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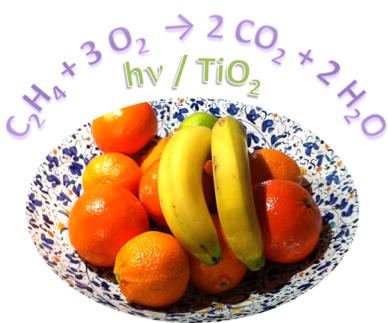
Ethylene Removal and Fresh Product Storage: A Challenge at the Frontiers of Chemistry. Toward an Approach by Photocatalytic Oxidation

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CONTENTS

1. Introduction and Outline	5030	3.2.5. Range of Volume To Be Treated and Air Circulation	5036
2. Ethylene Origin and Impact on the Storage of Perishables	5031	3.2.6. System Specification: Ethylene Load	5036
2.1. Origin and Destiny of Ethylene in Air	5031	3.3. Safety Issues	5037
2.1.1. Natural Sources	5031	4. Approaches for Controlling and Removing of Ethylene	5037
2.1.2. Anthropogenic Sources (Air Pollution)	5031	4.1. Action at the Plant Receptor Level by Genetic and Chemical Approaches	5038
2.1.3. Atmospheric Depletion of Ethylene	5031	4.1.1. Genetic Modifications	5038
2.2. Impact of Ethylene on Fruits, Vegetables, and Plants	5031	4.1.2. Chemical Inhibition of Synthesis/Action	5038
2.2.1. History of the Discovery of Ethylene As a Plant Hormone	5031	4.1.3. Strategies at the Plant Receptor Level	5038
2.2.2. Ethylene Synthesis and Action at the Plant Receptor	5032	4.2. Environment Level Actions	5039
2.2.3. Ethylene Effects on Plants	5032	4.2.1. Ventilation	5039
2.2.4. Storage Life with and without Ethylene Elimination	5033	4.2.2. Controlled Atmosphere (CA) Storage	5039
2.2.5. Economic Importance of Perishable Crops	5033	4.2.3. Modified Atmosphere Packaging	5039
2.2.6. Return on Investment in Reducing Ethylene Damage	5034	4.2.4. Coupling of CA Storage and MAP with Ethylene Removal	5039
2.3. Importance of Ethylene Control in the Cold Chain	5034	4.2.5. Hypobaric Storage	5039
3. The Fresh Product and Its Environment	5034	4.2.6. Ethylene Removal by Oxidation—Ethylene Scrubbers	5040
3.1. Product Characteristics	5034	4.2.7. Ethylene Adsorbents	5044
3.2. Storage/Transport Environment Characteristics	5034	4.2.8. Active Packaging	5047
3.2.1. Temperature	5034	4.3. Additional Operating Parameters of Interest in the Frame of the Strategy Aiming at Removing Ethylene from the Plant Environment	5048
3.2.2. Relative Humidity	5034	4.3.1. Heat Input from External Scrubbing Systems	5048
3.2.3. Ethylene Concentrations	5035	4.3.2. Air-Flow Patterns and Temperature Distribution	5048
3.2.4. Atmosphere Composition	5036	4.4. Comparison of Ethylene Removal Systems	5049
5. Photocatalytic Oxidation of Ethylene	5034	5. Photocatalytic Oxidation of Ethylene	5050
5.1. Introduction	5034	5.1. Introduction	5050
5.2. Unexpected Fruit Storage Applications as Driving Force for New Ethylene Removal Technologies	5050	5.2. Unexpected Fruit Storage Applications as Driving Force for New Ethylene Removal Technologies	5050
5.3. Reaction Mechanism and Influence of Reaction Parameters	5051	5.3. Reaction Mechanism and Influence of Reaction Parameters	5051
5.3.1. Reaction Mechanisms	5051	5.3.1. Reaction Mechanisms	5051
5.3.2. Influence of Reaction Parameters	5053	5.3.2. Influence of Reaction Parameters	5053
5.4. Photocatalytic Materials	5055	5.4. Photocatalytic Materials	5055

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5.4.1. Under UV Light	5055
5.4.2. Under Visible Light	5057
5.4.3. Immobilized Supported Photocatalyst	5058
5.4.4. Zeolite as TiO ₂ -Free Photocatalyst	5058
5.5. Photocatalysis and Fresh Product Storage Applications	5058
5.5.1. Ethylene as a Single and Short Carbon Chain Chemical Target	5058
5.5.2. A Flexible Use	5059
5.5.3. Global Nature of Photocatalysis toward Chemical and Airborne Pathogenic Biological Targets	5059
5.5.4. Low Operation Costs	5060
5.6. Research Efforts and Photocatalysis Coupling	5061
5.6.1. Coupling of Adsorption and Photocatalytic Oxidation	5061
5.6.2. Photoelectrocatalytic Degradation of Ethylene	5061
5.6.3. Microwave-Coupled Photocatalysis	5062
5.6.4. VUV/TiO ₂ Photocatalytic Degradation of Ethylene	5063
5.7. Targeting an Efficient Technology	5064
6. Conclusions	5064
Author Information	5064
Corresponding Author	5065
Notes	5065
Biographies	5065
Acknowledgments	5066
References	5066

1. INTRODUCTION AND OUTLINE

Ethylene (C_2H_4) is a natural ripening (or “aging”) hormone of plants which has numerous effects on growth, the development and storage life of many fruits, vegetables, and ornamental crops.¹ Its sources can include adjacent crops, automotive emissions, plastics, smoke, and fluorescent lights. Ethylene is physiologically active at extremely low concentrations measured in the parts-per-million (ppm, $\mu L\ L^{-1}$) to parts-per-billion (ppb, $nL\ L^{-1}$) range, and it acts positively under controlled conditions as a ripening agent, although, by contrast, even small amounts of ethylene during shipping and storage cause a faster deterioration of fresh produce.

The harmful impact of ethylene on fruits, vegetables, and ornamentals has been estimated to cause significant product losses (as high as 10–80%), which continues to be an incentive for active research and development for tools to mitigate this impact. One of the easiest ways to prevent the detrimental influence of ethylene on perishable crops, and thus to prolong their storage life, is to remove it from the storage and handling environment. Removing ethylene from the atmosphere surrounding ethylene-sensitive fresh products is one of the main challenges in postharvest handling of perishable products for maximizing their freshness, quality, and shelf life from the field to the table. Although the origin of the “ethylene problem” lies with domains such as postharvest biology, plant metabolism, and biochemistry, possible solutions can be found in the fields of photocatalysis, material science, adsorption, and chemical engineering.

This review will focus especially on the comparison of all existing ethylene control/removal methods and technologies (current and historical) applied to the food storage industry.

Many strategies have been developed for protecting postharvest commodities from the detrimental effects of ethylene, and they have been classified in different ways. Emphasis is given to ethylene photooxidation using photocatalytic materials and its possible coupling with ethylene adsorbers as well as to the multidisciplinary awareness required by this problem. Indeed, among different ethylene removal methods, the photocatalytic oxidation process can be considered as a promising alternative, used as a single technique or coupled with other approaches, and has already proven to be an efficient and reliable technology for chemically oxidizing (i.e., converting) organic molecules into carbon dioxide and water at room or even subambient temperatures (mineralization technology).

We highlight first the importance and the effect of ethylene on fruits, vegetables, and plants. Environmental conditions (temperature, gas composition, gas volumes) are outlined to define the operating conditions for a photocatalyst. For comparison, other existing ethylene removal methods are presented, divided into approaches based on plant level modifications and environment modifications.

Photocatalysis is an emerging and promising technology. Considered as a laboratory process for many years, it is now enjoying development resulting from simultaneous efforts by research laboratories and industrials in the search for innovative solutions to the environmental treatment of liquid and gaseous effluents, and surfaces. This results from the advantages that photocatalysis can offer to the targeted application fields foreseen by both academic and industrial partners involved in the implementation of ecotechnologies or sustainable technologies. However, although some commercial photocatalytic devices are already available, the wider industrial application of photocatalysis still requires an important research effort at both laboratory and industrial scales, by demonstrating its performance under different storage/transport conditions, taking into account critical variables such as the kind and amount of commodity, the storage duration, and the atmospheric composition. Similarly as for other gas purification processes, there is also great potential interest in coupling the widely used technique of ethylene removal by adsorption with ethylene photooxidation.

Bearing in mind that designing an efficient photocatalytic system requires multidisciplinary awareness and cooperation, we aim to provide here an outline for several interrelated subjects. First, after this short introduction, we present the background to the origins of ethylene and its effect on the storage of perishables, which is necessary in order to predict the usefulness of any anti-ethylene treatment (section 2). Particular attention is given to the importance of ethylene removal during the whole cold chain that encompasses all the critical steps and processes that food and other perishables must undergo in order to maintain product quality from field to consumer.

Section 3 points out the storage conditions encountered in practice and describes the working conditions of ethylene removal technologies. The important characteristics that are taken into account are temperature, relative humidity, ethylene concentration, and atmospheric composition, with the possible presence of other volatile organic compounds (VOCs).

The fourth section gives an overview of existing methods used for eliminating ethylene from the air for the long-term conservation of fruits, vegetables, and plants. Two strategies are distinguished: plant level actions to inhibit ethylene synthesis/action (genetic and chemical approaches) and environment level actions mostly related to ethylene removal from the

atmosphere by oxidation or adsorption (chemical approach with a destructive or recuperative technology, respectively). Each technique and approach is presented and described from both fundamental and applied points of view, with the different existing methods for ethylene control and removal being reported in order to be compared with the photocatalytic removal approach.

In the fifth section, special emphasis is given to the photocatalytic oxidation of ethylene. The influence of the main reaction parameters such as relative humidity, temperature, and ethylene and oxygen concentration are discussed, and the reaction mechanisms are reported. The photocatalytic materials used for the reaction are mentioned, and the research efforts aiming at the increase of the process efficiency by a coupling approach of photocatalysis are highlighted. Particular attention is given to the application of the photocatalysis technology to the fresh product storage, by putting toward the advantages of the technology in response to the fresh product storage requirements.

We claim that this review will serve as an encouragement for chemists, biochemists, plant physiologists, and food scientists to perform further research and systematic investigation in the field of ethylene adsorption and photocatalytic oxidation, and more generally in the field of worldwide food technologies at the frontiers of chemistry, so important from both the economical and health aspects. We think it could lead to the improvement of existing materials and technologies for ethylene removal and, thus, globally contribute to an increase in both food quality and availability by reducing postharvest losses of fresh produce.

