasion of the pathogens, and iii) preventing the degradation of natural antifungal substances. Combined imazalil treatment and seal-packaging of fruits enabled a marked reduction of decay (Ben-Yehoshua 1985; Hintlion and Hotchkiss 1986; Ben-Yehoshua et al. 1994). Imazalil could be applied in several ways: as a dip, spray, or by incorporating it into the plastic films. The films serve as a slow release reservoir of the fungicide to the produce, thus reducing the residue on the produce (Miller et al. 1986; Ben-Yehoshua et al. 1987). The film acts also as a physical barrier to slow the dissipation of volatile fungicides, such as imazalil, 2 aminobutane, and diphenyl. MAP thereby produces a micro atmosphere that can be enriched with a suitable volatile fungicide so that the sealed enclosure forms a fumigation chamber to control decay and control pathogen over a prolonged period.

Methods of creating MA conditions

MA within polymeric film packages can be established either passively by the commodity or intentionally via active packaging or a combination of the both (Kader *et al.* 1989; Mahajan *et al.* 2007).

Active MAP

In the case of active MAP an atmosphere is established by pulling a slight vacuum and replacing the atmosphere of the package with the desired gas mixture of O_2 , $\hat{C}O_2$ and N_2 . The advantage here is that the beneficial equilibrium atmosphere may be established more quickly in the package containing commodity. Additionally, absorbers or adsorbers may be included in the package to scavenge O_2 , CO_2 , or C₂H₄ to control the concentration of these gases. Commercially suitable absorbers for any gas should satisfy the following requirements: (1) must be effective and exhibit an appropriate rate of absorption of that gas, (2) must be harmless to human by direct or indirect contact (3) must have good storage stability, and (4) must be small in size but have large capacity for gas absorption (Kader et al. 1989; Labuza 1990; Ahvenainen 2000). The details of the absorbers used for active MAP for preservation and shelflife extension are summarized (Kader et al. 1989; Labuza and Breene 1989; Ahvenainen 2003) and presented in Table 12.

There are growing interests in developing time-temperature indicators (TTI), which would monitor the product temperature history to determine the remaining storage life (Jayas and Jeyamkondan 2002). Others like O_2 indicators, CO_2 indicator, microbial growth indicators/freshness indicator, pathogen indicators may be used for quality control of a packed commodity (Ahvenaine 2003). It may be mechanical, chemical or enzymatic. This will greatly improve the inventory control at the retail stores and also food safety (Labuza and Breene 1989; Ahvenaine 2003).

Passive MAP

In this case the modification of the atmosphere inside the package is attained/achieved by the natural interplay between two processes, the respiration of the products and the transfer of gases through the packaging that leads to an atmosphere richer in CO_2 and poorer in O_2 and it depends

Table 12 Absorbers used for active MAP for extending shelf life.

on the characteristics of the commodity and the packaging film (Smith *et al.* 1987; Mahajan *et al.* 2007). The MAP design requires the determination of intrinsic properties of the produce, i.e. respiration rate, optimum O_2 and CO_2 gas concentrations, and film permeability characteristics. The objective of MAP design is to define conditions that will create the atmosphere best suited for the extended storage of a given produce while minimizing the time required achieving this atmosphere. This can be done by matching the respiration rate of the packaged produce with the film permeation rate for O_2 and CO_2 . As different products vary in their behavior and as MA packages will be exposed to a dynamic environment, each package has to be optimized for specific demands (Chau and Talasila 1994; Jacxsens *et al.* 2000).

Respiration rate of the commodity

Fruits and vegetables are still living after harvest and still require O₂ for their metabolism. Aerobic respiration consists of oxidative breakdown of organic reserves to simpler molecules, including CO₂ and water, with release of energy. So in respiration process it consumes O_2 and evolves CO_2 . The exchange of gases between a plant organ and its environment can be considered in four steps as follows: (i) diffusion in the gas phase through the dermal system (ii) diffusion in the gas phase through the intercellular system (iii) Exchange of gases between the intercellular atmosphere and the cellular solution (cell sap), which is a function of the distribution of intercellular spaces and respiratory activities and (iv) diffusion in solution within the cell to centers of O₂ consumption or from centers of CO₂ and C₂H₄ production (Kader et al. 1989). As a result of respiratory metabolism CO_2 and C_2H_4 are produced in the cell sap, and this local increase in concentration will activate diffusion outward toward the cell wall surface adjacent to the intercellular space. These gases then move into the intercellular space and continue toward regions of lower concentrations until they reach the intercellular space below the dermal system. From there, CO₂ and C₂H₄ diffuse through the openings in the surface of the commodity to the ambient atmosphere (Button 1987; Kader et al. 1989; Irtwange 2006). The pattern of the gradient that is established for O_2 diffusion is the reverse of that for CO_2 and C_2H_4 . O_2 diffuses inward from the ambient air into the centers of consumption inside the cells.

| Packaging system | Example of working principle/mechanism/reagents | Purpose |
|----------------------------|--|--|
| Oxygen absorbers | Ferro-compound (iron powders), ascorbic acid, metal salt, glucose | Reducing/preventing respiration rate, mould, yeast and |
| (sachet, labels, films, | oxidase, alcohol oxidase | aerobic bacteria growth, prevention of oxidation of |
| corks) | | fats, oil, vitamins, colors. Prevention of damage by worms, insects and insect eggs |
| Carbon dioxide absorbers | Calcium hydroxide and sodium hydroxide or potassium hydroxide, | Removing excess carbon oxide formed during storage |
| (sachet) | calcium oxide, magnesium oxide, activated charcoal and silica gel | to prevent from fruit damage and bursting of package |
| Ethylene absorbers | Aluminum oxide and Potassium permanganate (sachets), Activated | Prevention of too fast ripening and softening |
| (sachets, films) | hydro carbon (squalane, apiezon) + metal catalyst (sachets), Builder- | |
| | clay powders (films), Zeolite (films), Japanese oya stone (films) and | |
| | other compound like silicones (phenyl- methyl silicone) | |
| Humidity absorbers (drip | Polyacrylates (sheet), polypropylene glycol (film), silica gel (sachet), | Control of excess moisture in packed produce, |
| absorbent sheets, films, | clays (sachet) | reduction of water activity on the surface of food in |
| sachets) | | order to prevent the growth of moulds, yeast and |
| | | spoilage bacteria |
| Absorbers of off flavours, | Cellulose acetate film containing narinaginase enzyme, Ferrous salt | Reduction of bitterness in fruit, improving the flavour |
| amines and aldehydes | and citric or ascorbic acid (sachet), specially treated polymer | and oil containing foods |
| (films, sachets) | | |
| UV-light absorbers | Polyolefins like polyethylene and propylene doped in the material | Restricting light induction oxidation |
| _ | with a UV-absorbent agent, Crystallinity modification of nylon 6 | |
| Reagents | Ferrous carbonate | For quickly developing an MA within a package. The |
| | $FeCO_3 + O_2 + 6 H_2O \rightarrow 4 Fe (OH)_3 + 6 CO_2$ | reaction, quickly builds up the CO_2 content of the |
| | | package while reducing the O_2 content somewhat |
| Preservative films | Preservative films diffuses slowly preservatives such as nisin, sorbate, | Control the microbial growth or suppression of |
| | glycol, antioxidants, antibiotics, ethanol or ethylene into the package | unwanted biochemical reactions |

Gas diffusion within a fruit or vegetable is determined by: respiration rate, maturity stage, physiological age, commodity mass and volume, pathways and barriers for diffusion, properties of the gas molecule, concentration of gases in the atmosphere surrounding the commodity, magnitude of gas concentration gradient across barriers and temperature (Banks 1984; Kader *et al.* 1989). In turn, the respiration rate of a commodity inside a polymeric film package will depend upon: kind of commodity, maturity stage, physical condition, concentration of O₂, CO₂, and C₂H₄ within the package, commodity quantity in the package, void volume of the package and temperature.

Respiration rates can be measured by observing the concentration of O_2 consumption or CO_2 evolution per unit time per unit weight of the produce. Various external factors such as O_2 concentration, CO_2 concentration, temperature and time affect respiration (Kays 1991; Lee *et al.* 1991; Hagger *et al.* 1992; Mahajan and Goswami 2001). The usual methods of respiration rate determinations are: the closed or static system, the flowing or flushing system and permeable system (Fonseca *et al.* 2002).

In the closed system, a gas-tight container of known volume is filled with commodity and the container, containing ambient air as the initial atmosphere is closed (Cameron *et al.* 1989; Gong and Corey 1994; Ratti *et al.* 1996; Maneerat *et al.* 1997; Menon and Goswami 2008). Changes in the concentration of O_2 and CO_2 over a certain period of time are measured and used to estimate respiration rates (Mahajan 2001; Bhande *et al.* 2008; Mangaraj and Goswami 2008) as follows:

$$R_{O2} = \left[\frac{(Y_{O2})_t - (Y_{O2})_{t+1}}{\Delta t}\right] \frac{V_f}{W}$$
(1)

$$R_{CO2} = \left[\frac{(Z_{CO2})_{t+1} - (Z_{CO2})_t}{\Delta t}\right] \frac{V_f}{W}$$
(2)

where R_{O2} is the respiration rate, cm³ [O₂] kg⁻¹h⁻¹, R_{CO2} is the respiration rate, cm³ [CO₂] kg⁻¹h⁻¹, Y_{O2} and Z_{CO2} are the gas concentrations for O₂ and CO₂ in volume fraction respectively, t is the storage time in h, Δt is the time difference between two gas measurements, V_f is the free volume of the respiration chamber in ml and W is the weight of the fruit in kg.

In the flow through system, the product is enclosed in an impermeable container through which a gas mixture flows at a constant rate (Prasad 1995; McLaughlin and O'Beirne 1999). The respiration rates are calculated from the absolute differences in gas concentrations between the outlet and the inlet when the system reaches steady state as follows:

$$R_{02} = \frac{\left(Y_{02}^{in} - Y_{02}^{out}\right) \times F_{gas}}{W}$$
(3)

$$R_{c02} = \frac{\left(Z_{CO2}^{out} - Z_{CO2}^{in}\right) \times F_{gas}}{W}$$

$$\tag{4}$$

where F_{gas} is the gas flow rate to the respiration container in $\mbox{cm}^3.\mbox{h}^{-1}$

In the permeable system, a package of known dimensions and film permeability is filled with product (Joles *et al.* 1994; Lee *et al.* 1996; Mahajan *et al.* 2007). The steadystate concentrations of O_2 and CO_2 are determined and a mass balance is performed on the system in order to estimate the respiration rates as follows:

$$R_{02} = \frac{P_{02} \times A}{L \times W} \left(Y_{02}^{e} - Y_{02} \right)$$
(5)

$$R_{c02} = \frac{P_{C02} \times A}{L \times W} \Big(Z_{C02} - Z_{C02}^{e} \Big)$$
(6)

where P_{O2} and P_{CO2} are the permeability coefficient for O_2 and CO_2 in cm³.mm m⁻².h⁻¹. [Conc. diff. of CO_2 in volume fraction]⁻¹), L is the film thickness in mm, and Y_{O2}^{e} and Z_{CO2}^{e} are the steady state concentration of O_2 and CO_2 in volume fraction respectively.

