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## Ozone Technology and Photo Catalysis - The Newer Effective Methods for Keeping the Fruits and Vegetables Fresh for A Longer Period

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### ABSTRACT

Fruits and vegetables form the major part of our balanced diet. The growth of the population has led to the considerable increase in the demand for more consumption of fruits and vegetables which has also culminated the illness associated with these fruits and vegetables. With the development of science and technology, people not only require the food to be safe, but also they require it to keep their original flavour and nutritional value intact. Fungal contamination and some post harvest handling are the most common causes of the spoilage of fresh produce. Countermeasures include the synthetic fungicides, pesticides and pre packaged sanitation treatments including the use of chlorine and bromine. The traditional chemical storage method became unsuccessful to satisfy the growing demand of the people. Newer novel methods like ozone storage, plasma fresh keeping technology, electrolyzed reduction water technology, ultrasonic processing technology, photo-catalysis, super ice-temperature technology and ice film storage technology are now in focus. Ozone storage and photo-catalysis are the two promising fresh keeping technology for keeping the fruits and vegetables fresh along with their original flavour and nutritional value. Ozone is a viable alternative to those fungicides and pesticides as it is effective against a wide spectrum of microorganisms and does not leave any residues on the treated produce. In order to implement this technology and to know about its mode of action, it is necessary to study about ozone, its production, its concentration, the way of product packaging, standardizing the working conditions and the units to measure ozone concentration. Ethylene causes unwanted ripening, spoilage and financial losses. Photo-catalysis offers the greatest potential for removing ethylene preserving the produce both on Earth and also during spaceflights. In this method a catalyst and light acts together to remove ethylene by converting it into carbon dioxide and water.

**Keywords:** ozone, ethylene, photo catalysis, carbon dioxide, water

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## INTRODUCTION

Horticulture plays a significant role in Indian agriculture. In India and other countries of the world, vegetables and fruits are important food items. India is the second largest producer of fruits and vegetables (Sudheer et al. 2007)<sup>1</sup>. They are important because they form an essential part of our balanced diet (Chinenye 2011)<sup>2</sup>. Fruits and vegetables are important sources of minerals, vitamins especially A and C, carbohydrates and proteins. In India, the fruits are placed at high honour, being offered to God at every festival. Their lesser recognised benefit relate to their role in kidney functions, prevention of cancer and cardiac disorders through contribution of ascorbic acid, B-carotene and non-starch polysaccharides besides the bio-chemical constituents like phenol, flavonoids and alkaloids (Sudheer et al. 2007)<sup>1</sup>. In developing countries like India, agriculture constitutes the main informal sector of Economy (Chinenye 2011)<sup>2</sup>. Due to the growing standards of people the fruits and vegetables requirement for consumers is also high (Ji et al. 2012)<sup>3</sup>. People require them to be fresh at the same time they also need them to keep their original natural flavour and nutritive value (Lei ji et al. 2012)<sup>3</sup>. A considerable loss is found in fruits and vegetables due to improper post harvest operations owing to which there is a huge gap between the gross production and net availability (Chadha 2009)<sup>4</sup>. A very small fraction of fruits and vegetables are utilized for processing (< 1%) and exported (fruits- 0.5% and vegetables- 1.7%) in India (Chadha 2009)<sup>4</sup>. Post harvest losses in fruits and vegetables are very high (20-40%) (Chadha, 2009)<sup>4</sup>. About 10-15% fresh fruits and vegetables shrivel and decay lowering than market value and consumer acceptability (Sudheer et al 2007)<sup>1</sup>. Improper handling and storage causes physical damage due to tissue breakdown (Chinenye 2011)<sup>2</sup>. Mechanical losses include bruising, cracking, cuts, microbial spoilage by fungi and bacteria, whereas physiological losses include changes in respiration, transpiration, pigments, organic acids and flavour (Sudheer 2007)<sup>1</sup>. Today the improvement of preservation technology is of immense importance. With the development of modern science and technology physical technology has been widely applied in technology which causes chemical pollution, doesn't destroy the food nutrition, structure, nature and flavour due to which it has received extensive attention in the application of food industry and related research (Ji et al. 2012)<sup>3</sup>.