2. ETHYLENE ORIGIN AND IMPACT ON THE STORAGE OF PERISHABLES

2.1. Origin and Destiny of Ethylene in Air

Ethylene may come from natural sources, plants, and plant products (i.e., fruits, vegetables, flowers) or from anthropogenic sources (air pollution) (Figure 1). Sawada and Totsuka,³ in

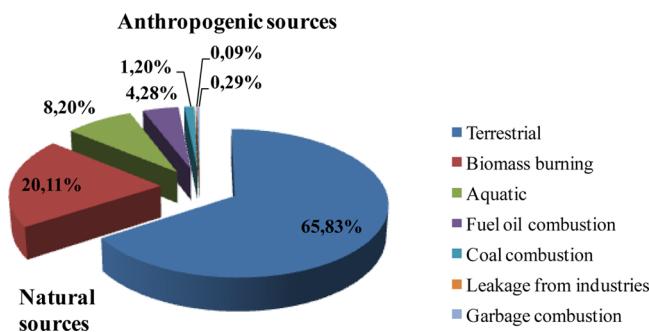


Figure 1. Ethylene natural (terrestrial and biomass burning) and anthropogenic (aquatic; fuel oil, garbage, and coal combustion; leakage from industries) sources.

their study of the dynamics of atmospheric ethylene, estimated the yearly total global ethylene emission at $(18-45) \times 10^6$ tons, of which 74% and 26% are released from natural and anthropogenic sources, respectively.

2.1.1. Natural Sources. Major natural sources are emissions from vegetation of all types. Ethylene is produced by nearly all vascular plants at low levels, and in addition, many plants show an enhanced production of ethylene during ripening and as a general response to environmental stress.

Other sources of ethylene include microbial production and horticultural production.

The ethylene produced by ripening fruits is a signal to other plants to synchronize ripening so as to maximize their appeal to their seed disseminators (e.g., birds), thus assuring the dispersal of their seeds. Even after harvest, fruits, vegetables, and flowers are still alive, continuing their biochemical processes, including ripening and ethylene generation.

Bruising or cutting some fruits and vegetables can cause them to increase their ethylene production. It can come as well from rotting or decomposing plant materials. For instance, aging flowers, dead foliage in the containers, and any plant debris in the cooler must be continually removed, as they give off large quantities of ethylene that will prematurely age everything else in the cooler container.

2.1.2. Anthropogenic Sources (Air Pollution). Ethylene is a byproduct of hydrocarbon combustion, for which the main anthropogenic release includes exhaust gases from internal combustion engines/heaters; air pollution due to coal combustion, oil, natural gas, or biomass; smoke, including cigarettes; welding; and natural gas leaks. A single propane-powered forklift can cause serious damage to highly ethylene sensitive commodities. Some examples of ethylene concentrations in exhaust gases are given in Table 1. Although ethylene is one of the main products of the chemical industry, industrial release remains a minor contribution to total emissions.

Table 1. Examples of Ethylene Concentrations in the Gases Issued from Different Combustion Anthropogenic Sources

source	ethylene conc (ppm)
butane fueled forklift exhaust	150
diesel motor exhaust	60
gasoil motor exhaust	200
cigarette smoke	100–200

The range of ethylene concentrations encountered in the environment and in storage areas will be discussed further.

2.1.3. Atmospheric Depletion of Ethylene. The fate of atmospheric ethylene emitted from natural and anthropogenic sources has been estimated by Sawada and Totsuka.³ Ethylene is destroyed mainly in the troposphere by reacting with OH radicals (89%) and O₃ (8%), and its atmospheric lifetime has been estimated between 2 and 4 days.

2.2. Impact of Ethylene on Fruits, Vegetables, and Plants

This section introduces some important notions related to the role of ethylene in plant physiology and illustrates the importance of removing ethylene in the storage of horticultural produce. Starting with a historical perspective, we present an outline of ethylene autocatalytic synthesis by plants, its action at the plant receptor level, and its effect on the quality of fresh produce. Understanding the relationship between the plant and its environment is essential for designing an efficient ethylene removal method. We believe that this goal can only be obtained by a close relationship between different research areas at the frontier between plant physiology, food technology, chemistry, and chemical engineering.

2.2.1. History of the Discovery of Ethylene As a Plant Hormone. The crucial role of ethylene as a plant growth regulator has only been established over the last 50 years, although its effects have been known for centuries.^{4,5} Ethylene

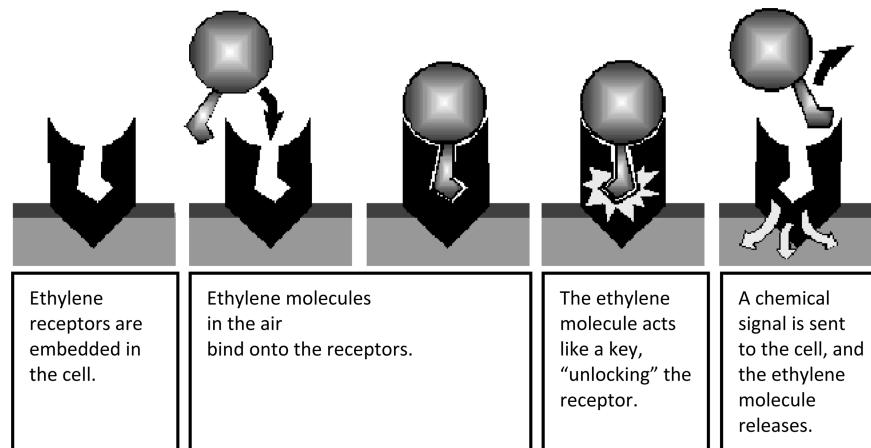


Figure 2. Binding of ethylene molecule with the receptor “unlocks” the receptor and leads to a chemical reaction in the plant tissue. Diagram adapted with permission from ref 14. Copyright 2004 American Association for the Advancement of Science.

has been used since the time of ancient civilizations, for example, the Egyptians, who would gas figs in order to stimulate their ripening, or the ancient Chinese, who would burn incense in closed rooms to enhance the ripening of pears.⁶ In 1864, leaks in illuminating gas containing ethylene caused the premature senescence and defoliation of plants in greenhouses and of trees near gas lines. Although a Russian plant physiologist, Neljubow, claimed in 1901 that the active component was ethylene,⁷ and in a report of the Jamaican Agriculture Department in 1910 Cousins claimed that oranges produce a gas that could ripen bananas, chemical proof that plants produce ethylene was not provided until 1934 by Gane, who analyzed the gases released by ripening apples.⁸ In 1935, Crocker et al. proposed that ethylene was the plant hormone responsible for fruit ripening as well as inhibition of vegetative tissues.⁹ Modern research on ethylene production by plant tissues and on the biological activity of ethylene began with the introduction of gas chromatography,¹⁰ which permitted accurate and rapid determination of trace amounts of ethylene.

2.2.2. Ethylene Synthesis and Action at the Plant Receptor. Both the synthesis and action of ethylene involve complicated metabolic processes, which require oxygen and are sensitive to elevated CO₂ concentration. An overview of basic studies on ethylene synthesis and sensitivity was reported by Klassen and Bugbee.¹¹ The state-of-art at both biochemical and genetic levels was recently reviewed by Zegzouti.⁶

Synthesis. The synthesis of ethylene in plants starts with the conversion of the amino acid methionine into 1-amino-cyclopropane-1-carboxylic acid (ACC) as a key intermediate and two key enzymes, ACC synthase and ACC oxidase.¹² This pathway was elucidated completely in 1979.¹³ The production of ethylene is autocatalytic in many plants, meaning that the presence of ethylene in the atmosphere or in the plant tissue causes a positive feedback, leading to a rise in the production of the hormone.

Action at the Receptor in Plant Tissue. The model for both ethylene perception and signal transduction pathways has been recently reviewed by Alonso and Stepanova.¹⁴ Ethylene is perceived by receptors located in the plant cell membrane.¹⁵ Its binding “unlocks” the receptor (Figure 2) and leads to a series of chemical reactions in the plant tissue resulting in changes in color and in tissue softening or leading to autocatalytic ethylene synthesis for which the effects will be developed further in paragraph 2.2.3.

Both the high binding affinity and specificity of the ethylene receptors are achieved with the help of a copper cofactor. Rodriguez et al.¹⁶ proposed that ethylene interacts with a Cu(I) cofactor in an electron-rich hydrophobic pocket formed by the membrane spanning helices of the ETR1 protein, whose N-terminal hydrophobic end forms a dimer linked by a S–S bond, as previously reported by Shaller and Bleeker.¹⁷ Although different models have been proposed, the exact structure of the ethylene binding site has not yet been fully elucidated. It is worth noting that when its structure will be solved, this natural, highly ethylene selective binding site could serve as a model for designing efficient ethylene adsorbents.

2.2.3. Ethylene Effects on Plants. Understanding how ethylene affects plants requires taking into account the ethylene origin together with the interactions between the plant and its environment (Figure 3), strongly depending on the type of fresh produce.

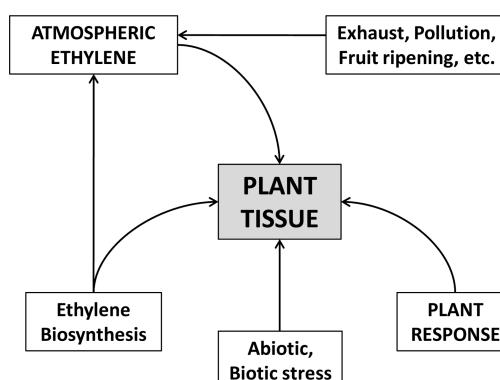


Figure 3. Schematized interactions between the plant and its environment. Redrawn and reprinted with permission from ref 1. Copyright 1999 Elsevier.

Climacteric and Nonclimacteric Fruits/Flowers. In terms of ethylene production, there are two classes of fresh produce:¹⁸

- “Climacteric” products are those that ripen after harvest (e.g., tomato, banana, avocado) and are characterized by consecutive *preclimacteric* and *climacteric* periods. During the *preclimacteric* period, when the fruit remains firm, both respiration and ethylene production are low, and therefore, removing outside sources of ethylene will

prolong this period. By contrast, an external source of ethylene will trigger autocatalytic ethylene production and thus accelerate the *climacteric* period, characterized by rapid ripening, high respiration, and high ethylene production. The removal of outside sources of ethylene will thus not slow down the ripening.

- “Nonclimacteric” fruits (such as leafy vegetables, strawberry, grape, lemon, or orange) are those for which ripening does not occur after harvest. Exposure to ethylene will generally shorten shelf life.