Modelling of respiration rates

For fresh commodities, both O2 and CO2 concentrations have an influence on quality and shelf-life. High CO₂ concentrations can reduce the O₂ consumption rate of a number of fruits and vegetables. The principles of enzyme kinetics have been suggested as being applicable to the respiration rate of fresh produce and Michaelies-Menten equation has been fitted to respiration rates (Lee et al. 1991). The role of CO_2 in respiration is suggested to be mediated via inhibition mechanism of the Michaelis-Menen equations. This can be modelled by four types of inhibition in an enzyme kinetics model (Lee et al. 1991; Song et al. 1992; Pepelenbos and Leven 1996; Mangaraj and Goswami 2009; Tariq et al. 2009): (1) the competitive type; (2) the uncompetitive type; (3) a combination of competitive and uncompetitive types; and (4) the non-competitive type. All these models describe the effects of inhibitor (CO_2) on respiration rate.

(1) Competitive type

Competitive inhibition occurs when both the inhibitor (CO_2) and the substrate compete for the same active site of the enzyme. An increase of O_2 at high CO_2 concentrations would then strongly influence the O_2 consumption rate. Thus the maximum respiration rate is lower in high CO_2 concentrations. The model with competitive inhibition can be described as:

$$RR = \frac{V_m \times Y_{02}}{k_m \times \left(1 + \frac{Z_{C02}}{k_i}\right) + Y_{02}}$$
(7)

(2) Uncompetitive type

The uncompetitive type of inhibition occurs where the inhibitor (CO₂) does not react with the enzyme, but with the enzyme-substrate complex. In this case the increase of O₂ at high CO₂ concentrations has almost no influence on the O₂ consumption rate (when O₂ concentrations are not very low). Thus the maximum respiration rate is not much influenced at high CO₂ concentration. The model with uncompetitive inhibition can be described as:

$$RR = \frac{V_{m} \times Y_{O2}}{k_{m} + \left(1 + \frac{Z_{CO2}}{k_{i}}\right) \times Y_{O2}}$$
(8)

(3) Non-competitive type

The non-competitive type of inhibition occurs where the inhibitor reacts both with the enzyme and with the enzyme-substrate complex. This leads to O_2 consumption rates at high CO_2 concentrations which lie in between those obtained by the previously described inhibition models. The model with non-competitive inhibition can be described as:

$$RR = \frac{V_{m} \times Y_{02}}{\left(k_{m} + Y_{02}\right) \times \left(1 + \frac{Z_{C02}}{k_{i}}\right)}$$
(9)

(4) A combination of competitive and uncompetitive type

When enzyme reactions are described, only one enzyme is involved. The complete respiratory pathway, however, involves many enzyme reactions. This means that the 'overall' type of inhibition describing gas exchange can be a combination of both competitive and uncompetitive types. The non-competitive type of inhibition describes such a combination, but in such a way that assumes both types to be equally active. Therefore, an equation is given with a combination of the competitive and uncompetitive type, where each type differs in its relative activity:

$$RR = \frac{v_m \times Y_{O2}}{k_m \times \left(1 + \frac{Z_{CO2}}{k_i}\right) + \left(1 + \frac{Z_{CO2}}{k_i}\right) \times Y_{O2}}$$
(10)

where RR is the respiration rate for O_2 consumption and CO_2 evolution, cm³ kg⁻¹ h⁻¹, Y_{O2} and Z_{CO2} are the gas concentrations for O_2 and CO_2 respectively in percentage, v_m , k_m , and k_i are the maximum respiration rate for O_2 consumption and CO_2 evolution, the Michaels-Menten constant for O_2 consumption and CO_2 evolution, % O_2 and the inhibition constants for O_2 consumption, CO_2 evolution, and % CO_2 , respectively.

Temperature has a major effect on the respiration rate, which has not been considered in the above equations. The dependence of model parameters of uncompetitive inhibition kinetics on storage temperature are expressed using Arrhenious equations (Lakakul *et al.* 1999) as follows:

$$R_{m} = R_{p} \exp\left[\frac{-E_{a}}{R \times T_{abs}}\right]$$
(11)

where R_m is the model parameter of enzyme kinetics, R_p is the respiration pre-exponential factor, E_a is the activation energy, kJ/g-mole, T_{abs} is the storage temperature, K, and R is the Universal gas constant (8.314 kJ/kg-mole-K).

Film characteristics and permeability

The factors that determine the gas diffusion characteristics of films are: film structure, film permeability to specific gases, thickness, area, concentration gradient across the film, temperature and differences in pressure across the film. Relative humidity may affect diffusion characteristics of some films (Kader *et al.* 1989; Prasad 1995).

Permeability is a measure of the ease with which an intact material (film) can be penetrated by a given gas or it is defined as the transmission of penetrant through a resisting material. Gases and vapor can penetrate through materials by macroscopic or microscopic pores and pinholes. In the absence of cracks, pinholes or other flaws the primary mechanism for gas and water vapor flow through the films is by a molecular mechanism known as activated diffusion. In activated diffusion, gas transport mechanism involves four distinct steps: (i) absorption of permeant gas into upstream face of the film, (ii) the penetrant dissolve in the film matrix at the high concentration side (solution in the film matrix), (iii) molecular diffusion through (to the down stream face) the film driven by virtue of concentration gradient and (iv) desorption from the downstream face (evaporate at the other surface of the film) (Karel et al. 1975; Sacharrow and Griffin 1980; Prasad 1995; Abdel-Bary 2003)

Koros (1989) described gas permeation through polymeric film as solution diffusion mechanism (Prasad 1995; Labthink 2008). The solubility coefficient is the ratio of equilibrium concentration of the dissolved penetrant to its partial pressures in the gas phase. The equilibrium concentration depends on polymer penetrant interaction (i.e. polarity and cohesive energy density) and the availability of free volume for hole filling. Differences in the solubility of specific gases in a particular film may determine which gas diffuses more readily across that film. In the diffusion process, the dissolved penetrant equilibrates with the film surface and then diffuses in the direction of lower chemical potential. It requires activation energy for generating an opening large enough to allow the penetrant molecule to perform a unit diffusional jump from one sorption site to another (Yasuda *et al.* 1968; Karel *et al.* 1975).

In particular, for the case of gas transport (gas transmission) in one direction from the atmosphere into the package, the diffusion law applies (Karel *et al.* 1975):

$$J = -DA \frac{dc}{dx}$$
(12)

where J is the flux of gas in appropriate unit (mole/sec or cm^3/sec), A is Area (cm²), D is the diffusion coefficient for the gas in the membrane (cm²/sec), c is concentration of the gas in the membrane (mole/cm³ or cm³/cm³), x is distance in membrane measured in direction of flow (thickness of film), (cm)

If D is a constant and steady state condition exist, then

$$J = DA \frac{c_1 - c_2}{\Delta x}$$
(13)

However, c_1 and c_2 are difficult to measure within the membrane. If Henry's law applies, we have:

$$\mathbf{c} = \mathbf{S}\mathbf{p} \tag{14}$$

where S is the solubility (moles/cm³/atm or cm³/cm³/atm) and P is the partial pressure of gas (atm). Then we can combine equation (13) and (14) to obtain:

$$J = DSA \frac{p_1 - p_2}{\Delta x}$$
(15)

The quantity DS is known as the permeability coefficient (P) or permeability, which is the product of diffusivity and solubility and is defined in terms of quantities as follows:

$$P = \frac{J \Delta x}{A(p_1 - p_2)}$$
(16)

$$P = \frac{(\text{Amount of gas})(\text{thickness})}{(\text{area})(\text{time})(\text{pressure difference})}$$

Hence the permeability coefficient (P) is the proportionality constant between the flow of the penetrant gas per unit film area per unit time and the driving force (partial pressure difference) per unit film thickness. The amount of gas penetrating through the film is expressed in terms of either, moles per unit time (flux) or weight or volume of the gas at STP. Commonly, it is expressed in terms of volume.

Gas permeation or gas transmission

Conceptually, gas permeation rate (GPR) or permeability is same as gas transmission rate (GTR). GPR are expressed on the basis of per unit film thickness while GTR are usually expressed for total thickness of the film. For composite films, it is more appropriate to use GTR values since permeation in composite films does not vary linearly with film thickness, usually. For some single material (polymer) films also, the relationship is not linear either. In such cases extrapolation may be erroneous (Nemphos *et al.* 1976).

The influence of temperature on permeability of polymeric films was quantified with the Q_{10}^{P} value, which is the permeability increase for a 10°C rise in temperature and is given by the equation as follows.

$$Q_{10}^{P} = \left(\frac{P_{2}}{P_{1}}\right)^{10/(T_{2}-T_{1})}$$
(17)

where Q_{10}^{P} is the temperature quotient for permeability (gas permeation rate increase for a 10°C rise in temperature), P_1 is permeability at temperature T_1 and P_2 is permeability at temperature T_2 .

Prasad (1995) has developed an empirical model for

prediction of gas transmission rates of some polymeric films. This model incorporate the most important parameter i.e. temperature which influence the gas permeability of films significantly. The empirical model is given by the following equations.

$$P_{O2} \text{ or } OTR = \alpha_0 + \alpha_1 T + \alpha_2 T^2$$
(18)

$$P_{CO2} \text{ or } CTR = \beta_0 + \beta_1 T + \beta_2 T^2$$
(19)

where P_{02} is O_2 permeability of the film, P_{CO2} is CO_2 permeability of the film, T is in absolute temperature, and $\alpha_0 \alpha_1$ α_2 and $\beta_0 \beta_1 \beta_2$ are the constants of the gas transmission model.

The temperature dependency of permeability is commonly described by an exponential equation (Arrheniustype equations) (Exama *et al.* 1993; Cameron *et al.* 1995; Yam and Lee 1995). The relationship of O_2 permeability and CO_2 permeability with temperature is depicted by this model. The generalized form of the Arrhenius equations is as follows.

$$P = P^{P} \exp\left[\frac{-E_{a}^{P}}{RT}\right]$$
(20)

where P is the permeability of O_2 and CO_2 temperature T, P^P is permeability pre-exponential factor for gas, $E_a^{\ p}$ is the activation energy of permeation for gas, R is gas constant and T is in absolute temperature

Generally, the above equations would accurately characterize a polymer's gas diffusivity/temperature behavior, except where there are strong interactions between the polymer and the gas molecules (e.g., water vapor and hydrophilic polymers). In addition, the above equation would only predict the effect of temperature above the gas transition temperature (T_g), since most films show a discontinuity of diffusion at the transition. At or below T_g , the polymer conformation is set and rotational movements responsible for diffusional properties are blocked (Cowie 1973).