### **Nature and causes of post harvest losses**

The loss of fruits and vegetables which occur after the harvesting is known as post-harvest loss of fruits and vegetables (Chadha 2009)<sup>4</sup>. It gradually starts from the field, after harvest, in gardening and packing areas, in storage, during transportation and in the whole sale and retail markets

(Chadha 2009)<sup>4</sup>. Such losses are caused mostly due to poor facilities, lack of knowledge, poor management, market dysfunction or the carelessness of farmers (Chadha 2009)<sup>4</sup>.

### Extent of post-harvest loss

Joint study conducted by the management consultancy firm, McKinsey and co. and (The confederation of Indian, Industry (CII), at least 50% of the production of fruits and vegetables in the country is lost due to wastage and value destruction (Verma and Joshi 2000)<sup>5</sup>. The loss of the estimated waste is about Rs. 23,000 crores each year. Another committee named as Swaminathan committee (1980) reported the post-harvest handling account for 20-30% of the losses at different stages of post-harvest application (Verma and Joshi 2000)<sup>5</sup>. India loses about 35-45% of the harvested fruits and vegetables during handling, storage, and transportation leading to the loss of Rs. 40,000 crores per year (Chadha, 2009)<sup>4</sup>.

### Important sites of post-harvest losses

Some of the important sites of post-harvest losses are noticed in India are-

Farmer's field (15-20%)

Packaging (15-20%)

Transportation (30-40%)

Marketing (30-40%)

### Estimated loss of fruits

Fruit	Estimated loss (%)
Papaya	40-100%
Grapes	27%
Banana	20-28%
Citrus	20-95%
Avocado	43%
Apple	14%

### Estimated loss of vegetable

Vegetable	Estimated loss (%)
Onion	25-40%
Garlic	8-22%
Potato	30-40%
Tomato	5-34%
Cabbage and cauliflower	7.08-15%
Chilli	4-35%
Radish	3-5%
Carrot	5-9%

### Causes of post-harvest losses

Horticultural crops have a very high moisture content, tender texture and high perishability (Chadha 2009)<sup>4</sup>. If not taken care properly its nutritious product gets deteriorated and gradually rots within a few days or hours. The major causes of post-harvest causes are follows-

**Metabolic** - The natural process like respiration and aging of the organs.

**Mechanical** - Due to their tender texture and high moisture content, fresh fruits and vegetables are more susceptible to mechanical injury. Taking poor care of those products easily causes bruising cutting, breaking, impact wondering and other forms of injury.

**Developmental** - It includes sprouting, rooting and seed germination.

**Parasitic diseases**- Mostly the loss are caused due to the invasion of fungi, bacteria insects and other organism. They attack fresh fruits and vegetables easily and can spread quickly as the product do not have much of a natural defence mechanism and has plenty of nutrients and moisture to support microbial growth.

**Physiological deterioration** -The physiological disorders due to minerals deficiency, concentration or high temperature injury or undesirable atmospheric conditions such as high humidity etc. This can also be a result of enzymatic action leading to each-ripeness and senescence.

**Lack of market demand**- Poor planning, inaccurate production and market information may lead to over production of certain fruits and vegetables, which can't be sold in time.

**Consumption**- Mainly due to inadequate presentation methods.

#### **Others**

Lack of infrastructure

Unorganized marketing

Poor storage facilities

Late realization of its importance

Inadequate technical support and

Lack of clear concept of packing house operations

#### **Impact of post-harvest losses**

The nutrition and economical status of the country is mostly affected.

**Nutrition**- The wastage of the fruits and vegetables causes heavy loss in the nutrition.

**Economy**- Careless harvesting and rough handling of perishable remaining can scar the skin, thus reduces the quality and market price of the fruits and vegetables. Such damaged products fail to attract the attention of the international buyers and ultimately results in huge economic loss for the country.