Ethylene Effects. As already mentioned, ethylene induces accelerated softening and ripening of fruits and senescence of flowers during transport and storage. When not desired, it shortens postharvest life and accelerates deterioration. Unless intentionally added to the storage environment, ethylene is considered as a contaminant and exposure should be minimized. Examples of the damages caused by ethylene include the following: decay (fresh produce and flower bulbs), russet spotting (leafy vegetables and eggplants), yellowing (cucumbers, broccoli, and brussel sprouts), odor (garlic and onions), wilting (vegetables and cut flowers), scald and loss of crunch (apples), and rind breakdown (citrus). An exhaustive description of the effects of ethylene and its role in postharvest management is given by Kader.¹⁹

Ethylene Concentration Affecting Plants. The typical dose response curve for ethylene does not show any effect below 0.01 ppm, with half maximal and maximal effects at 0.1 ppm and at 1 to 10 ppm, respectively.⁵ A concentration of ethylene in air of 0.1 ppm was often quoted as the threshold level for physiological activity. However, in recent studies on a wide range of fruits and vegetables, Wills et al. claim that any level of ethylene has a deleterious effect on produce, with the decrease of postharvest life being linearly related to increasing \log_{10} ethylene concentration.²⁰

Rates of Ethylene Production in Plants. The rate of ethylene production by horticultural produce varies widely depending on the commodity. Nonclimacteric produce usually generates ethylene concentrations lower than $1 \mu\text{L kg}^{-1} \text{ h}^{-1}$ at 20°C .²¹ By contrast, the ethylene production rates shown by climacteric fruits may strongly depend on the different stages of their postharvest life. During the preclimacteric period, they often generate ethylene with concentrations of $1\text{--}10 \mu\text{L kg}^{-1} \text{ h}^{-1}$, and when the fruit ripens, the respiration increases by 50% or more, with ethylene production increasing by at least 10-fold.²² The high production rate of climacteric fruits makes them dangerous for other ethylene-sensitive commodities, with such ripe fruits being themselves usually unresponsive to further ethylene. Thus, ethylene removal is generally only worthwhile: (1) with unripe climacteric fruits and other commodities with low production rates and (2) when mixed commodity handling is unavoidable, to protect commodities with low ethylene production from ethylene generated by produce with high ethylene production.²²

Examples of ethylene production and sensitivity levels for fruits, vegetables, and flowers with the main ethylene effects are shown in Table 2. One should add that the ethylene production rate also strongly depends on temperature (see section 3.2.1).

Ethylene produced by fruits and vegetables will tend to accumulate around the produce, as most postharvest handling entails restriction of ventilation. Even at a very low production rate of $0.01 \mu\text{L kg}^{-1} \text{ h}^{-1}$, a commodity occupying one-third of the volume of a closed room could accumulate in 24 h high

Table 2. Ethylene Production Rates, Sensitivity Levels, and Principal Effects for Some Fresh Commodities

fresh produce type	ethylene production rate ($\mu\text{L kg}^{-1} \text{ h}^{-1}$)	ethylene sensitivity ^a	principal reaction to ethylene
cherries	very low <0.1	L	softening
potatoes	very low <0.1	M	sprouting
cut flowers	very low <0.1	H	sleepiness, leaf curl
cucumber	low 0.1–1.0	H	yellowing
kiwi fruit			decay
banana	moderate 1.0–10	H	decay
tomato	moderate 1.0–10	H	shrink, decay
apricot, avocado	high 10–100	H	decay
apple	very high >100	H	scald, lose crunch
passion fruit	very high >100	H	decay

^aEthylene sensitivity (ppm): H = high (0.01–0.5); M = moderate (0.5–3); L = low (3–5).

ethylene levels around 0.12 ppm. In addition, ethylene produced by other commodities or from man-made sources will compound the problem.

2.2.4. Storage Life with and without Ethylene Elimination.

Low levels of ethylene promote the ripening of climacteric fruit and vegetables, but one should note that even very low levels of ethylene (e.g., 0.02 ppm) can adversely affect the storage life of nonclimacteric vegetables.²³ Indeed, the storage life of a range of nonclimacteric fruits and vegetables was assessed by Wills et al. during storage at ambient temperature (20°C) and low temperature ($0\text{--}5^\circ\text{C}$), using ventilation as the removal method with air containing ethylene at concentrations within the range <0.005–10 ppm.²⁴ Among 23 kinds of produce, about a 60% extension in postharvest life was observed for storage in an atmosphere with ethylene concentrations lower than 5 ppb compared to produce stored in air containing ethylene at 0.1 ppm concentration (the commonly considered threshold level for ethylene action). It was suggested that the threshold level of ethylene action on nonclimacteric produce is well below 5 ppb and that the level of ethylene accumulated around commodities in all commercial situations is always much greater than 5 ppb. Hence, any postharvest action that reduces the accumulation of ethylene around nonclimacteric produce during marketing will result in an increase in postharvest life.

This implies that there is no “safe” level of ethylene for which no deleterious effect on postharvest life could be observed.

2.2.5. Economic Importance of Perishable Crops.

Inhibiting the action of ethylene can have tremendous commercial benefits for the storage of sensitive commodities. Let us take as an example only the fruit market. According to the Food and Agriculture Organization of the United Nations (FAO) statistics from 2003, world fruit production reached 379.15 millions of tons, with an increase greater than 20% compared to 1990.²⁵ Throughout the world, the total export value was greater than 11 billion US\$ in 2003 and continues to grow rapidly, mainly due to an increased consumption demand and to the development of technologies facilitating the trade of fresh products. The invention and adoption of new transportation and controlled atmosphere technologies allow fresh fruits to travel greater distances while still maintaining freshness. In the United States of America, the sole value of fresh fruit exports (<9% of total fruit production) in 2003 was over 2.2 billion US\$, amounting to nearly 3 millions of tons.

Taken as an example, in a refrigerated cargo ship with a load weighing 8000 tons, a single percent waste equates to 80 000 kg! The magnitude of losses for perishable food crops has been reviewed in ref 26.

2.2.6. Return on Investment in Reducing Ethylene

Damage. Investigation conducted at the California University showed that the use of an ethylene scrubber in storage facilities significantly reduced russet spotting for lettuce.²⁷ The difference in value for lettuce protected from ethylene compared to that which was exposed to ethylene was estimated to be around 20% to 25%, largely greater than the cost of the ethylene scrubber. Similar results were found with kiwi fruits, which soften very rapidly when exposed to ethylene levels as low as 50 ppb.

2.3. Importance of Ethylene Control in the Cold Chain

Perishable fruits, vegetables, and ornamentals are living, respiring commodities, which give off mainly heat, carbon dioxide, and ethylene and begin to lose quality as soon as they are harvested. The cold chain encompasses all the critical steps and processes that foods and other perishables must undergo in order to maintain product quality from field to consumer. It has been schematized by the worldwide Food and Agriculture Organization of the United Nations (FAO) into a stepwise sequence as follows: harvest, cooling/temporary storage, transport to market, handling at destination, and handling at home or food service outlet.²⁷ Like any chain, the cold chain is only as strong as its weakest link. Ethylene can have an influence at several points during the progress of a commodity in the cold chain. Although produce may only spend a small proportion of their postharvest life in each marketing situation (storage, transportation, and distribution), the effects of elevated ethylene levels are cumulative. The end result of successive expositions to even moderate ethylene levels throughout marketing can be a very short life in the hands of the consumer.

Provided that handling, storage, temperature, and relative humidity (RH) management are correct, ethylene control or removal remains a key factor in all storage and transport stages of the cold chain for targeting the reduction of both losses and quality degradation.²⁸ The following section outlines the significant parameters and the environmental conditions encountered in different links of the cold chain, and that should directly and strongly impact on the design of an ethylene removal method.

3. THE FRESH PRODUCT AND ITS ENVIRONMENT

3.1. Product Characteristics

When designing cost-effective systems for removing ethylene, it is first essential to know precisely the ethylene response characteristics of the target product (see section 2.2.3.). Taking this into account, it is possible to define an adequate concentration of ethylene in the store, the duration for which this concentration can be maintained, and the ethylene production rate which can be expected under specified storage conditions. For a given production rate, the size of a scrubber will be inversely proportional to the required (acceptable) ethylene concentration. Specifying a lower concentration than necessary, or operating the system for longer than required, will not only increase the running costs, but may also increase the product moisture loss, which in some cases leads to a loss in quality.

3.2. Storage/Transport Environment Characteristics

There is also a crucial need to determine the characteristics of the store and its environment. There are six storage environment parameters that can be managed in order to get good quality products to market: the duration, the temperature, the relative humidity (RH), and the different concentrations of ethylene, O₂, and CO₂ (atmospheric composition).²⁹

Examples of usual storage conditions in terms of temperature and relative humidity are reported in Table 3, for which the classification made by Thompson and Kader has been adopted, by dividing fruits and vegetables into three groups with respect to short-term storage.³⁰

Table 3. Ranges of Temperature and Relative Humidity for Short-Term (7 days^b) Transport and Storage of Fruits and Vegetables^a

group	description	T (°C)	RH (%)
1A	most leafy vegetables, Cole crops	0–2	90–98
1B	temperate-origin fruits and berries	0–2	85–95
2	citrus and subtropical fruits and many fruit-type vegetables	7–10	85–95
3	common root-type vegetables, winter (hard-rind) squashes, and most tropical fruits and melons	13–18	85–95

^aData taken from ref 30. ^bEthylene concentrations should be kept below 1 ppm in storage area.

3.2.1. Temperature. The temperature remains the most important factor that influences the impact level of the others (i.e., relative humidity, ethylene concentration, and atmospheric composition). It is noteworthy that the optimal storage temperature depends strongly on the horticultural commodities. At a minimum temperature level, the metabolism of fruits is significantly slowed and does not respond significantly to ethylene, while the deterioration rate of perishables increases 2- to 3-fold for each 5 °C increase in temperature. As an example, Table 4 shows the impact of temperature on the ethylene production rates observed for apples.

Table 4. Temperature Dependence of Ethylene Production Rates for Apples

temp (°C)	0	5	10	20
rate of ethylene production ($\mu\text{L kg}^{-1} \text{h}^{-1}$)	1–10	2–20	5–40	20–125

3.2.2. Relative Humidity. Relative humidity (RH) is the ratio of the water vapor pressure in air to the saturated water vapor pressure at a given temperature and pressure, so that 100% relative humidity is defined as the saturated vapor pressure of water at 25 °C, thus corresponding to about 24 Torr, i.e. about 3% relative to the total atmospheric pressure. The water content of air at sea level can become as high as 3% (30 000 ppm) at 30 °C compared to no more than about 0.5% (5000 ppm) at 0 °C. The relative humidity can influence water loss, decay development, and physiological disorders, as well as the uniformity of fruit ripening. Low relative humidity can induce water stress, increasing ethylene production rates. To prevent possible weight loss associated with the drying-out of surfaces, high relative humidities are beneficial. According to Kader and Rolle, the appropriate relative humidity range for the storage of fruits is 85% to 95%, whereas that for vegetables usually varies between 90% and 100%.²⁷ Examples of the

optimal relative humidity for different commodities are given in Table 3.

3.2.3. Ethylene Concentrations. The ethylene concentration parameter is very important to take into account. It concerns the ethylene concentration inside and outside the store, and requires also a consideration of both internal and external leakage rates of the storage volume.