Desirable characteristic of films for MAP

The selection of a polymeric film should be based on the expected respiration rate of the produce at the transit and storage temperature to be used and on the known optimum O_2 and CO_2 concentrations for the produce that will result in a favorable MA with shortest possible time (Kader *et al.* 1989). For most produce (expect those which tolerate high CO_2 levels), a suitable film must be much more permeable to CO_2 than to O_2 . In fact, most commercially available films are indeed more permeable to CO_2 than to CO_2 (Crosby 1981; Kader *et al.* 1989; Exama *et al.* 1993; Abdel-Bary 2003).

The desirable characteristics of polymeric films for MAP of fruits and vegetables are as follows:

- 1. The film should match the required permeabilities for different gases
- 2. Good gas transmission properties
- 3. High ratio of CO_2 / O_2 permeability
- 4. Low permeability to water vapor
- 5. Good transparency and glossy
- 6. Light weight
- 7. High tear strength and tensile strength
- 8. Low temperature heat sealable
- 9. Nontoxic and chemically inert
- 10. High resistance to chemical degradation
- 11. Soft, nonfogging and durable
- 12. Non reactant with produce
- 13. Good thermal and ozone resistance
- 14. Good weatherability
- 15. Commercial suitability
- 16. Ease of handling
- 17. Ease of printing for labeling purpose
- 18. Heat shrink films are extra advantageous

19. Maintain product quality 20. Low cost / inexpensive.

*

Equilibrium gas concentration

In MAP a definite quantity of commodity is sealed in the selected polymeric film packages. After a certain period of time, steady-state conditions is established inside an intact polymeric film package once the respiration rate of the produce match with the permeability of packaging films to O₂ and CO₂. O₂ inside the package is consumed by the produce as it respires and an approximately equal amount of CO_2 is produced. The reduction in O₂ concentration and increase in CO_2 concentration create a gradient causing O_2 to enter and CO_2 to exit the package. Initially, however, the gradient is small and the flux across the package is not sufficient to replace the O₂ that was consumed or to drive out all of the CO₂ that was generated. Thus, inside the package, the O₂ content decreases and CO2 content increases. As this MA is created inside the package, respiration rates start to fall in response to reduction of the O₂ content and elevation in the CO2 content. Thus, new equilibrium concentrations of the gases surrounding the fruit are established (Geeson et al. 1985; Smith et al. 1987; Geeson et al. 1989; Kader et al. 1989; Talasila et al. 1994). When the rate of consumption of O_2 by the commodity equals the rate of O_2 permeates into the package and rate of evolution of CO₂ equals the rate of CO₂ permeates out of the package, steady-state equilibrium is achieved (Kader and Zagory 1988; Cameron et al. 1989; Kader et al. 1989; Mammapperuma et al. 1989; Prasad 1995; Talasila and Cameron 1997; Jacxsens et al. 1999; Fonseca et al. 2000, 2002; Paul and Clarke 2002)

Many researchers have calculated the required O_2 and CO₂ permeability for various fruits and vegetables to create optimal gas concentrations in the MA packages. These calculations were based on the steady state respiration rate whereas in MA package the respiration rate changes as the atmosphere is modified (Cameron et al. 1989; Renault et al. 1994). Hence, the design should take into consideration not only steady-state conditions (product respiration rate and film permeability), but also the dynamic process, because if the product is exposed for a long time to unsuitable gas composition before reaching the adequate atmosphere, the package may have no benefit (Kader et al. 1989; Cameron et al. 1989; Merts et al. 1993). Storage temperature is never constant in the distribution chain of fresh produce. Due to the temperature dependence of the respiration rate and of the gas permeability of a packaging film, fluctuating temperatures result in changes of the internal O2 and CO2 concentrations (Kader et al. 1989; Exama et al. 1993; Jacxsens et al. 2000). Because of the difference in the rates of change of permeability and respiration rate with temperature, a film that produces a favorable atmosphere at the optimal storage temperature may cause excessive accumulation of CO2 and/or depletion of O₂ at higher temperatures, a situation that could lead to metabolic disorders (Kader et al. 1989; Beaudry et al. 1992; Cameron et al. 1993; Exama et al. 1993; Čameron et al. 1994; Joles et al. 1994)

A package poorly designed may actually reduce the product shelf-life and even induce anaerobiosis, with the possible growth of pathogens and concomitant effects on product safety. Hence a systematic theoretical design and modeling is needed to establish which commercially available plastic films would be most suitable for MAP of a particular produce (Exama et al. 1993). Such a design and analysis could provide closely the respiration rate of the commodity, matching/suitability of polymeric films, optimized packaging conditions. It can also point out potential limitations, and help minimize the number of experimental trials: as the trial and error approach is extremely time consuming procedure. Simulation of a MAP system is the most appropriate method to allow a correct MAP design and consequently obtain a successful commercial product (Cameron et al. 1989; Geeson 1989; Makino et al. 1997; Del Nobile et al. 2007).

External factors

Temperature is one of the most important external factors, which govern the rate of metabolic process in living plant tissues. Any change in temperature will affect the rate of respiration and the equilibrium conditions within the package unless the rate of diffusion of gases through the film is changed by temperature to exactly the same extent as respiration. A decrease in the internal concentration of O₂ and an increase in the internal concentration of CO₂ within the package with increase in temperature have been observed (Maxie et al. 1974; Prince et al. 1986; Kader et al. 1989; McLaughlin and O'Beirne 1999; Petracek et al. 2002). At constant relative humidity it has been shown that an increase in temperature causes an immediate increase in the transpiration rate of the commodity as well as the condensation of water (Hintlian and Hotchkiss 1986; Hotchkiss 1989; Beaundry et al. 1992).

On the whole, respiration is roughly doubled or tripled for every rise of 10°C (Kader et al. 1989) with a slightly lower value under reduced O_2 atmosphere (3% O_2) (Exama et al. 1993). The permeability of films has been reported to rise from two to five times with increase in temperature of every 10°C (Kader et al. 1989), but Exama et al. (1993) has reported that the permeability of commercial films rise from one to two time with every 10°C increase in temperature over the temperature range of 0-10°C. However, since the Q_{10}^{R} in 3% O_2 is lower, MA condition would tend to minimize any difference. If film/micropore combinations were used to provide optimal gas concentrations, the diffusivity of gas in micropores is not a strong function of temperature and would only change by a factor of 1.08 for an increase of 10°C (Cussler 1984). Thus, such combined systems would not be effective to maintain appropriate gas permeability during temperature fluctuations. Therefore a film resulting in a favorable atmosphere at a low temperature may result in a harmful atmosphere at higher temperatures. Generally speaking films having low permeability to water vapor are used for MAP. The high relative humidity formed within the package can cause condensation and development of molds and bacteria (Hotchkiss 1989)

Tano *et al.* (2007) studied the effects of temperature fluctuation on quality during MAP of mushroom, broccoli and matured green tomatoes. They found that temperature fluctuations had a major impact on the composition of the package atmospheres and on product quality. The quality of the products stored under the temperature fluctuating regime was severely affected as indicated by extensive browning, loss of firmness, weight loss increase, the level of ethanol in the plant tissue, and infection due to physiological damage and excessive condensation, compared to products stored at constant temperature.

MAP was shown to develop and maintain proper atmospheres around tulip bulbs at 20°C with resulting increased quality during storage (Prince *et al.* 1986). Fluctuations in temperature did not result in detrimental package atmosphere, probably due to change in film permeability compensating for changes in respiration rates (Prince *et al.* 1986; Exama *et al.* 1993).

MAP design

MAP is a dynamic system during which respiration and permeation occur simultaneously. Factors affecting both respiration and permeation must be considered when designing a package (Cameron *et al.* 1989; Mannapperuma *et al.* 1989; Yam and Lee 1995; Jacxsens *et al.* 2000). Commodity mass kept inside the package, storage temperature, O_2 , CO_2 and C_2H_4 partial pressures and stage of maturity are known to influence respiration in a package (Kader *et al.* 1989; Beaudry *et al.* 1992; Ben-Yehoshua *et al.* 1994; Das 2005). Type, thickness, unintended holes, and surface area of the packaging film that is exposed to atmosphere and across which permeation of O_2 and CO_2 takes place, volume of void space present inside the package, as well as temperature, relative humidity, and gradient of O_2 and CO_2 partial pressures across the film, are known determinants of permeation (Ashley 1985; Beaudry *et al.* 1992; Renault *et al.* 1994; Kader *et al.* 1997; Das 2005).

In a MAP packaging system, fresh fruits are sealed in perm selective polymeric film packages. Due to respiration of the packaged fruits, O₂ starts depleting and CO₂ starts accumulating within the package because of the consumption of O_2 and the production of CO_2 in the respiration process. Consequently, respiration begins to decrease while O₂ and CO₂ concentration gradients between package and ambient atmosphere begin to develop. The development of concentration gradients induced ingress of O₂ and egress of CO_2 through the packaging material i.e. polymeric films. Simultaneously respiration rate decreases with decrease in O_2 level and increase in CO_2 level, provided the variations in O₂ and CO₂ levels are within safe limits. The decrease in respiration rate decreases the rate of increase of concentration gradient. Transmission of O₂ and CO₂ through the film further reduces concentration gradient. As the rate of increase in concentration gradient retards, respiration tend to retrieve which again increases the gradients. The increase in concentration gradient again decreases respiration and increases gas transmission. Thus the cyclic process continues until a steady state is established (Cameron et al. 1989; Merts et al. 1993; Chau and Talasial 1994; Renault et al. 1994; Prasad 1995; Mahajan et al. 2007).

In a properly designed MAP, after a period of transient state (the state at which the O₂ and CO₂ concentration changes continuously within the package with time) an equilibrium state is established. At equilibrium, the amount of O_2 entering (ingress) into the package and that of CO₂ permeating out (egress) of the package become equal to the amount of O_2 consumed and that of CO_2 evolved by the packaged fruit respectively (Jacxsens et al. 2000; Del Nobile et al. 2007; Techavises and Hikida 2008). The package atmosphere is then considered to be in dynamic equilibrium with external atmosphere. Hence, Package equilibrium or steady state is defined as the point at which the commodity O₂ consumption and CO₂ production rates (respiration rates) are equal to the permeation rates of the respective gases (O₂ and CO₂) through a package at a given temperature (Das 2005; Del-Valle et al. 2009). Once established, the equilibrium gas concentrations remained nearly constant throughout the stipulated period of storage unless there is considerable variation in ambient conditions. The period from sealing of fruits in the packaged to the establishment of steady state or equilibrium state is called transient period or equilibrium time. The O₂ and CO₂ concentration levels of package atmosphere at which dynamic equilibrium establish are called as O₂ equilibrium concentration and CO₂ equilibrium concentration respectively. An ideal package system will equilibrate and maintain at the levels of O₂ and CO₂ are known to be optimal for storage, transport and handling through out the market chain for a specific commodity (Jacxsens et al. 1999; Fonseca et al. 2000; Paul and Clarke 2002; Mahajan et al. 2007).