### **Ozone (O<sub>3</sub>)**

Ozone is derived from a Greek word “Ozein” which means “to give off odour” (Carletti et al. 2013)<sup>6</sup>. Ozone is a strong, naturally taking place oxidising agent (Suslow 1998)<sup>7</sup>. It is used as disinfectant in municipal water, process water, bottled drinking water and swimming pools (Suslow 1998)<sup>7</sup>. Recently it is applied in the treatment of waste water, dairy and swine effluent, cooling towers, hospital water system and tools, aquariums and aqua culture, water theme parks and public and in house spas (Suslow 1998)<sup>7</sup>. At the concentration of 0.5 to 2ppm, it acts as an effective sanitizer (Botzenhart et al. 1993)<sup>8</sup>. Ozone is insoluble in water in water (0.0003g/100ml at 20°C [68°F] (Suslow 1998)<sup>7</sup>. Its effective disposal is essential for antimicrobial activity (Botzenhart et al. 1993)<sup>8</sup>. Its purifier activity is maintained at a water P<sup>H</sup> from 6 to 8.5 (Suslow 1998). At concentrations above 4ppm ozone is extremely corrosive to equipment and lethal to humans on long-lasting exposure. At 1ppm ozone has a pungent odour and causes exasperation in eyes and throat. Newer electrode probes that measure oxidation reduction potential (ORP) of the water or colorimetric kits are being used to examine the concentration of ozone (Suslow 1998)<sup>7</sup>.

### **Ozone in air of storage rooms**

Ozone concentration in air which can be breathed for a longer period of time without showing any kind of irritation does not provide any kind of effective sanitation of fruits and vegetables surfaces or storage rooms (Smilanick et al, 1999)<sup>9</sup>. The ozone concentration exceeding 0.1ppm has an effective action on pathogen spores and requires specific precautions for the workers employed (Smilanick et al. 1999)<sup>9</sup>. Sometimes it functions by removing ethylene and spores from an airstream that passes through the device (Smilanick et al. 1999)<sup>9</sup>. Ethylene destruction in air by the action of ozone in air is a better phenomenon (Dickson et al, 1992)<sup>10</sup>.

### **Ozone in water systems**

Ozone in water is an effective alternative to hypochlorite as a disinfectant or sanitizer (Smilanick et al. 1999)<sup>9</sup>. Ozone is sparingly soluble in water (Smilanick et al. 1999)<sup>9</sup>. Its maximum solubility at 20°C (68°F) is 29.9 µg/ml (Smilanick et al. 1999)<sup>9</sup>. Ozone in water above in concentrations of 1 µg/ml liberates ozone into the air that exceeds safe levels (Smilanick et al. 1999)<sup>9</sup>. Some of the major advantages of ozone in water are that it decomposes quickly into oxygen, leaving no residues and it has more potential activities against bacteria, cysts of protozoa, viruses and fungal spores as compared to hypochlorites (White 1992)<sup>11</sup>. Ozone has a mode of action to control a plant pathogen which is not based solely on its anti-microbial activity (Smilanick et al. 1999)<sup>9</sup>. Ozone controlled *Rhizopus stolonifer* and induced resveratrol and pterostilbene phytoalexins in table grapes which made those berries resistant to subsequent infection (Sarig et al. 1996)<sup>12</sup>. Ozone

oxidises many organic compounds mostly those with phenolic rings or unsaturated bonds in their structure (Razumonski and zaikov 1984)<sup>13</sup>. It has a role in reducing pesticide residues in processed water (Nicklos and Varas 1992)<sup>14</sup>. It can also reduce mycotoxins in durable commodities (McKenzie et al. 1997)<sup>15</sup>.