Ethylene Levels during Storage and Transport. Table 5 summarizes the classical ethylene levels encountered in the

Table 5. Classical Ethylene Levels in Ambient and Storage/Transport Atmospheres^a

area	ethylene concentration (ppb)
In Air ³¹	
rural areas	<1–5
urban areas	<50
heavy traffic	<1000
industrial production and use	<160
petrochemical plants	up to 4300
Fruit and Vegetable Holding Areas ³²	
supermarket stores	17–35
wholesale markets and distribution centers	60
domestic refrigerators containing apples	200
domestic refrigerators without apples	29
controlled atmosphere apple and pear stores	250000 ³³
air apple and pear stores	up to 30000 ³³
inside packages (e.g. MAP) ^b	<48000
refrigerated shipping container	up to 50000 ³³

^aData taken from refs 31–33. ^bMAP = modified atmosphere packaging.

atmosphere and in some holding areas for fresh produce. Ethylene concentrations in ambient air at rural and remote sites worldwide are extremely low, generally in the range of <1–5 ppb, and ethylene is rapidly destroyed by soil microorganisms and solar radiation.³¹ In urban and indoor air contaminated

with combustion products, ethylene concentrations typically range from a few up to about 50 ppb. However, measurements of ethylene levels in heavy traffic can reach values around 1000 ppb or even more. In confined spaces such as greenhouses, cold storage rooms, packages, and transport vehicles, ethylene can easily accumulate up to 10–100 times its ambient air level. Wills et al. have indexed the ethylene levels in the atmosphere of fruit and vegetable holding areas, taking over 700 measurements in wholesale markets, distribution centers, supermarket retail stores, and domestic refrigerators over a 3-year period.³² Ethylene measurements in commercial environments were also reported by Lawton.³³

Wills's results suggest that most products are held during the marketing step at ethylene levels between 15 and 100 ppb, for which 10% or 30% of potential postharvest life is lost, respectively.

Much higher ethylene levels are reported in commercial controlled atmosphere (CA) apple stores, where the hermetic seal leads to ethylene accumulation.³⁴ In this case study, ethylene levels ranged from 160 ppm to 550 ppm, with a maximum of 1400 ppm in one room at storage temperatures ranging from –0.5 to 4 °C. Lawton indicated that high ethylene levels have been observed in mixed cargoes, which could lead to product deterioration.³³ In mixed shipments on refrigerated container ships, levels of 50 ppm have been detected (emanating from apples) and, consequently, could contaminate other supposedly isolated areas: indeed, this has been unfortunately evidenced, with contamination ethylene levels of 0.5 ppm in neighboring holds.

It should be stressed that ethylene can permeate many materials, such as cardboard shipping boxes, wood, and even concrete walls. As shown in the study of Wills et al., ethylene at high concentrations can diffuse easily from one storage room to another.³² Thus, even if ethylene producing crops are stored separately from those which are ethylene sensitive, the unremoved ethylene can cause serious problems.

Ethylene Monitoring throughout the Whole Cold Chain. There are relatively few published case studies on ethylene concentrations throughout the whole cold chain. Ethylene

Table 6. Ethylene Levels in the External Atmosphere and in Packed Cartons with Lettuce at Various Cold Chain Locations between Field and Consumption^a

sample location	ethylene conc (ppm)			potential sources
	range	mean	no. of samples analyzed	
field	E <0.01–0.12		21	air pollution
field to cooler	I 0.03–0.11	0.7	3	mechanically injured lettuce, exhaust from truck, other pollution
holding areas prior to vacuum cooling	E 0.01–0.61	0.05	47	exhaust from trucks and forklifts
	I 0.01–0.80	0.16	12	
immediately following cooling	I 0.1–0.29	0.12	11	(vacuum cooling removes much ethylene from the carton)
cold storage rooms at vacuum coolers	E 0.01–2.78	0.33	144	exhaust from forklifts, other commodities
	I 0.01–1.56	0.22	73	
inside rail cars at destination	E 0.01–0.19	0.06	14	decay, other pollution sources
	I 0.01–0.02	0.01	3	
inside truck units at destination	E 0.04–0.22	0.08	9	decay, other pollution sources
	I 0.08–0.11	0.09	4	
distribution centers and warehouses	E 0.03–2.49	0.25	22	exhaust, other commodities
	I 0.01–0.78	0.08	43	
retail storage areas	E 0.02–2.95	0.36	19	other commodities
	I 0.06–2.88	0.41	18	
home refrigerator	E 0.02–1.58	0.25	33	other commodities

^aData taken from ref 35. E = atmosphere external to carton, I = inside carton.

concentrations measured throughout postharvest handling were published in the 70s-80s by Morris et al.³⁵ for lettuce (Table 6) and by Schouten³⁶ for mixed vegetables (Table 7). There is,

Table 7. Ethylene Accumulation in Consignment of Mixed Vegetables during Transit^a

time (h)	location	ethylene conc (ppm)	
		closed truck	ventilated trailer
0	loading bay	0	0
12	loading bay	4.5	1.2
18	on road	4.1	0.3
26	on ferry	4.3	0.3
34	on ferry	5.8	1.7
44	arrival	6.5	0.1
58	unloading	10.4	0.5

^aData taken from ref 36.

however, a crucial need for more complex and exhaustive empirical studies highlighting the quantitative ethylene evidence in transit and short-term holding spaces along the marketing chain. The relationship to basic studies and action on commodities could thus be drawn for establishing impact scales and further designing appropriate ethylene removal methods. Therefore, a wider range of case studies for particular commodities is needed, supplemented by a survey of ethylene levels at particular stages: refrigerated containers, wholesale markets, supermarkets, etc., with background information on the quantities, the types of commodities involved, and the time elapsed since harvest and spent at each stage.

3.2.4. Atmosphere Composition. The presence of organic molecules other than ethylene in the atmosphere surrounding the products could result in competitive adsorption at the surface of the material used in the ethylene removal process. Understanding of this competitive process is determinant for successfully applying removal methods under real working conditions, for instance in the case of recuperative adsorption, and for photocatalytic technology especially. Thus, the nature and quantity of other gases should be taken into account.

CO_2 Produced by Commodity Respiration. As an example, Table 8 shows the temperature dependence of the CO_2

Table 8. Temperature Dependence of the CO_2 Production Rates for Apples^a

temp (°C)	0	5	10	20
rate of CO_2 production ($\text{mL kg}^{-1} \text{h}^{-1}$)	1.5 – 3	2.5 –	7.4	11–22.7

^aData taken from ref 37.

production rate observed for apples,³⁷ and a summary of both respiration and ethylene production rates can be found in the work of Echeverría et al.³⁸

Volatile Compounds. Present in extremely small quantities, volatile organic compounds are responsible for the characteristic aroma of fruits. The total amount of carbon involved in the synthesis of volatile compounds is lower than 1% of that expelled as CO_2 . In climacteric fruits, ethylene accounts for 50–75% of the total carbon content released to the gas phase, but by definition, it is not included in the list of volatile organic compounds. By contrast, volatile organic compounds (odors) are largely esters, alcohols, aldehydes, ketones, and hydro-

carbons.^{38–40} Figure 4 shows some volatile organic compounds and their sources in fruits and vegetables.⁴¹

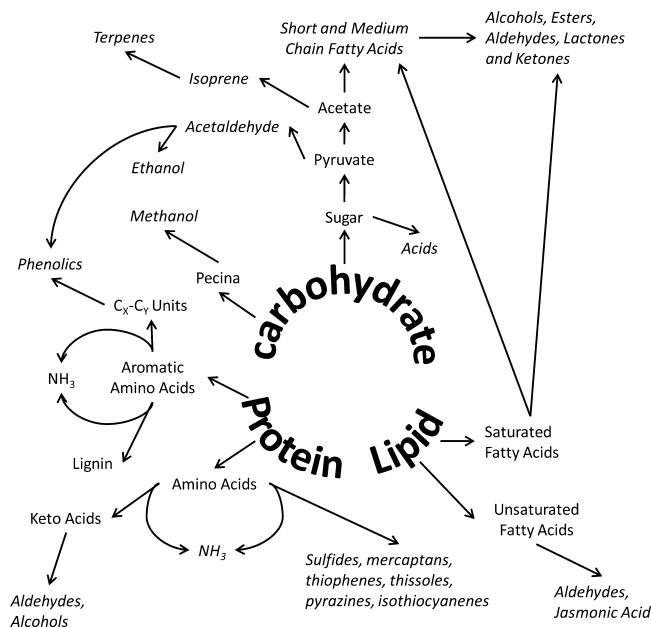


Figure 4. Sources of volatile organic compounds in fruit and vegetable tissues. Redrawn and reprinted with permission from ref 41. Copyright 1997 Elsevier.

The presence of volatile compounds is an important factor that should be taken into account in designing a suitable antiethylene technology, and an efficient catalytic or photocatalytic ethylene removal material, or, even more generally, for building a long-term conservation technology such as modified atmosphere packaging (MAP) or active packaging (AP). As shown in paragraph 4.2.2 for MAP or AP technologies, small confined spaces induce the accumulation of volatile organic compounds to high levels. This highlights another important requirement, since some of these compounds should be completely removed in order to avoid impacts on, for example, taste or odor changes in commodities. Photocatalysis can therefore be potentially a very interesting method for this application due to its global mineralizing approach.

3.2.5. Range of Volume To Be Treated and Air Circulation. Ethylene scrubbers can be used to remove ethylene from circulating air within the vehicle or the storage room. When applying an ethylene removal technology, the characteristics of the storage container have to be taken into account for designing an efficient removal system. This led to the concept of ethylene load on the removal system (see paragraph 3.2.6).

The load volume is usually ~85% of the container capacity. Table 9 shows different air volumes to be treated in different cold chain links.

In addition, the air circulation rate depends on the commodity type; for example, air should be circulated at a low velocity within a floral cooler (if air circulates too rapidly, flowers can dry out), inside which there should be at least one complete exchange of air every hour.

3.2.6. System Specification: Ethylene Load. The specification of an ethylene removal system can be considered in terms of the ethylene load and its variation, as proposed by Dover.⁴² The ethylene load (analogous to the heat load for a

Table 9. Examples of Volumes To Be Treated

cold chain stage	air volume (m ³)	load-carrying capacity (tons)	air exchange (m ³ /h)
road transport (trailers)	120	25	
shipping container	39–78	30	0–75
domestic refrigerators	typically 0.14	-	

refrigeration system) can be defined from a general ethylene removal equation, taking into account the different components as represented in Figure 5.

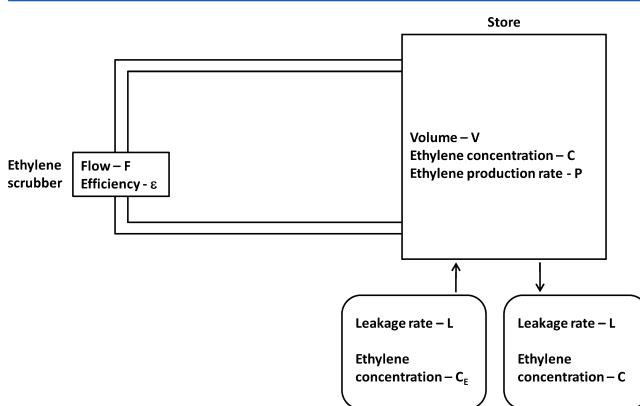


Figure 5. Components of the ethylene removal equation. Redrawn and reprinted from ref 42. Copyright 1989 International Society for Horticultural Science.