Design methodology

MAP design requires the determination of intrinsic properties of the produce, i.e. respiration rate, optimum O_2 and CO_2 gas concentrations, and film permeability characteristics (Cameron *et al.* 1989; Talasila and Cameron 1993). The ultimate aim of this design process is to select suitable films for a given product, its area and thickness, filling weight, equilibrium time, and the equilibrium gas composition at isothermal and non-isothermal conditions. When several films can be suitable for MAP, their cost will be a major selection factor. The maximum possible protection a film can provide regardless of cost can be a target, but some type of balance or of compromise may also need to be evaluated if the best solution appears excessively onerous (Ahvenainen 2003; Mahajan *et al.* 2007).

Mathematical modeling of gaseous exchange in MAP system

When the fresh commodity is sealed in a selected polymeric film packages, it constitute a dynamic system where, respiration of the product and the gas permeation through the film takes place simultaneously. In the respiration process O_2 is consumed and the produce evolves CO_2 . A small amount of C_2H_4 also emanates from the climacteric commodity during climacteric period. Usually the relative humidity in the internal package atmosphere is higher than the external atmosphere. Hence some amount of water vapor may permeate out of the package, depending upon the water vapor transmission rate (WVTR) of the packaging polymeric film. However, the mathematical modeling of gaseous exchange for respiratory gases only (i.e. O_2 and CO_2) has been considered prime important for modeling the MAP system.

The simplest concept is that the plastic film serves as the regulator of O_2 flow into the package and the flow of CO_2 out of the package. For a considerably small length of transient period and at a given temperature, the rates of O_2 consumption (R_{O2}) and the rate of CO_2 evolution (R_{CO2}) of the packaged commodity depend greatly on O_2 concentration (Y_{O2}) and CO_2 concentration (Z_{CO2}). Considering that there is no gas stratification inside the packages and that the total pressure is constant, the differential mass balance equations that describe the O_2 concentration changes in a package containing respiring product are:

Rate of O_2 entry into package space – Rate of O_2 consumed by product

= Rate of O_2 accumulation inside package space

$$A_{p}P_{02}(Y_{02}^{a}-Y_{02}) - W_{p}R_{02} = V_{fp}\left[\frac{dY_{02}}{dt}\right]$$
(21)

or,

$$\frac{dY_{02}}{dt} = -\left(\frac{W_{p}}{V_{fp}}\right)R_{02} + \left(\frac{A_{p}P_{02}}{V_{fp}}\right)(Y_{02}^{a}-Y_{02})$$
(22)

Similarly, the CO_2 concentration changes in a package can be written as:

Rate of CO_2 generated by the fruits – Rate of CO_2 leaving out of the package space

= \bar{R} ate of accumulation \bar{CO}_2 inside package space

i.e.,

$$W_{p}R_{CO2} - A_{p}P_{CO2} \left(Z_{CO2} - Z_{CO2}^{a} \right) = V_{fp} \left(\frac{dZ_{CO2}}{dt} \right)$$
(23)

or,

$$\frac{\mathrm{d}Z_{\mathrm{CO2}}}{\mathrm{d}t} = \left(\frac{\mathrm{W}_{\mathrm{p}}}{\mathrm{V}_{\mathrm{fp}}}\right) \mathrm{R}_{\mathrm{CO2}} \cdot \left(\frac{\mathrm{A}_{\mathrm{p}}\mathrm{P}_{\mathrm{CO2}}}{\mathrm{V}_{\mathrm{fp}}}\right) (\mathrm{Z}_{\mathrm{CO2}} \cdot \mathrm{Z}_{\mathrm{CO2}}^{\mathrm{a}})$$
(24)

where A_p is the Area of the package through which the O_2 and CO_2 permeates (m²), Y_{O2}^{a} and Z_{CO2}^{a} are the O_2 and CO_2 concentration in the atmospheric air (cm³ per cm³ of air) respectively, Y_{O2} and Z_{CO2} are the O_2 and CO_2 concentration in side the package (cm³ per cm³ of air) respectively, P_{O2} and P_{CO2} are the O_2 and CO_2 permeability of packaging material (cm³.m⁻².h⁻¹. [Concentration difference of O_2 in volume fraction]⁻¹) respectively, W_p is the weight of the fruit kept inside the package (kg), R_{O2} and R_{CO2} are the respiration rate for O_2 consumption and CO_2 evolution by the fruits, (cm³.kg⁻¹.h⁻¹) respectively, V_{fp} is the free volume in the package (cm³), t is the storage time (h) and dY_{O2}/dt and dZ_{CO2}/dt are the rate of change of O_2 concentration ' Y_{O2} ' and CO_2 concentration ' Z_{CO2} ' within the package at time 't' of storage (cm³ per cm³ of air. h⁻¹) respectively.

Equations (22) and (24) coupled to the model that describes the dependence of respiration rate on gas composition, temperature (and eventually time) and models that

describes the dependence of packaging material on temperature, constitute the basic of MAP design (Exama *et al.* 1993; Chau and Talasa 1994; Fishman and Ben-Yehoshua 1994; Prasad 1995; Jacxsens *et al.* 2000; Das 2005; Del Nobile *et al.* 2007; Mahajan *et al.* 2007; Torrieri *et al.* 2007).

Polymeric films in use for MAP

Package design and construction plays a significant role in determining the shelf-life of commodity. The right selection of the packaging materials and technologies maintains product quality and freshness during distribution and storage. Recent advances in the design and fabrication of polymeric films made it possible to create films with specific and differential permeabilities to O_2 and CO_2 (Marsh and Bugusu 2007; Siracusa *et al.* 2008). The permeability of some of the polymeric films available for MAP to O_2 , CO_2 at ambient temperature (23°C) and permeability to water vapour at 38°C and R.H. at one side of approximately 0% and the other side (high-pressure side) of 95% are presented in **Table 13** (Abdel-Bary 2003; Massey 2003).

These films display a wide range of characteristics in terms of gas permeability, water vapor transmission rate, antifogging properties, strength and stretch-shrink properties (Smith et al. 1987). Table 13 presents gas permeability and water vapor transmission properties as well as the ratio of CO₂ to O₂ permeability for a number of plastic polymers currently available for use in the fabrication of flexible plastic films. The ranges of permeabilities presented for some films are quite broad, reflecting high variability in the measurement of film permeabilities, differing conditions during permeability measurements and variations in fabrication among manufactures and even among batches from the same manufacturer of similar film types (Oswin 1975; Crosby 1981; Kader et al. 1989). In addition gas permeability is sensitive to changes in temperature and relative humidity (Karel et al. 1975; Prince et al. 1986; Exama et al. 1993)

Relatively few kinds of polymers are routinely used in the fabrication of flexible films for packaging of fresh commodity, with the most important being plasticized PVC, polyethylene, polypropylene, polyvinyledene chloride, polyester, ethylene vinyl acetate, polybutylene and polystyrene (Benning 1983; Kader *et al.* 1989; Exama *et al.* 1993; Abdel-Bary 2003; Siracusa *et al.* 2008). The polyolefins are the predominant plastics used for packaging (Marsh and Bugusu 2007). This group includes polyethylene, polypropylene and polybutylene as well their copolymers and ionomers. The polyolefins film possesses good water vapor barrier properties, relatively high gas permeabilities and shows favorable response to heat sealing. The detailed summary of the properties, environmental issue and cost of polymeric films for MAP are presented in **Table 14**.

Polyethylene films are the most commonly used polymers in the packaging of fresh agricultural commodity. The polyethylenes are of several types i.e. LDPE, MDPE and HDPE, classified according to their specific gravity. Polyethylene although do not possesses great tensile strength, however it displays excellent teat strength, high resistance to chemical degradation and relatively high gas permeabilites (Table 14). The particular importance for MAP is that polyethylene; particularly LDPE tends to have a high ratio of CO₂ to O₂ permeabilities. This is of importance in allowing O₂ concentration to decrease with out an associated excessive built up of CO_2 inside the package. A numbers of formulation of PVC are also available as flexible films. The PVC films are soft, clear, none fogging and durable. PVC films are highly gas permeable and moderate level of water vapor permeability. Also PVC films have very high ratio of CO_2 to O_2 permeability, this fact is making them very well suitable for MAP of fresh commodities (Crosby 1981; Ben-Yehoshua 1985; Kader et al. 1989; Abdel-Bary 2003; Massey 2003).

Polystyrene is another polymer with high gas permeabilities and relatively high ratio of CO_2 to O_2 . Polystyrene is chemically inert and possesses high degree of clarity. It is