Adequate mixing and sensitive process monitoring are essential for the treatment with the low concentrations applied to water for post-harvest uses (Suslow 1998)<sup>20</sup>. The ozone generator provides the line interfaces with the processed water supply or return line at a venturi-type injection dispersor unit (Suslow 1998).<sup>20</sup>

### **Mechanism Of action**

The bactericidal action of ozone was studied on a wide variety of micro-organisms, including gram positive and gram negative bacteria as well as spores and vegetative cells (Carletti et al. 2013)<sup>6</sup>. In recent years it has been seen that ozone is efficient against Venezuelan equine encephalo myelitis virus, hepatitis A, influenza A, vesicular otitis virus and infectious bovine rhino-tracheitis as well as reversal strains of bacteriophage (Seydim et al. 2004)<sup>16</sup>. In case of virus and bacteria and in some prazozoa and insects, ozone acts by the catalytic oxidation of proteins and lipopolysaccharides by destroying their structure (Carletti et al. 2013)<sup>6</sup>. Ozone oxidizes the organic matter present in the bacterial membranes, further weakening cellular walls and causing cell damage and gradual death of the cell due to the effect of nucleic acid destruction, ozone action causes death of the cell (Kim et al. 1999)<sup>17</sup>. Ozone is safer than other food additives, as it has a very short life span in water and air and no residues remain in the food (Kim et al. 1999)<sup>17</sup>.

### **Ethylene**

Ripening is the general phase in the maturation process of fruits and vegetables. The old adage that one bad apple can spoil the whole bag of apples is true as damaged or diseased apples produces high levels of ethylene and stimulate the other apples to ripen too quickly. As the ripening of the fruits is higher it causes the disease.

The ripening of freshly fruits represents the only unique pathway that involves the coordination of developmental and biochemical pathways leading to changes in colour, texture, aroma and nutritional quality of mature seed bearing plant organs (Barry and Giovannoni 2007)<sup>18</sup>. Ethylene is the only gaseous plant hormone which plays a key regulatory role in ripening of many fruits (Barry and Giovannoni 2007)<sup>18</sup>.

### **Effect of ethylene on fruits and vegetables**

Some of the ethylene effects include

1. Russet spotting of lettuce in the mid rib of the leaves;

2. Discoloration in snap beans;
3. Increased roughness in turnips and asparagus spears;
4. Carrots and parsnips become bitter;
5. In the leaves of broccoli, cabbage, Chinese cabbage and curly flower yellowing and abscission is seen;
6. Increased softening of cucumbers, acorn and submersed squash;
7. Watermelons and sweet potatoes show discolouration, softening and off flavour development;
8. Eggplant pulp and seed show brownie and discolouration;
9. Sprouting is seen in potatoes;
10. Increased ripening and softening is seen in matured green tomatoes; and
11. Raspberries and blackberries show shattering.

### **Ethylene bio-synthesis and its regulation**

Fruits are generally divided into two groups on the basis of ethylene production. Fruits that undergo ethylene production and show an increased in respiration rate at the onset of ripening are called climacteric fruits and this group includes tomato, apple, peach and banana, whereas fruits which do not produce increased level of ethylene are known as non climacteric fruits and this group includes citrus, grape and strawberry. These differences are not correct as the so called non climacteric fruits may or may not show elevated ripening characteristics in response to exogenously applied ethylene.

Basically there are two systems of ethylene production defined in plants. In the first case, it is produced during normal growth and development and also during stress responses, whereas in second case it is produced during floral senescence and fruit ripening.

Ethylene production can be regulated primarily by “switching off” or decreasing the production of ethylene in the fruit by the following ways:-

- a. The enzyme responsible for the conversion of s-adenosylmethionine (SAM) to 1-aminocyclopropene-1-carboxylic acid (ACC) is ACC (1-aminocyclopropene-1-carboxylic acid) synthase; this is for the second to the last step in the ethylene bio-synthesis (Barry and Giovannoni 2007)<sup>18</sup>. This enzyme’s expression can be hindered by an insertion of the antisense (“mirror-image”) or truncated copy of the synthase gene into the plants genome (Barry and Giovannoni 2007)<sup>18</sup>.
- b. The ACC deaminase gene encoding for the enzyme is obtained from converse ACC to another compound there by reducing the availability of ACC for ethylene production (Barry and Giovannoni 2007)<sup>18</sup>.