The concept of the ethylene load can be used to illustrate the impact of the storage environment characteristics, such as the store atmosphere leakage, the external concentration, and the transient conditions, on the removal system specification (eq 1):

$$V \frac{dC}{dt} = P + L(C_E - C) - \varepsilon FC \quad (1)$$

where V is the free volume of the store, C is the concentration of ethylene inside the store, P is the ethylene production rate of the product, L is the leakage rate, C_E is the concentration of ethylene outside the store, ε is the ethylene removal efficiency,

and F is the flow rate through the removal system. Thus, $V \frac{dC}{dt}$ is the rate of change in ethylene within the store, $L(C_E - C)$ is the influx minus the efflux of ethylene due to leakage, and εFC represents the removal rate by a scrubbing system. The detailed analysis of the influence of different system characteristics, such as duration, CA storage, air storage, etc., was described by Dover.⁴²

3.3. Safety Issues

Ethylene was used as an anesthetic for many years before having been replaced by more modern anesthetics, mostly due to high explosion risk. Relevant studies on ethylene have indicated a low toxicity, and no risk to human health has been identified. The explosive limits for ethylene in air are 2.75–28.6 vol % at 0.1 MPa and 20 °C.⁴³ The odor threshold is 299 ppm and 4600 ppm, for low and high odor levels, respectively.⁴⁴

4. APPROACHES FOR CONTROLLING AND REMOVING OF ETHYLENE

Many strategies have been developed for protecting postharvest commodities from the detrimental effects of ethylene. There are different ways to classify those methods. According to Sherman, they can be separated into three major categories: avoidance, removal, and inhibition.⁴⁵ We prefer to distinguish two approaches. The first one (section 4.1) deals with actions at the *plant level to inhibit both ethylene synthesis and action* (genetic and chemical approaches), whereas section 4.2 concerns actions at the *environment level, mostly related to ethylene removal from the atmosphere* by oxidation or adsorption (chemical approach with a destructive or recuperative technology respectively). Within this second approach, we respect the method nomenclature of Sherman. Indeed, avoidance of ethylene exposure is the most obvious approach for maintaining fresh produce quality and can also be considered as an environment level action. One should note that the controlled or modified atmosphere concept is included in section 4.2, although it is related to both approaches, by acting as ethylene action inhibition through atmosphere modification. After an outline of the plant level modifications, this third part focuses especially on the ethylene removal approach. The different existing removal methods are presented in order to be compared with photocatalytic removal. Figure 6

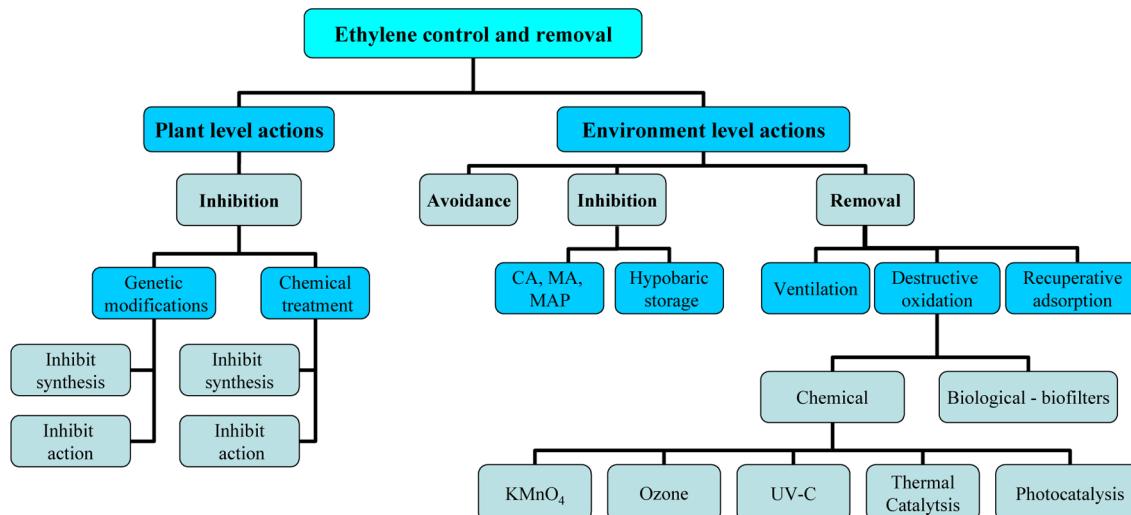


Figure 6. Main methods of ethylene control and removal.

summarizes the different methods of ethylene control and removal presented in section 4.

Application of a specific method may depend on the stage in the cold chain, the size of the storage area, the commodity, the storage atmosphere, etc. Moreover, one should remember that ethylene control/removal is only one link of the cold storage puzzle. Maintaining product quality in an economically viable way will require taking into account a global view of the possible cold storage technologies, such as recently reviewed by Ekman et al.⁴⁶

4.1. Action at the Plant Receptor Level by Genetic and Chemical Approaches

Plant (receptor) level actions or modifications, covering both genetic modification of ethylene biosynthesis and perception, have been reported for fruits⁴⁷ and flowers^{48,49}. In this paragraph we briefly outline this approach, which, although being slightly out of the main scope of this review, should be taken into consideration as a possible alternative or complement to ethylene removal and to environment modification methods.

4.1.1. Genetic Modifications. Ethylene Synthesis Inhibition. Recent advances in molecular biology unravelling the complexities of both ethylene biosynthesis and action have allowed the modification of genes that code the two key ethylene synthesis enzymes (ACC synthase and ACC oxidase) to be performed. This produces fruits for which maturation proceeds normally, but with completely inhibited ethylene synthesis. Transgenic modification of ethylene biosynthesis has been demonstrated to be feasible, and therefore, the control of fruit ripening by suppression of ethylene biosynthesis is currently being explored for commercially useful applications, with tropical fruit species with a very short shelf life being one of the main valuable targets.

Ethylene Action Inhibition. Another approach is the creation of ethylene-resistant crops by modifying the gene encoding the ethylene “binding site”, the “trigger” for the ethylene action in plants. As an example, we can cite the isolation of the mutant gene from the ethylene-resistant plant, *Arabidopsis thaliana*, and its insertion into commercial crops, which demonstrated that the harmful effect of ethylene could be removed.

4.1.2. Chemical Inhibition of Synthesis/Action. Ethylene Synthesis Inhibition. The chemical inhibition of ethylene synthesis occurs through the inhibition of the ethylene key-precursor, i.e. the ACC synthase enzyme. This is obtained by using mainly aminoethoxyvinyl glycine (AVG), which complexes the pyridoxal phosphate cofactor of the ACC synthase enzyme.⁵¹

Ethylene Action Inhibition. Ethylene action can be blocked also at the receptor level by compounds including CO₂, Ag⁺, and a number of unsaturated cyclic olefins such as the 1-methylcyclopropene. Working at the receptor level is possible by considering the advances made by molecular biologists as well as by both chemical and biochemical approaches.

A. 1-Methylcyclopropene (1-MCP). Investigations of ethylene binding have resulted in the identification of unsaturated cyclic olefins that effectively inhibit ethylene action by competing for the same binding site in the fruit or vegetable. Gaseous 1-MCP is almost the ideal compound to treat ethylene-responsive plants,⁵² since it is the most effective olefin, active at extremely low concentrations and protecting for extended periods of time, whereas it is nontoxic. Since the

impact of 1-MCP on climacteric or nonclimacteric fruits and vegetables as well as on fresh-cut products remains not fully understood (e.g. on physiological and pathological disorders that appear during the storage, especially), research is still being conducted in many fields, and up-to-date knowledge has been recently summarized by Lurie.⁵³

B. Silver. Silver is used to promote the longevity of ethylene-sensitive cut flowers, dipped or fed with, for example, silver thiosulfate (STS). The ethylene receptor contains a copper ion that coordinates the ethylene binding,¹⁶ and the STS action may be related to the copper/silver ion exchange in the receptor protein. Silver ions may occupy the binding site occupied by copper and then interact with ethylene.⁵⁴

4.1.3. Strategies at the Plant Receptor Level. Strategies dealing with actions at the plant receptor level are of high interest, since they would consequently get rid of the implementation strategy for the removal of ethylene from air. At this level, transgenic biotechnology is a very valuable approach. However, even if the transgenic modification of ethylene biosynthesis has been demonstrated to be feasible, the main challenge remains the reduction of its deleterious effect on the flavor, the color, and the nutritional content of fruits.⁴⁷ Further, when used for inhibiting the ethylene action, genetic manipulation of ripening suffers up to now from side impacts due to interferences with ethylene signaling,⁵⁰ as well as from an insufficient understanding of the genetic manipulation of both ethylene perception and response for allowing implementation of the technology into commercial applications, as put forward by Brummel.⁴⁷

More generally, biotechnology and genetically modified organisms (GMOs) are still considered with general public apprehension, especially in Europe. The technology suffers also from substantial research and development costs, at least in the early stages. The two main concerns of GMO crops are the food safety risks and the environmental impact of new biological elements in ecosystems, with decades being necessary to understand the involved phenomena.

Taking into account that difficulty to bring biotechnology-based products to the market, technological transfer of the approach dealing with the chemical inhibition of ethylene synthesis or action seems to be an easier task. In contrast to ethylene synthesis inhibition, which appears to be only a partial solution, considering the high ethylene levels due to automobile pollution in urban areas (30–70 ppb) in ambient air outside the holding areas,³² chemical inhibition of ethylene is more interesting, and 1-MCP was approved for commercial use in 2002 as a postharvest treatment on different climacteric fruits (e.g., the Smartfresh product). The technique benefits from a 10–14 day long effect, but facilities for the routine gassing of fruits with 1-MCP may be expensive and not available in many regions. However, although gaseous 1-MCP treatments have been approved, research still needs to be conducted, since 1-MCP seems to be almost the ideal compound to treat ethylene-responsive plants,⁵² being up to now the most effective nontoxic olefin, active at extremely low concentrations and protecting for extended periods of time. Today, crucial research covers important aspects that still need to be fully understood, such as the impact of 1-MCP on different fruits, the responses of fruits of different physiological ages to 1-MCP, the examination of the global impact of 1-MCP on physiological and pathological disorders that appear during the storage, the influence of 1-MCP on nonclimacteric fruits and vegetables, the investigation of the 1-MCP effects on fresh-cut products, as

well as the scale up of the technology from laboratory experiments to commercial store rooms. Besides the use of nontoxic 1-MCP, the use of silver is unfortunately limited to ornamentals, and as a laboratory tool, because of its toxicity, that precludes use on stored food crops.

4.2. Environment Level Actions

This subsection deals with the description of methods for controlling and removing ethylene, based on environment level actions. They include ventilation, both controlled atmosphere (CA) storage and modified atmosphere packaging (MAP), hypobaric storage, ethylene removal from the atmosphere by oxidation (destructive method), and ethylene removal from the atmosphere by adsorption (recuperative method).

4.2.1. Ventilation. The tried and trusted method is to ventilate storage rooms, packing houses, and retail areas with fresh air (e.g., one air exchange per hour). A major drawback of ventilation is that ambient air has to be cooled and dehumidified, leading to a significant extra load on the refrigeration system and to a consequent increase in running costs. In addition, in the presence of large amounts of water vapor in ambient air, frequent defrosting of the evaporator coils is required. Prior to and during a defrost cycle, temperature control and distribution in cargo can cause serious problems. The impact of ventilation with outside air remains limited by the contamination of outside air by ethylene from other sources, such as the pollution resulting from internal combustion engines. Taking into account the high ethylene levels in ambient air in some transport/storage locations, the efficiency of ventilation is significantly decreased. This method is usually impractical in controlled atmosphere (CA) and modified-atmosphere (MA) storage.