| Name of the film | Permeability (| (cm ³ . µm/m ² . h. atm) | Permeability (g. µm/m ² . h) | CO ₂ /O ₂ ratio | |
|--|-----------------------|--|---|---------------------------------------|--|
| | O ₂ | CO ₂ | Water vapor | - | |
| Polyvinyl Fluoride (PVF) | 50 | 179.16 | 54.16 | 3.58 | |
| Polyvinylidene Fluoride (PVDF) | 81.66 | 408.33 | 8.16 | 5.00 | |
| Polyamide (Nylon 6) | 105.83 | 423.33 | 640 | 4.00 | |
| Polycarbonate | 2829.17 | 18166.67 | 62.5 | 6.42 | |
| Polyethylene Terephthalate (PET) | 50-100 | 245.83-408.64 | 16.25-21.25 | 4.91 | |
| Polyamide | 416.66 | 708.33 | 20.83-56.25 | 1.70 | |
| Low Density Polyethylene (LDPE) | 11416.68 | 39958.33 | 18.75 | 3.49 | |
| Linear Low Density Polyethylene (LLDPE) | 2916.66-8333.34 | | 12.5 | | |
| Medium Density Polyethylene (MDPE) | 4083.33-8791.67 | 1625 -41000 | 11.66 | 4.66 | |
| Linear Medium Density Polyethylene (LMDPE) | 3666.66 | | 9.16 | | |
| High Density Poly Ethylene (HDPE) | 1640.41-3280.83 | 9841.67-11482.92 | 6.66 | 5.99 | |
| Ethylene Vinyl Acetate Coplymer (EVA) | 7500 | 45833.33 | 187.5 | 6.11 | |
| Ethylene Vinyl Alcohol Coplymer (EVOH) | 0.1 | 3.33 | 33.33-100 | 33.3 | |
| Polypropylene (Cast film) | 2458.33-2675 | 8166.67-13041.67 | | 3.32 | |
| Polypropylene (BOPP) | 2675 | 8833.33 | 6.25-11.25 | 3.30 | |
| Polybutylene | 6316.66 | 23375 | 19.58-30.83 | 3.70 | |
| Polyvinyl Alcohol (PVOH) | 3.75 | 1.66 | | 2.00 | |
| Polystyrene (PS) | 4875-6316.67 | 16375-23375 | 32.5 - 162.5 | 3.35 | |
| Mylar (Polyester) | 54.16-137.5 | 190.41-412.5 | | 3.51 | |
| Oriented Polystyrene (OPS) | 4100 | 11500-21958.33 | 145.83 | 2.80 | |
| Polyvinyl Chloride (PVC) -Plasticized | 422.5-32666.67 | 1633.33-49000 | 147.91-180.83 | 3.86 | |
| Polyvinylidene Chloride (PVDC) | 16.25 | 62 | 3.33 | 3.81 | |
| Cellulose acetate | 1919.58 | 14107.50 | 1230.84 | 7.34 | |
| Rubber Hydrochloride | 623.33 | 4724.16 | 8.25 | 7.57 | |
| Ethylcellulose | 32808.33 | 82020.83 | 328 | 2.5 | |
| Methylcellulose | 1312.08 | 6561.66 | 3280.83 | 5.00 | |
| Cellulose triacetate | 2460.41 | 14435.66 | 78.31 | 5.86 | |
| Vinylchlorideacetate | 246.25 | 902.5 | 65.61 | 3.66 | |
| Natural rubber | 63500 | 370416.66 | | 5.83 | |
| Silicone rubber | 1058333 | 6350000 | 72 | 6.00 | |

Sources: Karel 1975; Kader et al. 1989; Abdel-Bary 2003; Massey 2003

extensively used to wrap lettuce and tomatoes and is available as heat-shrink film (Sacharow and Griffin 1980). Polyvinyledene chloride films are of high gas barrier films and mostly used for MAP in combination with the low barrier films by tailoring of film laminates (Prasad 1995). Several polymeric films, such as saranex, nylon, mylar, polyester and several variants of polyvinyl (**Table 13**) have good clarity, strength and adequate gas permeability ratio, but their gas transmission rates are too low for which; these films are generally not suitable for MAP of fresh produce (Kader *et al.* 1989).

Orientation of polymeric films resulting in shrinkage when heat is applied (Benning 1983; Kader *et al.* 1989). Biaxial orientation results in shrinkage in both directions. Gas transmission rates and water vapor permeability of the crystalline polymer are affected and in fact reduced by orientation process. Most of the polyolefins films can be oriented to allow heat shrinkage (Salame 1986). Heat shrink films could be of use in MAP because the headspace around the commodity is greatly reduced after the film has been shrunk to fit. This would then result in a more rapid modification of the internal atmosphere of the package (Kader *et al.* 1989; Mannapperuma *et al.* 1989).

Recent advances in the polymer science and technology have made it possible to manufacture films with desired and well designed gas transmission rates especially for O₂. Plastic materials can be manufactured either as a single film or as a combination of more than one plastic. There are two ways of combining plastics: lamination and co-extrusion. Lamination involves bonding together two or more plastics or bonding plastics to another material such as paper or aluminum. Bonding is commonly achieved by use of water-, solvent-, or solid-based adhesive. After the adhesive are applied to one film, two films are passed between rollers to pressure bond them together. Lamination using laser rather than adhesives has also been used for thermoplastics (Kirwan and Strawbridge 2003). Laminations enables reverse printing, in which the printing is buried between layers and thus not subjected to abrasion and can add or enhance heat sealability. In co-extrusion, two or more layer of molten plastics are combined during the film manufacture. This process is more rapid but requires materials that have thermal characteristics that allow co-extrusion. Because coextrusion and lamination combines multiple materials, recycling is complicated. However combining materials results in the additive advantage of properties from each individual material and often reduces the total amount of packaging material required. Therefore, co-extrusion and lamination can be sources of packaging reduction (Marsh and Bugusu 2007).

Exama et al. (1993) has reported that all films (including the most common films used in the fruits and vegetables packaging such as LDPE and PVC) except those with barrier properties such as Saran, Mylar and Nylon etc. could satisfy the O₂ permeability requirement and the required CO_2/O_2 permeability ratio for low respiration rate produce such as apple, carrot, celery, cabbage, green pepper etc. with minor adjustments to film thickness and/or area of film packaging to weight ratio. For produce with moderate respiration rates (e.g. cauliflower), rubber type films (natural rubber, polybutadiene) would be adequate. Only silicone rubber films would provide the O_2 fluxes for high (e.g. strawberries, litchi) and very high (e.g. litchi, mushroom) respiration samples. The LDPE and PVC films also have the appropriate required CO₂/O₂ permeability ratio for high respiring Brussels sprouts. However, either the film area would have to be increased or the product weight decreased by a factor of about 10 for LDPE or a factor of 5 for PVC to produce the optimum MA conditions. Such configuration would be commercially impractical.

If the CO_2/O_2 permeability ratio for the films is much higher than those required by the product; even if the appropriate O_2 permeability were matched, the internal CO_2 concentrations would always be below optimum in the packages. Also for plastic films with high ratio of CO_2/O_2 permeability, the efflux of CO_2 is greater than the influx of

Table 14 Properties, environmental issue and cost of polymeric films for MAP.

| Type of | Product characteristics/food compatibility | | Consumer and | marketing issue | Environmental issues | | Cost |
|--|--|--|--|-----------------------------------|---|---|--|
| films | Advantages | Disadvantages | Advantages | Disadvantages | Advantages | Disadvantages | |
| LDPE | i. Flexible and strong ii. Good moisture barrier iii. Resistance to chemicals | i. Poor gas barrier | i. Light weight | i. Slight haze or translucency | i. Recyclable | i. Easily recycled in semi-rigid form but | i. Low cost |
| | iv. Heat sealable and easy to seal v. Relatively transparent and predominantly used in film application | | | | | identification and separation more difficult for films | |
| | vi. High ratio of CO ₂ to O ₂ permeability | | | | | | |
| HDPE | i. Flexible and strongii. Resistance to chemicals and moistureiii. Permeable to gasesiv. Easy to process and easy to form | i. Poor gas barrier | i. Light weight | i. Slight haze or translucency | i. Recyclable | i. Easily recycled in semi-rigid form but identification and separation more difficult for films | i. Low cost |
| Polypropyle ne (BOPP) | i. Stronger/harder, denser and more transparent than polyethylene ii. Moderate gas barrier iii. Good resistance to chemicals iv Good water vapor barrier v. Favorable response to heat sealing | i. Moderate to poor gas barrier | i. Light weight ii. High clarity, strength and durability as compared to LDPE | | i. Recyclable | i. Easily recycled in semi-rigid form but identification and separation more difficult for films | i. Low cost |
| Polyesters (PET/PEN) | i. Strong ii. With stand hot filling ii. Good resistance to chemical degradation iii. Good barrier to gases and moisture iv. Good resistance to heat, minerals oil, solvents and acids. v. Glass like transparency, adequate gas barrier for retention of carbonation, light weight and shatter resistance. | | i. High clarity ii. Shatter resistance | | Recyclable | i. Easily recycled in semi-rigid form but identification and separation more difficult for films | i. Inexpensive but higher cost among plastics |
| Plasticized Polyvinyl chloride (Plasticized PVC) | i. Strong (medium) ii. Transparent iii. Excellent resistance to chemicals oils/fats. iv. Largely used as packaging films | Poor gas barrier | i. High clarity | | Recyclable | i. Contains chlorine ii. Requires separating from other waste | i. Inexpensive |
| Polyvinylide ne chloride (PVdC) | i.Gigh barrier to gases, water vapor and fatty and oily productsiii. Heat sealableiv. Used in hot filling, retorting, low temperature storage and MAP | | i. Maintains product quality | | Recyclable | i. Contains chlorine ii. Requires separating from other waste | i. Inexpensive but higher cost among plastics |
| Polystyrene | i. Available in rigid, film and foam formii. Clear, hard and brittle | i. Poor barrier properties | i. Good clarity | | Recyclable | i. Requires separating from other waste | i. Inexpensive |
| Polyamide (nylon-6) | i. Strong ii. Good barrier properties iii. Good chemical resistance, toughness and low gas permeability iii. Mechanical and thermal properties similar to PET | | | | Recyclable | i. Requires separating from other waste | i. Inexpensive when used as thin films |
| Ethylene vinyl alcohol (EVA) | i. High barrier to gases and oil/fats specially to oxygen | i. Low moisture barrier/moisture sensitive | i. Maintains product quality for oxygen sensitive products | | Recyclable | i. Requires separating from other waste | Relatively expensive |
| Laminates/ Co- extrusions | i. Properties can be tailored for product needs | | Flexible in design and characteristics | | Often allows for source reduction | Layer separation is required | Relatively expensive but cost effective for purpose |

Sources: Benning 1983; Kader et al. 1989; Exama et al. 1993; Abdel-Bary 2003; Marsh and Bugusu 2007

 O_2 . If the film is flexible and hermetically sealed, this imbalance would cause a reduction of void volume. In bags the films would collapse around the produce (Exama *et al.* 1993).

The ultimate solution to achieve the desired flux and ratio of CO_2/O_2 permeability is to develop new films of desired permeabilities and required ratio of CO_2/O_2 permea-

bility. Model developed by Salame (1986) can predict the polymer transport properties and could be used to produce custom films (Exama *et al.* 1993). Unfortunately a film would need to be optimized for each commodity but strategies for combining films could minimize the number of required polymers. Developing the new polymer is time consuming and the potential results are uncertain, so the choice of films should be made from those commercially available (Exama *et al.* 1993; Prasad 1995).

When fluxes of both gases cannot be exactly matched (the usual case), the O_2 flux should take the priority because it is the limiting factor in MAP (Burton et al. 1987; Knee 1991; Exama et al. 1993; Cameron et al. 1995; Prasad 1995). Reduced O₂ level will decrease respiration rates, C₂H₄ biosynthesis and sensitivity to C₂H₄ (Burg and Burg 1965; Burton 1974; Isenberg 1979; Konze et al. 1980; Yang 1985; Kader et al. 1989; Exama et al. 1993). However, excessive depletion of O₂ inside the package can lead to anaerobiosis accompanied by undesirable metabolic reactions such as tissue breakdown, odour and off-flavors production (Hulme 1971; Bohling and Hansen 1984; Kader et al. 1989; Kays 1991; Kader 1997; Kays 1997). At extremely low O_2 levels, toxin production by anaerobic pathogen organisms can occur (Yang 1975; Hotchkiss 1989; Faber 1991). Thus precise control of internal O₂ concentration is very essential.