- c. Ethylene production is hindered when the SAM hydrolase gene is inserted. It reduces the amount of its precursor metabolite there by converting SAM to homoserine (Barry and Giovannoni 2007)<sup>18</sup>. This gene is obtained from *Escherichia coli* T<sub>3</sub> bacteriophage (Barry and Giovannoni 2007)<sup>18</sup>.
- d. Suppression of ACC oxidase gene initiates the oxidation of ACC to ethylene, which is the last step in the ethylene bio-synthetic pathway (Barry and Giovannoni 2007)<sup>18</sup>. Down regulation of this gene results in the suppression of ethylene production there by delaying fruit ripening (Barry and Giovannoni 2007)<sup>18</sup>.

Ripening can be delayed by modifying their ethylene receptors. The gene ETR1 encodes an ethylene binding protein, the plants with modified ETR1 lack the ability to respond to ethylene (Barry and Giovannoni 2007)<sup>18</sup>.

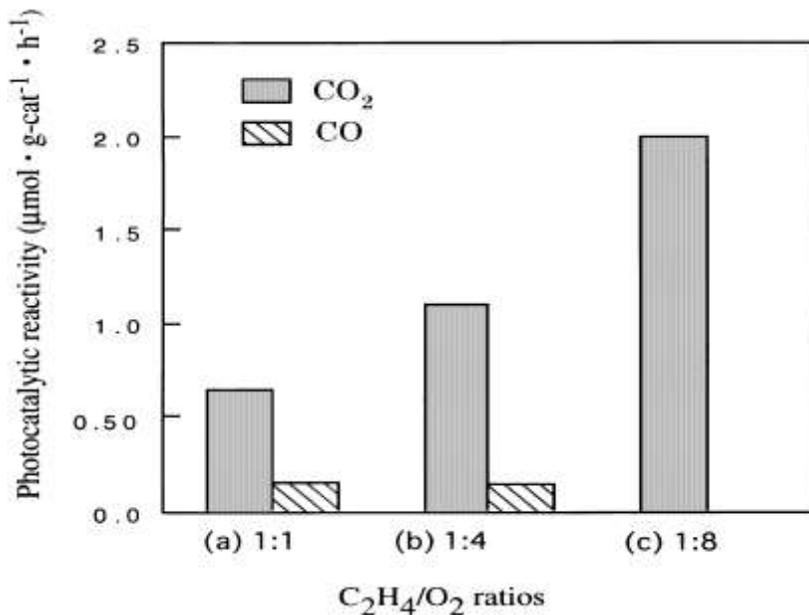
### **Photo-catalysis**

The word photocatalysis is derived from the Greek words “photo” meaning light and “catalysis” meaning to break apart or decompose. In case of photolysis light is absorbed by an adsorbed substrate. The photocatalysis activity (PCA) depends on ability of the catalyst to create electron lone pairs that generates free radicals (.OH) which are able to undergo secondary reaction. Practically it was applied by the discovery of water electrolysis by means of titanium oxide. The advanced oxidation process (AOP) is the commercially advanced process.

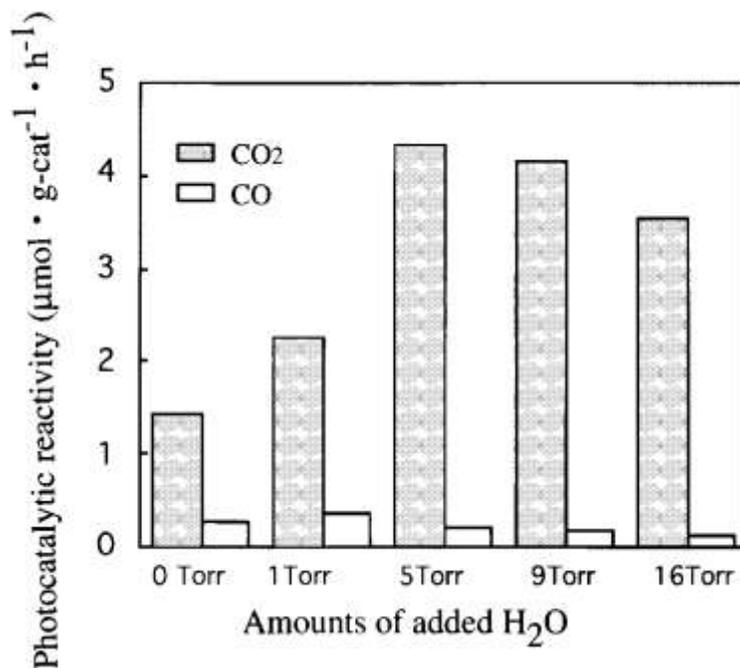
### **Mechanism of ethylene photo-catalysis**