4.2.2. Controlled Atmosphere (CA) Storage. Controlled atmosphere storage involves altering and maintaining an atmospheric composition different from that of air (~78% N₂, 21% O₂, 1% Ar, and 360 ppm CO₂), by simultaneously decreasing oxygen and increasing CO₂ concentrations. Generally, oxygen below 8% and CO₂ above 1% (1–25%) are used, depending on the commodity.⁵⁵ When used as supplements to keep fresh horticultural perishables within their optimum ranges of temperature and of relative humidity, controlled atmospheres as well as modified atmospheres can serve to extend the postharvest life of the products.

Optimum oxygen and carbon dioxide concentrations lower both respiration and ethylene production rates (ethylene production is reduced by about half at oxygen levels around 2.5%), reduce ethylene action, delay both ripening and senescence, retard the growth of decay-causing pathogens, and control insects.^{27,29} For example, controlled atmosphere storage may double the storage life compared to that of regular cold storage for several varieties of apples and pears by slowing down the natural rate of respiration. Atmospheres have therefore to be applied with great precision and accuracy in controlled atmosphere storage using an array of technologies that include nitrogen generators, ethylene and carbon dioxide scrubbers, computer sense-and-respond systems, and dynamic control systems.

Modified atmosphere (MA) storage is another type of controlled atmosphere storage. This term denotes the storage of horticultural products in a beneficial atmosphere other than air that is not under as close regulation as in controlled atmosphere storage. While controlled atmosphere systems actively manage the composition of the storage atmosphere,

modified atmosphere systems generally use product respiration and passive technology to generate the required atmosphere.⁴⁶ Modified atmosphere storage can be obtained in boxes of pears, apples, and cherries that are lined with polyethylene film, which acts as a barrier to the escape of carbon dioxide and to the introduction of external extra oxygen. Another method for obtaining a modified atmosphere storage is the addition of dry ice, which increases to some extent the carbon dioxide level in the atmosphere surrounding the products.

In both controlled and modified atmospheres, great care should be taken to obtain optimum modifications of the atmosphere and to avoid extremely low levels of oxygen and/or too high levels of CO₂, which would induce anaerobic metabolism and accelerate senescence and spoilage.^{56,57}

Although modified and controlled atmosphere storage have both been shown to be effective in extending the postharvest life of many commodities, their commercial application has been limited by the relatively high cost of these technologies. There are, however, a few cases in which a positive return on investment (cost/benefit ratio) can be demonstrated. Using controlled atmosphere during marine transportation extended the postharvest-life of those fruits and vegetables that would normally have a short postharvest-life potential, thereby allowing marine transportation instead of air transport for the shipment of such produce. In terms of cost and benefit, savings obtained with the use of marine transportation are much greater than the additional extra-cost introduced by the controlled atmosphere technology. It has been estimated that around 20–30% of cargo transported in refrigerated cargo ships is now carried under controlled atmosphere conditions.⁵⁸

4.2.3. Modified Atmosphere Packaging. While the terms *controlled* or *modified atmosphere storage* refer mainly to storage rooms or containers, the modified atmosphere packaging of fresh fruits and vegetables refers to the technique of sealing actively respiring produce in polymeric film packages to modify both oxygen and CO₂ levels within the package atmosphere.⁵⁹ It can be considered as a particular case of controlled atmosphere. Its use at the pallet, shipping container (plastic liner), and consumer package levels is growing. The beneficial effects of MAP for fresh-cut produce have been extensively reviewed by Ahvenainen⁶⁰ and Solomos.⁶¹

4.2.4. Coupling of CA Storage and MAP with Ethylene Removal. Controlled atmosphere storage, however, remains a technology based on a static atmospheric system, during which ethylene and other volatile compounds can readily accumulate, and for which ventilation is not possible. Therefore, ethylene removal remains still a great focus in controlled atmosphere storage and modified atmosphere packaging. Using ethylene, carbon dioxide, oxygen, and/or water vapor absorbers as part of the modified atmosphere packaging technology allows the storage life of products to be increased. Although much research has been done on the use of surface coatings to modify the internal atmosphere within the package, commercial applications are still very limited due to inherent biological variability of commodities. It is worth noting here that photocatalytic oxidation has a great potential utility for this application.

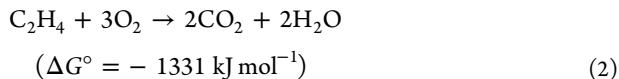
4.2.5. Hypobaric Storage. It has been known for a long time that hypobaric storage of fresh fruits and vegetables helps to keep their quality and extend their shelf life. The basic operational scheme consists of low atmospheric pressure, usually below 50 kPa, continuous ventilated air exhaust, and saturated humidity in the storage room, so that the process

suffers unfortunately from expensive costs and restrictive safety considerations. After the concept of hypobaric storage was introduced by Burg and Burg in 1966,⁶² positive effects of hypobaric treatments on delaying the senescence of many fruit and vegetables, such as apples, asparagus, avocados, bananas, mangoes, cucumbers, parsley, mushrooms, tomatoes, and strawberries, have been reported.^{63–66} The apparent effects have been retention in firmness, color, soluble solids, sensory quality, and nutrients, such as ascorbic acid and chlorophyll, extending storage life. Hypobaric storage has been reported to be effective not only for fresh produce but also for preserving fresh meat, such as pork by reducing microbial growth and retaining sensory quality.⁶³ Hypobaric treatment for a short time was also reported to inhibit or reduce the mold spoilage and decay of strawberries, grapes, and sweet cherries.^{67,68} It has been suspected that the subatmospheric treatment could induce resistance of the produce against pathogens. Pressure reduction, even for short times, may also have another additive effect of rapid vacuum cooling to preserve quality in the subsequent storage of fresh produce.⁶⁹

The enhanced preservation of fresh produce by hypobaric conditions is thought to be due to the modified low oxygen atmosphere and the removal of detrimental volatile metabolic products such as ethylene and α -farnesene from the storage facility's atmosphere;^{64,65,70} low oxygen can slow the respiration of fresh produce, and removal of ethylene and other volatile metabolic products can retard the progress of ripening and senescence. The volatiles α -farnesene and its oxidation product 6-methyl-5-hepten-2-one accumulating in the storage room are responsible for scald development of apple fruit, and thus, removal or lowered production of them can prevent scald.⁷⁰

However, the technology of hypobaric storage has not been widely accepted or used for storing fresh produce in industrial practice when compared with controlled atmosphere storage or modified atmosphere packaging. A possible explanation for the poor exploitation of this technology is that it is perceived to have no significant advantages in terms of beneficial effects or costs over other technologies. In an effort to overcome the limitations of hypobaric storage, a three-stage hypobaric storage system for preserving asparagus has recently been developed and applied.⁷¹ An improved variant of slowed evacuation has also been proposed by Burg to eliminate the artificial humidification step.⁷²

4.2.6. Ethylene Removal by Oxidation—Ethylene Scrubbers. The easiest way to prevent the impact of ethylene on perishable crops is to remove (scrub) it from the storage and handling environment. In contrast to a recuperative method such as adsorption, the use of a destructive technology, such as an oxidation process (eq 2), allows continuous and irreversible ethylene removal.



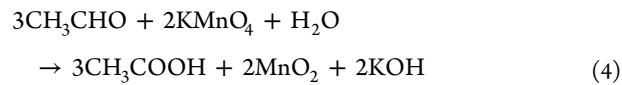
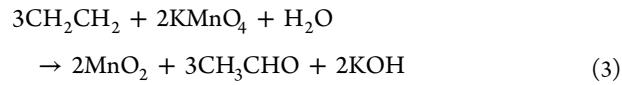
When the oxidizing agent is air (O_2), this thermodynamically favored reaction has to be activated thermally (at temperatures higher than 800 °C), catalytically (100–800 °C), photochemically by UV light, or photocatalytically by UV light through a solid semiconductive material. Both photochemistry and photocatalysis take place at temperatures lower than 100 °C (at ambient or even subambient temperatures).

For most oxidation technologies, it is essential for the air inside the room or the transit vehicle to be circulated past the

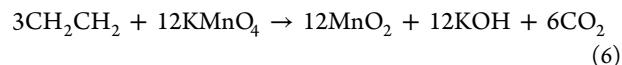
scrubber for effective ethylene removal. They can be thus considered as external scrubbing systems. After the description of the advantages/drawbacks of each oxidation technology, the necessary heat input related to the use of external scrubbing systems as well as unusual operational parameters such as air flow pattern and temperature distribution, will be presented in section 4.3.1.

KMnO₄. Potassium permanganate-based ethylene scrubbers are the most widely used technology. They are especially adapted to small volume storage rooms, since the potassium permanganate is rapidly consumed and must be replaced with a fresh supply several times during a conservation season.^{73,74} Potassium permanganate readily stoichiometrically oxidizes ethylene at ambient temperature to carbon dioxide and water, simultaneously forming manganese dioxide and releasing KOH which can be spent as organic fertilizer.

The ethylene stoichiometric oxidation reaction pathway can be schematized as follows, passing through the partially oxidized CH_3CHO and CH_3COOH intermediates:



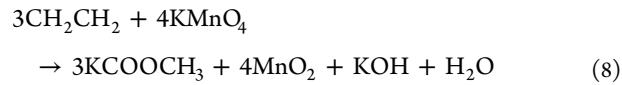
Combining eqs 3–5, we get the overall stoichiometric oxidation reaction:



Even if the oxidation (eq 6) is not complete, many of the intermediate products formed are irreversibly bound to the media or act as a reactant; for example, KOH will react with the acetic acid formed in eq 4 to produce potassium acetate:



Combining eqs 3, 4, and 7, we get:



To be effective in oxidizing very low concentrations of ethylene in the atmosphere surrounding the product, where natural convection and diffusion are the only driving forces giving contact between ethylene and the oxidant, the potassium permanganate needs to have a high surface area exposed to the atmosphere. This is achieved by supporting potassium permanganate on porous inert materials with high surface area, such as clays, zeolites, alumina and limestone, cement and silica gel, vermiculite, activated carbon, pumice, and brick.⁷⁵

A range of commercial potassium permanganate products is now available, usually with a carrier being alumina beads, for which one can note Purafil (Purafile, Doraville Ga.), Circul-Aire (Circul-Aire, Montreal), Ethylsorb (Molecular Products, Thaxted, Essex), Bloomfresh (Ausdel, Cheltenham, Victoria), or supported on zeolitic materials (ethylenecontrol). However, Wills and Warton claimed that these products are mainly used to remove organic contaminants from the atmosphere in

ducted air-conditioning systems and that there has not been any meaningful commercial use with horticultural produce.⁷⁶

The ability of potassium permanganate to reduce ethylene concentration in the atmosphere around horticultural produce was first demonstrated by Forsyth et al. on apples.⁷⁷ Since then, many studies have investigated the impact of laboratory-prepared or commercial potassium permanganate products, and mainly evaluated the effect of the product amount on a single produce, while rather no scientific studies were conducted on the concentration of potassium permanganate in the product, for determining the dominant parameters in the stoichiometric oxidative removal of ethylene and for investigating the effect of the ethylene concentration.