Even when the O_2 permeability requirement is satisfied the CO_2 would accumulate inside the package to different level depending upon the CO₂/O₂ permeability ratio of the films. A film with high ratio of CO_2/O_2 permeability (e.g. polybutadiene) would allow CO2 to accumulate to very low levels whereas a film with low ratio of CO_2/O_2 permeability (e.g. Pliofilm) would accumulate higher levels of CO₂. Elevated CO₂ levels could repress the respiration rates (Rhodes 1980; Kader 1986), antagonize the action of C₂H₄ (Yang 1985) and growth of pathogens (El-Goorani and Sommer 1981; Stewart 2003). However, the benefits of elevated CO_2 would be much less important at lower than optimum levels. Further more the effects of optimal CO₂ are generally reduced at lower O2 levels (Yang and Chinnan 1988; Makhlouf *et al.* 1989). On the other hand, if the CO_2 accumulates well above optimum levels, produce injury could occur (Kays 1991) especially with sensitive commodities such as lettuce (Stewart and Uota 1971; Siripanich and Kader 1985). However, almost all films examined have a high CO_2 to O_2 permeability ratio; hence such situation is very unlikely.

Current application of MAP for some fruits and vegetables

Many researchers have worked on MAP with varieties of fresh produce. Hardenburg (1957) used polyethylene box liners for reducing decay as well as weight loss and freshness in apple. In the early 1960's Duvekot, Moiseyeva, Sommer and a number of other scientists investigated extensively, the effect of package atmospheres ranging from 3-9% O₂ and 2-12% CO₂, on the shelf-life of the commodity (Henig 1975). The early work with apples demonstrated the feasibility of MAP even with the limited packaging materials available at that time. Marcellin (1974) put silicone rubber windows in polyethylene bag to increase permeability and tested such packages for the storage of artichokes, carrots, turnips and bell peppers but found that moisture condensation led to decay problems, which negated any salutary effects of the MAP.

A special package developed by G. G. Rumberger for various fresh fruits and vegetables was granted US patent as early as 1971 (Prasad 1995). Similarly, special packages developed by A. S. Cumin, H. Daun, S. G. Gilbert and Y. Henig for packaging lettuce and banana, were granted US patent in 1974 (Pintauro 1978). However, the skepticism about MAP technology pertaining to the risk of commodity spoilage caused by varietals difference and temperature abuses during distribution impeded the adoption of MAP technology particularly in America, in its initial phase of development (Lioutus 1988). However, the continued research on the subject provided much needed support for eliminating the skepticism about MAP technology in developed countries.

The apples were found to be greatly benefited from CA storage and hence researchers devoted time for the study on MAP for apples and its perspectives. Most workers used polyethylene specially low density polyethylene, and PET as the packaging materials and studied the effects of package surface area, temperature, film permeability to O_2 and CO_2 , film perforations/pin holes and R.H. on package gas concentrations including the state of equilibrium conditions achieved and their effects on quality (Anzueto and Rizvi 1985; Smith *et al.* 1987). Smith *et al.* (1988) studied the effect of harvest date /maturity level of apples on MAP and their shelf-life. They found that later-harvested apples developed higher CO_2 and lower O_2 concentrations within the package, apparently due to their higher respiration rate (Smith *et al.* 1988).

Rocha et al. (2004) stored apple in MAPs using polypropylene of 100 µm during 6.5 months at 4°C and 85% relative humidity and found that apples packed in MA lost less weight, presented better colour, and preserved better firmness than fruits stored in air. Prasad (1995) developed MAPs of apple by tailoring of film laminates. The MA packed apples were reported to have retained orchard freshness for longer period of time. The shelf-life of MA packed apples was reported be 1.45 to 2.25 times higher than that of unpacked apples. The incidence of bitter pit that developed during controlled and MA storage (polyethylene bags containing different numbers of 9-mm holes) of apple for 5 weeks at 2°C was progressively reduced from 50% to less than 5% as the number of holes per bag decreased (Hewett 1984). Fruit in polybags had less weight loss, higher firmness and improved quality compared with air-stored fruit.

Micro-perforated low density polyethylene (LDPE, 30 μ m) liners, closed by envelope folding, provided effective, favorable atmospheres for Bramley apples during a simulated 4-week marketing period under ambient conditions and the shelf-life benefit was observed (Geeson 1994).

Qiang et al. (2004) packed apples in optimal MA package, had good quality after storage at 0 and 10°C (transferred to 0°C after 100 days) for 7 months with reduction of scald rate. Scald rate, ethanol and acetaldehyde content increased with packaging quantity and temperature became greater. Rocculi et al. (2006) used and tested a new general respiratory model based on the Michaelis-Menten type enzyme kinetics to describe changes in aerobic respiration of minimally processed apple packed in multilayer pouches after dipped in an antioxidant solution (1% ascorbic acid, 1% citric acid), stored at 4°C. The proposed model successfully fitted the experimental data, adequately describing the aerobic respiration of apple slices. The dipping reduced the overall respiration rate (for about 10 h of storage). The active MA decreased the rate of O₂ consumption compared with passive MA, in particular at the beginning of storage.

Valero et al. (2006) developed active packaging by adding eugenol or thymol to table grapes stored for 56 days under MA condition. The sensory, nutritional and functional properties losses were significantly reduced in packages with added eugenol or thymol. In addition, lower microbial spoilage counts were achieved with the active packaging. Artés-Hernández et al. (2006) studied the quality of superior seedless table grapes stored for 7 days at 0°C followed by 4 days at 8°C + 2 days at 20°C under MAP using microperforated and oriented polypropylene films and reported that SO₂-free MAP kept the overall quality of clusters close to that at harvest. Artés-Hernández et al. (2006) stored white seedless table grapes under several gas treatments for up to 60 days at 0°C followed by 7 days in air at 15°C using microperforated polypropylene (PP) to generate a MAP system. It is concluded that the gas treatment could be an alternative to replace the use of SO_2 for keeping quality of 'autumn seedless' grapes and MAP provided the best results at a lower cost. Wu et al. (2007) investigate the effects of high atmospheric O₂ on berry drop in 'Kyoho' grapes, changes in fruit detachment force (FDF), berry abscission and enzyme activities in the abscission zone (AZ) during 60 days of storage in air (control), $40\% O_2 + 30\% CO_2$ or 80% O_2 at 0°C and 95% relative humidity. High O_2 suppressed the activities of cellulase, PG and PE, maintained higher FDF, and reduced berry abscission during storage.

The benefit of MAP of citrus fruits is not from modification of O_2 and CO_2 concentrations but from maintenance of high relative humidity in side the package and hence reduction of shrinkage (Barmore *et al.* 1983; Ben-Yehoshua 1985; Smith *et al.* 1987). Packaging citrus fruits in polyethylene films also reduced low O_2 damage to fruit by excluding decaying fruit, which respire rapidly and consume more O_2 (Barmore *et al.* 1983).

Jacomino et al. (2001) observed that multilayer co-extruded polyolephinic film with selective permeability (PSP) can prolong storage of guava up to 3 weeks, while low density polyethylene film with incorporated minerals (LDPEm) is suitable for guava storage to 14 days at 10°C with 85-90% relative humidity. A similar study was performed by Gaspar et al. (1997) with Kumagai guava wrapped either in polyvinyl chloride plastic film (PVC) or low density polyethylene bags (LDPE), stored for two and three weeks at 8°C. LDPE hindered the development of peel colour and the loss of firmness, showing itself superior to PVC. LDPE was also used in the research of Mohamed et al. (1994) to study the effects of different chemical treatments on guava skin. Guavas were stored at 10°C and the best results in reducing weight loss and keeping the texture was observed in shrink-wrapped LDPE, however, color of the skin was best preserved by LDPE packaging along with sucrose ester and palm oil emulsion dips.

Sanjuka et al. (2003) compared MA storage of guava with four levels of silicon membrane size, with storage under regular atmosphere at high humidity (HRA) in which fruits were packaged in plastic bag with small holes and to regular atmosphere (RA) at 11° C and found that guavas stored with the membrane had the best overall quality after storage and after ripening. MAP of fresh guava in polyethylene terephthalate (PET) containers at 5°C for 24 days had a strong influence on color preservation and weight loss of the guavas (Pereira et al. 2004). Paul et al. (2002) observed that controlled atmosphere storage of guava reduced the rate of respiration and C₂H₄ evolution to variable extent and the fruit could be stored well in unripe condition for one month. CA storage reduced the weight loss, maintained firmness and colour and alleviated chilling injury. Combrink et al. (2004) reported that non-perforated polyethylene bags maintained guava fruit quality better than perforated bags. Polyethylene bags impregnated with natural mineral compound absorbed free moisture in the packs and created a MA, which increased shelf-life. Despite a MA in non-perforated regular bags, impregnated bags had a greater beneficial effect on keeping quality than regular bags (Combrink et al. 2004).

Jacomino *et al.* (2001) packed guavas fruits in plastic bags employing passive MAP and stored at 10°C and 85-90% RH during 7, 14, 21 and 28 days and found that the LDPE film with mineral incorporation (LDPEm) provided an atmosphere of 3% O₂ and 4.5% CO₂ inside the packages, which kept the fruit with good sensorial characteristics for 14 days. The multilayer coextruded polyolefin film with selective permeability (PSP) provided an atmosphere that was sufficient to maintain the fruit with good sensorial characteristics for 28 days. Chitarra *et al.* (2002) used both tight and perforated (0.1% perforated area) LDPE bags (CFfilm impregnated with C₂H₄ absorber) in guava during 30 days of cold storage (10°C and 90% RH) and found that the major beneficial effect was the reduction of mass loss with out affecting the skin color or chlorophyll content.

The respiration rate of tomatoes was found to be varying greatly depending on variety, maturity, and the onset of climacteric respiration. Hence results of the MAP of tomatoes are not consistent. The mature green tomatoes packed in polyvinyledene film and stored at 15°C, failed to ripen either in package or after removal from the package while in cellulose-acetate film, they ripened fully with better appearance (Ayers and Pierce 1960; Saguy and Mannheirn 1975). Geeson *et al.* (1985) developed MA packages for tomatoes with various types of plastic films. PVC film packages were found to have maintained 3-9% concentra-

tions of both O₂ and CO₂ at 10°C which resulted in slow ripening and better quality retention. Nakhasi et al. (1991) found that breaker tomatoes could be packed in LDPE film and stored safely at 15°C up to 23 days. Most workers have used polyethylene (Ayers and Pierce 1960; Saguy and Mannheim 1975) or PVC (Saguy and Mannheim 1975; Geeson 1985) films to extend tomato shelf-life up to 21 days, although other films have also been tested (Ayers and Pierce 1960; Geeson 1985). Persistent problem with development of adverse flavors or decay have been reported in tomato packages (Geeson 1985). Nevertheless, several type of MAP for tomatoes has been patented. Geeson et al. (1985) found that off-flavors and decay developed in films with low gas permeabilities but that such problems did not occur when permeabilities were high enough to allow adequate gas exchange. The value of MAP for tomatoes is not likely to be fully realized until researchers conduct experiments where they assay package gas concentration and relate them to quality parameters at given temperature.