Photo-catalysis of other titanium oxide semi conductors has received good response in relation to a variety of application for environmental issues such as the purification of polluted air and water (Ollis and Al-Ekabi 1993)<sup>21</sup>. The photo-catalytic degradation of hazardous waste is one of the most desirable and challenging aim in the research of the development of environmentally friendly catalysts (Ollis and Al-Ekabi)<sup>21</sup>. As we know C<sub>2</sub>H<sub>4</sub> is harmful to all fruits and vegetables in order to keep enough food fresh in the CELSS (Controlled Ecological Life Support Systems), it is necessary to remove ethylene, which is released from plants. In this context photo-catalyst are considered as they are referred to as advanced oxidation process (Anpo and Yamashita 1997)<sup>19</sup>. The total photocatalytic oxidation of C<sub>2</sub>H<sub>4</sub> with O<sub>2</sub> into CO<sub>2</sub> and H<sub>2</sub>O has been done on an ultrafine powdered TiO<sub>2</sub> photo-catalyst (Park et al. 1999; Fig. 1)<sup>19</sup>. The addition of H<sub>2</sub>O was found to increase the rate of the reaction (Park et al. 1999; Fig. 2)<sup>19</sup>. The detail mechanism of the photo-catalytic reaction had been studied by IR, ESR and by analysing the reaction products (Park et al. 1999). On UV irradiation of the photo-catalyst at 275K leads to the photo-catalytic oxidation of C<sub>2</sub>H<sub>4</sub> with O<sub>2</sub> into CO<sub>2</sub>, CO and H<sub>2</sub>O (Park et al. 1999)<sup>19</sup>. The large surface area of photo-catalyst

is one of the important factors in achieving the photo-catalytic oxidation of  $C_2H_4$  (Park et al.1999)<sup>19</sup>. The photo formed OH species as well as  $O_2^-$  and  $O_3^-$  anion radicals play a key role as active species in the complete photo-catalytic oxidation of  $C_2H_4$  with  $O_2$  into  $CO_2$  and  $H_2$  (Park et al. 1999)<sup>19</sup>.



**Figure 1** Photocatalytic oxidation of ethylene with oxygen  $TiO_2$  powder, (a) (ethylene 7 'mol, oxygen 7 'mol) (b) (ethylene 3 'mol, oxygen 12 'mol), and (c) (ethylene 3 'mol, oxygen 24 'mol) (c) Park et al. 1999)<sup>19</sup>.



**Figure 2** the addition of  $H_2O$  enhances the rate of reaction (Park et al. 1999).

## CONCLUSION

Comparing the traditional storage technology with that of modern preservation technique, which can retain food nutrients and the original flavour are the most promising techniques. The application of modern preservation techniques in fruits and vegetables fresh keeping has huge production potential and a better prospect (Ji et al. 2011)<sup>3</sup>. Post-harvest handling is the final stage in the process of producing high quality fresh produce (Ji et al. 2011)<sup>3</sup>. The modern fresh keeping techniques require a further study so that the mechanism behind the techniques could be thoroughly understood. Being able to maintain the level of freshness from the field to the dinner table presents many challenges, which can be best achieved by focussing on the best research mechanism.

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