The main disadvantages of using KMnO_4 -based scrubbers are related to the recuperative nature of the technology and to the release of non-negligible amounts of byproducts such as KOH. Even if KOH could be further used as organic fertilizer, it should further be recovered from the spent product, also containing the spent MnO_2 and the support carrier intimately mixed together. KMnO_4 also requires frequent replacement (e.g., for every journey in cargo transport, or several times during the conservation season), and the necessary amount depends on the ethylene production. Indeed, it has also been shown by Blanpied et al. for a 200 t Empire apple store,⁷³ that removal efficiency decreased quickly with the storage duration. Twelve days of continuous use led to a decrease in removal efficiency to 25% with a very restrictive regular replacement which is not practical during shipment. This strong reduction in efficiency was, however, more related to the side impact of the detrimental absorption of water rather than to the full consumption of the permanganate.

According to Wills and Warton, the lack of systematic studies on the ability of potassium permanganate to remove ethylene has strongly hindered its commercial use with horticultural commodities.⁷⁶ The lack of such studies caused the absence of any useful recommendations related to the amount of potassium permanganate needed for achieving either a calibrated decrease in ethylene concentration or an increase in the postharvest life of a commodity. It should also be noted that the labels of commercial products unfortunately do not mention the concentration of potassium permanganate inside the products, although Abeles et al.⁴ have reported a typical value of 4–6 wt %.

In order to provide such data, Wills and Warton carried out a systematic study on the ability of potassium permanganate to remove low levels of ethylene from the atmosphere. Ethylene removal was studied at 20 °C using a flow system with 0.7 ppm of ethylene in air flowing at 20 L h⁻¹ (corresponding to 14 μL of ethylene per h), passing through a 4 L container with an absorbent weight in the 1–50 g range. With an absorbent containing 4 wt % of KMnO_4 , 1 g of adsorbent allowed 760 μL of cumulative ethylene to be removed for 14 days, after which the activity dropped to lower than 10%. This value can be considered as the removal capacity. The ethylene removal, at 70% relative humidity, increased linearly from 30% to 90% when the absorbent amount increased from 1 to 50 g. The competitive effect of water is highly detrimental to the ethylene removal efficiency, and increasing the relative humidity from 70% to 90% led to a drastic 50% loss in efficiency.

The authors determined a removal efficiency of 168 $\mu\text{L h}^{-1}$ kg_{adsorbent}⁻¹. Taking this into account, for produce held at 20 °C in an atmosphere of 90% relative humidity and generating 1 $\mu\text{L kg}^{-1} \text{h}^{-1}$, reducing the ethylene concentration by 90% requires

the use of 6 g of absorbent per 1 kg of produce, while 60 g of absorbent per kg of produce is required when ethylene is generated at 10 $\mu\text{L kg}^{-1} \text{h}^{-1}$. Using a potassium permanganate absorbent would thus appear to be possible for packages of produce that have a low level of ethylene production. By contrast, suitability for a 20 kg package of produce generating ethylene at 10 $\mu\text{L kg}^{-1} \text{h}^{-1}$ is highly questionable, since 1.2 kg of absorbent would be required, with the simultaneous formation of 0.8 kg of KOH byproduct directly within the solid body.

The authors also studied the efficiency of ethylene removal with time on stream and evidenced that the initial efficiency of ethylene removal could be maintained at a 29% steady state for about 24 h before ethylene removal strongly declined to only 10% after 14 days (using 1 g of absorbent), although 44% of the initial quantity of potassium permanganate still remained unused in the beads. Those results suggest that the loss of efficiency was not due to the lack of potassium permanganate and rather to the difficulty of ethylene diffusion into internal parts of the bead after oxidation of the surface layer, which formed a used-skin. This strongly diminishes the efficiency of potassium permanganate for the long-term storage of high ethylene-generating produce. This pointed out that the (nano)material approach should be introduced for designing high efficiency products, by tuning the bulk and surfaces of permanganate-based material for increasing, for example, its resistance to water or ethylene diffusion within the material body.

Biofilters—Microbial Ethylene Removal. An interesting alternative for ethylene removal is the use of biological filters for purifying air, suggested as a method for removing ethylene from industrial waste gas and from horticultural storage facilities.^{78,79}

Biofiltration is a complex technological process which involves many physical, chemical, and biological phenomena.⁸⁰ The air flows through a packed bed, and the pollutant transfers into a thin biofilm at the surface of the packing material. Since contaminated gases pass through the reactor, pollutants are transported and further immobilized into the biofilm, where they are used by the microorganisms as a carbon source or an energy source, or both. Through oxidative reactions, organic contaminants are converted to odorless compounds, such as carbon dioxide, water vapor, and organic biomass. Very few papers have been published on this kind of ethylene removal, and no application can be found in real storage/transport conditions.

A prerequisite for successful biofiltration is the existence of ethylene-degrading microorganisms (bacteria, fungi, ...) with sufficient activity at low temperatures. Elsgaard reported microbial ethylene removal at temperatures below 10 °C with biofilters based on ethylene-oxidizing bacteria immobilized on peat-soil (i.e., organic soils containing more than 20% organic matter in various degrees and states of decomposition).⁸¹ A biofilter of 687 cm³ was designed for an air flow of about 73 mL min⁻¹ with 2 ppm ethylene in the inlet air. The ethylene removal efficiency decreased from 99.0% to 98.4% when the temperature dropped from 20 to 5 °C. This corresponded to ethylene levels of 0.022 ppm to 0.032 ppm in the biofilter outlet air. At 2 °C, the average ethylene removal efficiency decreased to 83%. The ethylene removal rate was maximum at 26 °C (0.85 μg of C_2H_4 g [dry weight]⁻¹ h⁻¹) and remained at levels of 0.14 μg to 0.28 μg of C_2H_4 g [dry weight]⁻¹ h⁻¹ at 0 to 10 °C. Complete ethylene oxidation by microorganisms was

evidenced at 15 °C, whereas lower temperatures, such as 5 °C, led to substoichiometric CO₂ production, with a probable accumulation of undetected intermediate products inside the filter.

In addition to the choice of microorganisms, the selection of an appropriate filter medium is another key factor in biofiltration efficiency. The major drawbacks of soil biofilters are their small surface area, low permeability, and a limited sorption capacity resulting in poor performance.⁸² The disadvantages of compost and peat biofilters include the replacement of filter media and the requirement of a large installation space.⁸³ In order to overcome this problem, Kim used a biofilter based on granular activated carbon (GAC) inoculated with *Pseudomonas* strains as the ethylene-degrading microorganism.^{84,85} The use of GAC provides advantages such as greater surface area and porosity ($S = 900\text{--}1100 \text{ m}^2 \text{ g}^{-1}$; bulk density = 0.4–0.5 g mL⁻¹). The removal efficiency was determined by the initial ethylene concentration of inlet air flow. Relatively high concentrations were applied to the biofilter, since such high levels are frequently encountered in industrial emission sources. Poor biodegradation (10–15%) was observed at a relatively high inlet ethylene concentration (517 ppm), probably due to the limited adsorption on the biofilm, whereas 100% removal was reached after a few days of run and maintained for about 20 days at the lower inlet concentration of 331 ppm. Improved performance in terms of subsequent days of efficiency might have occurred because the necessary microbial enzymes were induced during the use of the filter, as a result of the growth of the initially small population of ethylene-degrading microorganisms.

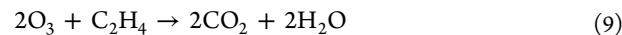
The biofilter studies were evaluated in terms of ethylene elimination capacity, defined as the amount of ethylene degraded per unit of reactor volume and of time. With an inlet ethylene concentration of 331 ppm, the maximum elimination capacity shown by this study was 34 g C₂H₄ m⁻³ day⁻¹, whereas the capacity in Elsgaard's study was 21 g C₂H₄ m⁻³ day⁻¹. This difference could be due to the selection of activated carbon and *Pseudomonas* strains, indicating that all parameters have to be taken into account.

It is worth noting that a biofilter remains a relatively simple device to build, and could operate as a cost-effective solution provided the pollutant is biodegradable, at fairly low concentration and at a reasonable temperature. For high air flows, a biofilter may be an interesting and cost-effective solution. In addition, there is no secondary pollution (compared to incineration technology) and the degradation products (for VOCs) are additional biomass, carbon dioxide, and water. Very large air flows may be treated (rates up to 100 000 m³ h⁻¹), although a huge area is then required—a large biofilter may occupy as much or more land than a football field—this being one of the major drawbacks of the technology.

Another limitation of the biofiltration process is the removal of molecules with lower biodegradability such as—unfortunately—ethylene. Photocatalysis is here an interesting solution to put forward due to its efficient action, enhancing the removal of VOCs, especially nonbiodegradable (biorecalcitrant) molecules. An improvement could come from using UV photocatalysts upstream of the biofilters. The synergistic effect of the coupled UV and biofiltration has already been demonstrated for some VOCs.

Ozone. Ozone is a powerful oxidant/disinfectant which remains technically more difficult to use, especially due to its toxicity. It can be easily generated using light generators or

corona discharge systems. Conceivable benefits of adding ozone to air in packing houses and storage rooms include the control of postharvest diseases on fruit, the delay of spore production from decaying fruits, the sanitation of surfaces, and ethylene removal. Forney recently reviewed this subject.⁸⁶ Ethylene oxidation with ozone can be written as follows:

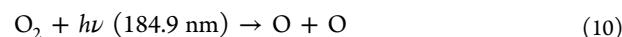


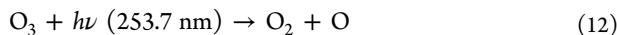
Ozone can be effective also against a wide range of microorganisms, including bacteria, viruses, fungi, and spores, but it can also cause serious and irreversible destruction of human and plant tissues. It can be used as a complementary measure with other ethylene removal methods or alone.

Crisosto et al evaluated the ability of the OxtomCav⁸⁷ corona discharge ozone generator to remove ethylene from an empty 60 m³ refrigerated export container.⁸⁸ Ethylene and ozone levels were measured over a 24 h period after introducing an initial concentration of 3.8 ppm of ethylene at 0 °C. The ethylene reduction rate was proportional to the ozone production rate. At its highest settings, the ozone generator reduced the ethylene level in the container at a rate of 145 ppb h⁻¹ compared to 35 ppb h⁻¹ for the control blank experiment without generator (due probably to container leakage). For comparison, the ethylene reduction rate measured for the potassium permanganate filter was similar to that of the control treatment. The ethylene and ozone levels after 24 h were 0.2 ppm and 3.9 ppm, respectively. Taking into account the toxicity of ozone, the safety issues are here of crucial importance. The current exposure limits established by the U.S. Occupational Safety and Health Administration (US-OSHA) for a 8 h workday are 0.1 ppm ozone; the short-term exposure limit (15 min) for ozone is 0.3 ppm, while long-term exposure to concentrations above 1 ppm causes irreparable damage and even death. The concentration that is “immediately dangerous to life and health” (IDLH) is 5 ppm, which corresponds to the maximum concentration for which self-contained breathing equipment is not required. However, concentrations could become much more than this in export containers, which can stay closed for long durations. Other exposure designs include generation of ozone in day–night cycles to minimize workers’ exposure to ozone⁸⁹ or circulation of the room air through an ozone reaction chamber.⁹⁰

The simultaneous sensitivity of plant tissues to ozone remains an irreversible drawback, and both ozone monitoring and control features will be necessary to ensure effective decay control, provide for human safety, and prevent fruit damage. Since ozone disappearance is not complete, the introduction of a technology which cannot be considered as human- and environment-friendly seems nowadays—and relative to the state-of-the-art of the process—prohibited.