Shantha (1993) observed that the shelf-life of pomegranate increased to 70 days at 8°C by individual shrink wrapping. Deily and Rizvi (1981) used a model to optimize packaging parameter for peaches in order to design a retailsize package. Their approach was to calculate the film permeabilities necessary in order to achieve a predetermined package atmosphere based on peach respiration value. They determined respiration rate and resulting package atmosphere experimentally to verify the assumptions behind their calculation. They then measured some of the quality attributes of packaged and control peaches after various storage duration. Their analytical, integrated approach to MAP could serve as a good example for other researchers for developing packages for other types of fresh produce. Rij and Ross (1987) worked on the MA packaging of peaches in various film at different temperature and found that peaches respond well to MAP.

Banana is greatly benefited from MAP due to reduced C_2H_4 sensitivity associated with high CO₂ and low O₂ (Young 1962; Daun *et al.* 1973; Banks 1984, 1985; Bhande 2007). The benefits to banana of MA are apparently Aradyha *et al.* (1993) inferred that the shelf-life of MA packed banana could be extended up to 6 weeks at 13°C as against 3 weeks of control samples. CO₂ and O₂ levels in MA packages varied from 3.8 to 6.35% and 15.7 to 11.8%, respectively.

The fruit litchi easily loses its commercial value after harvest due to pericarp browning, desiccation, quality deterioration and decay (Ray 1998; Tian et al. 2005). Browning of litchi pericarp was thought to be due to degradation of anthocyanidin by polyphenol oxidase (PPO) and peroxidase (POD) (Nip 1988; Chen and Wang 1989) and was primarily the result of PPO activity degrading the anthocyanins and producing brown-colored by-products (Huang et al. 1992). In general, sulfur dioxide treatments have been widely used to control saprophytic surface fungi and prevent peel browning of litchi fruit (Huang et al. 1990; Underhill et al. 1992). SO₂ fumigation followed by a dip in hydrochloric acid can preserve red skin color (Paull et al. 1998). Careful application can avoid an increase in aril sulfite residues and avoid off-flavors (Paull et al. 1998). Sulfites are not approved on fresh produce in the US, except for grapes. Most other countries have sulfite residue limits for edible portions (Tongdee 1994). Jiang et al. (2004) reported that litchi treated with 1% HCl for 6 min and packed in polyethylene films and stored at 25°C for 1 day and -18°C for 12 months preserved the red colour with minimal damage.

MAP has been considered to be beneficial to maintain high humidity, essential for prevention of water loss and browning of litchi pericarp (Kader 1994; Pesis *et al.* 2002; Tian *et al.* 2005; Sivakumar and Korsten 2006). CA, with low-O₂ and high-CO₂, has been successfully used to reduce decay, maintain quality and extend storage life in many fruits (Beaudry 1999; Mahajan 2001). In recent years, high O₂ treatment was considered to be effective in inhibiting enzymic discoloration, preventing anaerobic fermentation reactions, and limiting aerobic and anaerobic microbial growth (Day 1996; Duan et al. 2004; Tian et al. 2005).

An atmosphere of 3 to 5% $O_2 + 5\%$ CO_2 is recommended at 5 to 7°C (Mahajan 2001) for litchi. Higher levels of CO_2 (10 to 15%) can lead to off-flavors. MAP has been tried with sealed polyethylene and PVC films (Chaiprasart 2003) with or without SO₂ treatment (Scott *et al.* 1982; Paull and Chen 1987). The effect of using polyethylene film bags is probably to prevent dehydration that leads to rapid skin browning. Paull and Chen (1987) reported that litchi pericarp browning was reduced by storage at 2 and 22°C in a closed polyethylene bag (0.25 mm) but decay became a problem 20 days after harvest. MAP using PVC film wrapping might be more effective for extending the shelf-life of the lychee fruits (Chaiprasart 2003).

Sivakumar and Korsten (2006) reported that the MAP of litchi fruits using BOPP film after post harvest treatment minimized the rate of transpiration, preventing weight loss and deterioration of fruit quality. Among the combination treatments, *B. subtilis* + BOPP had the best potential to control decay, retain the colour and the overall litchi fruit quality during a marketing chain of 20 days (Sivakumar *et al.* 2008). Jiang and Fu (1999) investigated the postharvest browning of litchi fruit caused by water loss in relation to anthocyanin content, polyphenol oxidase (PPO) activity, pH value, and membrane permeability and observed that storage at 1°C under controlled atmosphere (3-5% O₂ and 3-5% CO₂) at 90% RH gave good browning control and fruit quality maintenance.

Tian et al. (2005) stored litchi fruit in air, MAP and CA at 3°C to determine the effects of different O2 and CO2 atmospheres on physiology, quality and decay during the storage periods. The results indicated that CA conditions were more effective in reducing total phenol content, delaying anthocyanidin decomposition, preventing pericarp browning, and decreasing fruit decay in comparison with MAP treatment. The fruit stored in CA conditions for 42 days maintained good quality without any off-flavour. Persis et al. (2002) monitored the emission of the metabolites, acetaldehyde (AA) and ethanol, from litchi fruit during maturation and storage by packed in laminated films, creating MAP. They suggested that mature litchi fruit deteriorated when kept longer on the tree during the harvesting season and this may be ascribed to a fermentation process that began on the tree and caused deterioration during MAP storage.

Packaging of straw berries PVC film shown a considerable improvement in quality in terms of fruit firmness, weight loss, desiccation and decay (Aharoni and Barkai-Golan 1987). Strawberries are relatively tolerant of high CO₂ concentrations which can reduce botrytis decay during storage, hence high CO₂ atmospheres are used commercially to reduce decay and maintain quality during shipping (Aharoni and Barkai-Golan 1987; Kirklanda et al. 2008). Van der Steen et al. (2001) studied the effect of the combination of high O₂ atmosphere and equilibrium MAP on the shelf-life of two non-climacteric red fruits, particularly strawberries and raspberries, at 7°C. The packaging systems compared were: (1) the conventional method of packaging in a macro perforated high-barrier film (air conditions), (2) equilibrium MA (EMA, i.e. 3-5% O₂ and 5-10% CO₂ balance N_2) and (3) two novel MAs: high O_2 atmosphere (HOA, i.e. > 70% O_2 - balance N_2) in a high-barrier film and (4) HOA in an EMA film with an adjusted film permeability. LDPE, PVC and polypropylene films were used for the MAP study. The shelf-life of the fruits was determined by evaluating the evolution of the internal O₂, CO₂ and C_2H_4 concentrations in the packages, the microbial and sensorial quality during the storage, the loss of weight due to transpiration and respiration of the fruit and the loss of marketable fruit due to visual decay or to Botrytis growth. The high O₂ atmosphere in the EMA film re-established after five days to an equilibrium of 3% O₂ and 5% CO₂. The High O₂ atmosphere in the high-barrier film remained high during the first five days of storage, but decreased then

rapidly to anaerobic conditions, resulting in off-flavors and odors. To avoid an accumulation of C₂H₄ inside the highbarrier package, an C₂H₄ adsorbing monolayer was added. Shelf-life of strawberries and raspberries, packed in air conditions, was limited by growth of moulds and yeasts, rather than by sensorial unacceptance (Stewart et al. 2003). On the other hand, sensorial properties limited the shelf-life of the fruits packed under MA (Renault et al. 1994; Stewart et al. 2003). Especially High O_2 atmosphere improved the microbial quality, due to the inhibiting effect on yeasts and moulds (Zheng 2008). However, when O2 was depleted and CO_2 had accumulated, sensorial quality (odour, taste and firmness) was deteriorated. As this is not the case with high O_2 in an EMA film, the high O_2 atmosphere can be assumed as a promising configuration for respiring fresh produce, combining the beneficial effect of high O_2 and EMAP. The beneficial effect of film perforation on gas content during MAP of strawberry fruit was observed and found to be potential for storage (Sanz et al. 2000).

A number of researchers have worked on the development of MAP for cherries and other similarly perishable fruits including blueberries and raspberries (Beaudry *et al.* 1992; Gorris *et al.* 1992; Cameron *et al.* 1995; Reed *et al.* 1995; Moyls *et al.* 1998; van der Steen *et al.* 2001; Almenar *et al.* 2008). MA film technology has utilized micro perforated films or films that are unperforated but have a selectively permeability to O_2 and CO_2 (Crisosto *et al.* 1993). Some commercial films have incorporated C_2H_4 scrubbing agents in their design while others have simplified sealing through the use of twist ties or tape rather than heat (Kupferman 1995). The cherries after harvest are rapidly cooled and humidified to preserve the quality; also cherries respond well to elevated CO_2 level (Chen *et al.* 1981).

Meheriuk *et al.* (1995) suggested that sweet cherry shelf-life may benefit from MAP, but success will be dependent in practice provided that the low O_2 concentration and/or high CO_2 concentration in the package suppress mold growth, respiration, and other metabolic processes without stimulating anaerobic respiration.

Petracek *et al.* (2002) examined the influence of O_2 , CO_2 partial pressures and temperature on sweet cherry fruit respiration in MA using low-density polyethylene film packages stored at 0-25°C and found that sweet cherry may benefit most for MAP through the reduction of water loss and the protection from physical damage. In contrast, low temperature storage reduces respiration rate and controls mold development. Temperature above 15°C there is no such beneficial effect of MAP for cherry. From a practical viewpoint strict control of temperature is the best tool for prolonging shelf-life of sweet cherries. Thus MA is not a substitute for cold temperature in extending postharvest life of cherry. The next generation of films will be 'smart' films that create different permeability rates based on ambient temperature (Cameron *et al.* 1994).

MAP can store several vegetables. Both high CO₂ (5-20%) and low O_2 (down to 1%) concentrations retard respiration and senescence of broccoli heads (Serrano et al. 2006). Increasing CO_2 seems to be more effective than decreasing O₂. Broccoli maintains its quality longer in both perforated and sealed polyethylene packages than did nonpackaged controls (Aharoni et al. 1987; Granado-Lorencio et al. 2008). Rij and Ross (1987) determined that wrapping broccoli in selected PVC films with proper gas permeabilities could serve to generate an appropriate equilibrium atmosphere to retard spoilage. Yoshio and Takashi (1997) have reported that a biodegradable laminate of a chitosancellulose was found suitable as a packaging material for MAP and storage of broccolis. Christie et al. (1995) successfully used a commercially available $35 \pm 3 \ \mu m$ film and a $25 \pm 5 \,\mu\text{m}$ experimental low density polyethylene (LDPE) films impregnated with inorganic particles for the MAP of broccoli. MAP does not affect significantly the in vivo bioavailability of carotenoids and tocopherols from broccoli, supporting its convenience for use by the food industry and consumers (Granado-Lorencio et al. 2008).

Serrano *et al.* (2006) packaged broccoli (*Brassica ole-racea* L.) heads using 3 types of polypropylene films: macro-perforated, micro perforated and non-perforated, and then stored at 1°C for 28 days and observed that, especially for micro perforated and non-perforated films, all changes related with loss of quality were significantly reduced and delayed with time. Jacobssona *et al.* (2006) studied the sensory quality of broccoli stored in MA using BOPP, PVC, and LDPE film packages at 10°C and inferred that overall, including all the sensory properties studied, broccoli packaged in LDPE that contained an C_2H_4 absorber was perceived to be the sample most similar to fresh broccoli.

It is inferred that biological structures influence the transpiration rats of the commodities. Because of the large surface area of peppers (*Capsicum annuum* L.) they are very much susceptible to water loss and thus it is desired to carry out film packaging to prevent from water loss (Bussel and Kenigsbergers 1975; Irtwange 2006). It is observed that packaging with plastic films can extend the post harvest life of pepper but the major benefit appear to be mediated by the maintenance of high relative humidity and not by modification of the atmosphere (Miller *et al.* 1986; Watada *et al.* 1987).

MAP is the most simple, economical, and effective way of extending shelf-life of fresh mushrooms. Kim et al. (2006) worked on the shelf-life of mushroom in MAP using PVC wrap and polyolefin films and found that, polyolefin film packages had the lowest weight loss. Nichols and Hammond (1973) reported that packaging with PVC film increased the shelf-life of mushrooms by retarding cap opening, discoloration, and reducing weight loss. Seal packaging of mushrooms in PVC films were generally associated with reduced respiration and reduced internal browning and, consequently resulting to higher quality. Results varied according to films permeability and number of perforation holes (Nichols and Hammond 1975). Roy et al. (1995) found that 2% O₂ and 5% CO₂ were optimum for MAP for prolonging shelf-life of mushrooms. Although a low concentration of O₂ may have many advantages, less than 2% could cause anaerobic microbial growth significantly, such as Clostridium botulinum (Herr 1991) and Staphylococcus aureus (Martin and Beelman 1996). Ántmann et al. (2008) packed shiitake mushrooms under air in two macro perforated packages (A, 9.0×10^3 perforations/m², 0.1 mm^2 surface and B, 17 perforations/m², 0.1 mm² surface) and under two gas mixtures (15 and 25% O_2) in polyethylene packages, and stored at 5°C for 18 days. Results suggested that during the first 6 days of storage all the evaluated packaging conditions were useful for reducing mushroom deterioration rate. The shelf life of mushrooms in active modified atmosphere was extended up to 12 days

González-Aguilar et al. (2004) reported that MAP could be used to maintain quality attributes of fresh-cut peppers for up 21 days at 5°C. Chilling injury was reduced in matured green bell pepper fruits stored at 2°C when MAP was used, particularly with the less permeable film. MAP also led to less pronounced increases in 1-aminocyclopropane-1carboxylic acid (ACC), putrescine (Put), and abscisic acid (ABA) levels as compared with fruit stored without film (Maria Serrano et al. 1997). Conesa et al. (2007) reported that 50-80 kPa O₂ combined with 20 kPa CO₂ could be used in innovative MAP of pepper dices to avoid fermentation and inhibit growth of spoilage microorganisms. Montero-Calderona et al. (2008) studied the influence of packaging conditions on fresh-cut 'Gold' pineapple shelf-life during 20 days of storage at 5°C. Fresh-cut fruit pieces were packed in polypropylene trays and wrapped with 64 µm polypropylene film under active (high 40% or low O_2 , 11.4%) or passive MAs (air or cut fruit coated with 1%, w/v alginate). Texture profile analysis parameters, did not significantly change over time, suggesting that structural characteristics of fresh-cut pineapple pieces were preserved throughout storage. The shelf-life of 'Gold' fresh-cut pineapple was found to be 14 days. Koide and Shi (2007) compared the effects of polylactic acid (PLA) based biodegradable film packaging on the microbial and physicochemical quality of green peppers with the effects of LDPE, and perforated LDPE film packaging. Each package containing green peppers was heat-sealed and stored for 7 days at 10° C. Results indicated that the physicochemical properties and microbial levels did not show remarkable changes during storage period. It is suggest that the biodegradable film with higher water vapor permeability can be used to maintain the quality and sanitary conditions (protection from microbial and insect contamination) of freshly harvested green peppers in MAP (Siracusa *et al.* 2008).

FUTURE RESEARCH PERSPECTIVES

For many years researchers have carried out packaging studies of fruits and vegetables utilizing the MAP. All such attempts can be classified by their single specific purpose, namely to find an appropriate package for a particular commodity. It would be more beneficial if the research approach is more comprehensive where studies are based on a rational understanding of principles and process and the packaging attempts grow logically from a conceptual model of MA instead of design of MAP for particular commodity every times with some specific purpose that take into accounts only a few of the salient variables. A through understanding of the interactions of temperature, O_2 and CO_2 concentrations and their effects on respiration rates, film permeability, and commodity diffusion resistance (process) and their effects on quality parameters would lead to a more rational selection of packaging materials for MAP system. During the last 15 years several mathematical models have been proposed and tested, but few of them are used commercially. However researchers (at public and private institutions) have identified the following topics which are identified under 'future research needs' and are necessary prior to the more appropriate/ systematic work on MAP is under taken:

- (1) Most data on film permeability are generated at a single or few more temperature and often at very low relative humidity. The response of film permeability to temperature between 0-30°C and relative humidity between 85-95% must be determined.
- (2) The respiration rates of most of the commodities at specific temperatures and gas composition are available. For many commodities, respiration rates in air and in a single CA/MA are available, but very few information is available in several CA/MA conditions. Hence more information on the respiration rates of fresh commodities in MA and at various temperatures must also be generated.
- (3) Several mathematical models developed for MAP describes the variation of O₂, CO₂ over a period of time within the package at a particular temperature. The C₂H₄ produced during this period and the amount of water vapor which may permeate out of the package may also be correlated and included in the MAP design process.
- (4) The additive effects of reduced O_2 and increased CO_2 on respiration and C_2H_4 production needs to be investigated keeping in mind, the overall quality of stored produce.
- (5) The MA packages for commodities are generally designed for a particular atmosphere and temperature. There is evidence that exposure or transfer of this package subsequently to air or another MA condition can affect their respiration and C_2H_4 production rates. Since MAP will expose a commodity to a continuously changing atmosphere until equilibrium is achieved, more information is needed on how this residual effect of MA modifies the predicted behavior from steady-state experiments.
- (6) The RQ depends on the atmospheric composition and temperature. That is as the O_2 and CO_2 are changing in the package atmosphere the ratio of CO_2 produced to O_2 consumed may it shelf be changing. In reality MAP of

produce would expose to a continuously changing atmosphere before the steady state is achieved. The, change in respiratory quotient in response to changing atmosphere could have a great effect on evolving atmosphere inside package including the establishments of equilibrium state; and hence so should be studied further.

- (7) On the whole, respiration is roughly doubled or tripled and permeability of films has been reported to rise from two to five times for every 10°C rise of temperatures. Thus, the MAP of commodity in the selected films would not be effective to maintain appropriate gas permeability during temperature fluctuations because; a film resulting in a favorable atmosphere at a low temperature may result in a harmful atmosphere at higher temperatures. Hence efforts should be made to produce films to equilibrate the Q_{10}^{R} and Q_{10}^{P} to balance the temperature fluctuations.
- (8) Additional information is needed on the resistance of fruits and vegetables to diffusion of O_2 , CO_2 and C_2H_4 under different atmospheric and temperature conditions. The models that describes the respiration rates of the commodity, film permeability, and commodity diffusion resistance be incorporated in the differential mass balance equation that describe the O_2 and CO_2 concentrations changes in packages containing the respiring commodity.
- (9) The temperature fluctuations during transport and storage in most cases would be transient. Hence a compensation methodology, which encounters the respiration rate of the produce and permeabilities of the films, is real need of the hour. The option using a safety device, a valve or membrane would be universal. If a temperature fluctuation were encountered, such device would open, and exchange gases, thus preventing excessive O₂ depletions and CO₂ accumulations. However, the benefits of MA may be temporarily lost. If MA packaging is to be become a viable commercial system some efficient device that would cause a drastic change in gas transfer with a slight change in temperature is needed.

CONCLUSIONS

MAP is used as a supplement to low-temperature preservation of fruits and vegetables. It is mainly used to reduce respiration rate and retard ripening process, thereby increasing resistance to diseases for the host. Commercially, MA is successful for storage of apples, pears, fresh cut (minimally processed) fruits and vegetables and for highly perishable and high value commodities, such as cherry, fig, raspberry, strawberries, litchi, capsicum, mushroom, etc. A marginal increase in storage life and quality by MA storage is not enough for the added cost of implementing MA technology commercially for most fruits and vegetables. An important problem in the commercial application of MA in fruits and vegetables is that the effect of MA is different for the same cultivar grown in different locations or under different cultural practices or different seasons. Therefore, trial-anderror studies have to be conducted to determine the optimum atmosphere for each cultivar in a given place and season. The packaging of films of any desired values of permeability to O_2 , CO_2 and water vapour are available in developed nations, however, it is not so with the developing countries. Models describing the respiration rate of fresh fruits/vegetables and gas permeability be developed. Based on the model, and critical design of MAP system it is possible to maintain an optimum atmosphere recommended for safe storage and extending the shelf-life of commodities. As fruits and vegetables are more sensitive to environmental conditions, accurate design of the MAP is highly required to achieve superior product quality and the development of models for different fruits and vegetables is a pre-requisite. Research is also needed in integrating active packaging with MAP to make this technology economically viable. Current C₂H₄-removing techniques (catalytic or chemical

oxidation) are not commercially successful. Active packaging involving C_2H_4 -absorbing substances should be studied. MAP and related technology can be selectively used in postharvest handling of fresh fruits and vegetables with good results. There is need for commercial application of the technology by processors and fresh produce retailers. Also there is need for MAP and related technology research for local crops under local conditions in developing countries.

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