Photochemistry under Ultraviolet Light. It has been shown by Shorter and Scott that ethylene can be removed by the use of UV-C germicidal lamps.^{91,92} The lamps emit ultraviolet radiation at 184 and 254 nm, though it is at the wavelength of 184 nm that the degradation of the ethylene is the most efficient. The ultraviolet radiation appears to be indirectly responsible for the degradation of ethylene and not the ozone, which is also produced as a byproduct. A model describing the UV-initiated photochemical and chemical processes leading to the destruction of ethylene was developed by Jozwiak et al.⁹³ and can be described by the following series of reactions:





where the symbol M denotes an inert third body.

The ozone can be removed either by a UV lamp emitting at 254 nm or by rusty steel wool. The major contribution to the rate of ethylene removal comes from the reaction of ethylene with atomic oxygen (eq 14).⁹⁴ The reaction of ethylene with ozone is practically negligible (very low O₃ concentration, eq 15), although its contribution increases slightly with initial concentrations of molecular oxygen. Lawton examined the efficiency of an ultraviolet ethylene remover located in a fruit store.³³ The system used little energy and did not contribute greatly to the heat load on the refrigeration plant. However, its overall efficiency remained very low: the ethylene level was found to be around 0.086 ppm in the store and 0.080 ppm in the outlet air stream exhausted from the scrubber, corresponding to a removal efficiency of only about 7%. According to the manufacturer of this particular unit, the scrubber efficiency drops markedly for very low ethylene levels. Moreover, due to very low oxygen concentrations, such ethylene scrubbers showed lower performances in ethylene decomposition than expected, at the commercial scale in controlled atmosphere (CA) room applications.⁹⁵

VUV Photolysis of Ethylene. The VUV photolysis of ethylene, corresponding to the VUV excitation and subsequent photodissociation of ethylene, has been the subject of extensive studies. Indeed, ethylene is the simplest molecule with a carbon bond, for which the excitation of an electron in a conjugated π system to a π^* orbital “unlocks” the double bond and allows bond torsion.^{96–98} That is why ethylene is usually considered as a model system for hydrocarbon dissociation dynamics, so that experimental and theoretical investigations on the VUV ethylene photodissociation are mainly performed for elucidating the mechanism and pathway in the molecular decomposition of ethylene in the 58–197 nm wavelength range. Basically, the dissociation of ethylene under high energy photon excitation involves many primary photodissociation channels, observed for different energy thresholds and associated to dihydrogen molecule and hydrogen atom elimination. The relative branching ratio for the atomic and molecular hydrogen elimination channel is an interesting issue, and the triple dissociation channel remains complicated in the case of the atomic hydrogen elimination. However, yet even this simple case of ethylene displays rich internal conversion dynamics. Details can be found in the review of Sato reporting on investigations in gas-phase photodissociation dynamics, with a focus on the photodissociation of unsaturated aliphatic hydrocarbons such as ethylene.⁹⁹ One has to point out that the investigations on the VUV photolysis of ethylene are usually favored due to the simple and model nature of the ethylene molecule and due to its importance in astrophysics, combustion, and atmospheric science, rather than for studying and implementing a possible technology for removing ethylene from air.^{100–104}

Catalytic Oxidation. Among the complementary ethylene removal techniques used for storing fruits and vegetables and

described in the previous paragraphs, only two have actually met the requirements for being successfully used on a commercial scale. Compared to the use of potassium permanganate, based on ethylene chemisorption, the catalytic oxidation of ethylene (eq 2) at high temperature (200–250 °C) appeared as an economically viable alternative, especially for treating large volume storage rooms.¹⁰⁵ Such a process was carried out on expensive catalysts based on platinum, copper, or a copper/zinc mixture. Wojciechowski,¹⁰⁶ Dilley,¹⁰⁷ Blanpied et al.,⁷³ and Dover and Sharp¹⁰⁸ attempted to modify and to apply the typical techniques of catalytic gas combustion to ethylene removal. There is, however, very little information on the wider application of these techniques in practice.

As an example of this technique, we can cite the catalytic gas purification process called “Swingtherm” adapted to ethylene removal and developed by Wojciechowski.¹⁰⁶ Figure 7 shows a schematic view of a “Swingtherm” converter for removing ethylene from storage chambers and evidences the symmetry of the process.

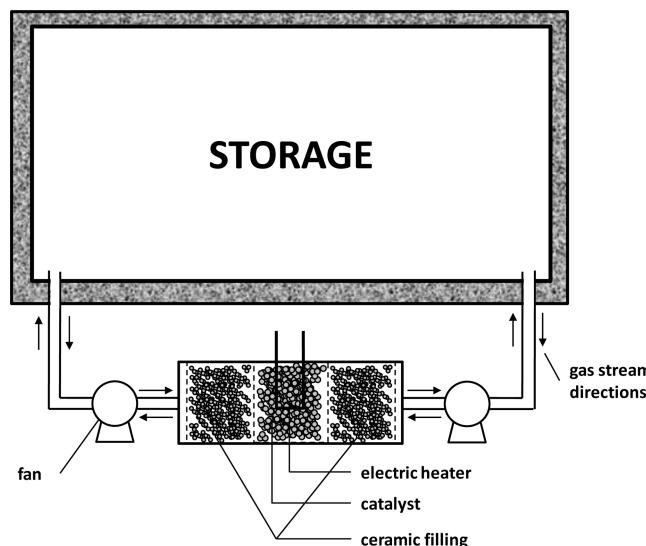


Figure 7. Scheme of the ethylene removal by means of a catalytic oxidation-based Swingtherm converter. Redrawn and reprinted with permission from ref 106. Copyright 1989 International Society for Horticultural Science.

Air contaminated with ethylene is drawn by one of the two fans and pumped through the catalytic reactor in which it passes consecutively through one layer of ceramic filling, the catalyst bed, and a second layer of ceramic filling, before finally being injected back into the storage chamber through the second fan. The direction of the gas flow is cyclically reversed, at constant time intervals by means of the consecutive operation of the two fans. Electric heaters supply heat continuously to the middle part of the catalyst bed, in which it accumulates due to the cyclical changes in gas flow direction, resulting in the required increase of the bed temperature up to 180–250 °C. The platinum catalysts used in this system claim to have 97% efficiency at a load of 10.000 L per liter of catalyst per hour (i.e., an hourly space velocity of 10000 h⁻¹). The ethylene conversion rate does not change in the concentration range of 0.1 ppm to 50 ppm. The average difference between the inlet and outlet gas temperature is about 10–15 °C.

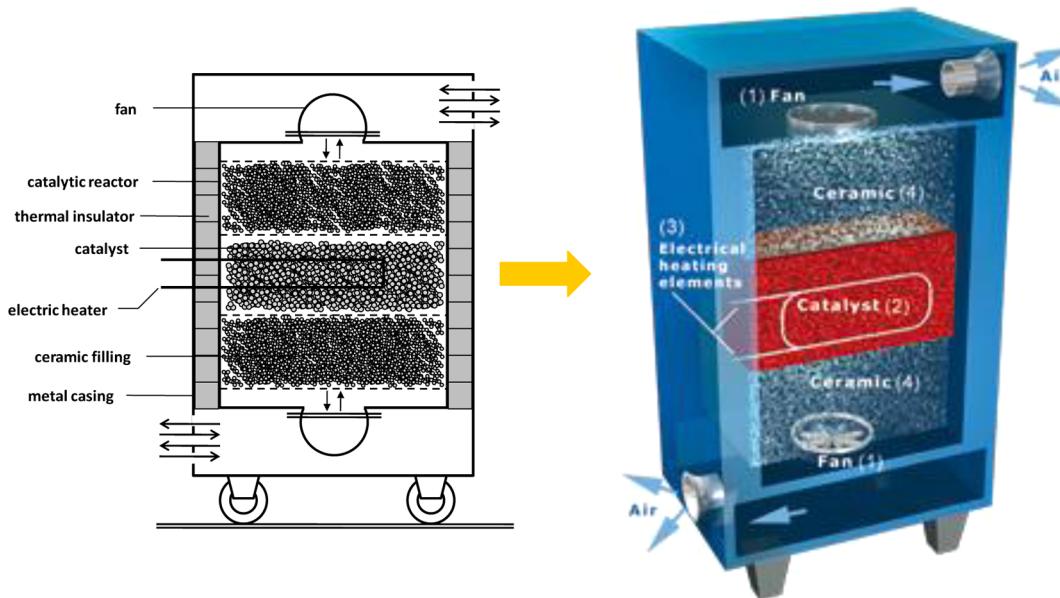


Figure 8. Mobile Swingtherm ME ethylene converter based on catalytic oxidation. The catalyst used consisted of platinum particles obtained from a diluted solution of chloroplatinic acid, supported on commercial refractory oxide grains. Redrawn and reprinted with permission from ref 106 and 109. Copyright 1989 International Society for Horticultural Science. See <http://www.absoger-controlled-atmosphere-nitrogen-generator.com/>.

An example of a commercial converter device that has found a wide use in storage applications is the Swingtherm ME (Figure 8—e.g. Absoger ethylene scrubbers¹⁰⁹).

The specifications, cost, and examples of beneficial effects of the use of such converters for the storage of various horticultural crops can be found in ref 106. A more recent study on the catalytic combustion of ethylene at low temperature (100–130 °C) was performed by El Blidi et al.¹¹⁰ The authors used mixtures of metallic oxides as catalysts (Mn and Cu oxides, with or without a substantial amount of MnCO₃, manganese carbonate), also incorporating a minor organic fraction and promoters such as sulfur, potassium, and calcium, responsible for enhancing the catalytic activity. It is worth noting that a transfer of the catalytic technology was performed, from the laboratory pilot scale, optimized by experimental design in terms of catalysis temperature and initial ethylene concentration, to an industrial prototype containing 90 kg of catalyst, for which the ethylene removal efficiency was evaluated in a large volume storage room (1800 m³) filled with Golden Delicious apples (282 t).¹¹¹

It should be noted that commercializing devices based on the combustion technology requires the use of ceramic heat exchangers for preheating the inlet flow before the catalytic combustion chamber and for cooling the air flow after the ethylene treatment before reinjecting the air at a temperature close to that of the storage room.

Scrubbing units based on the catalytic oxidation of ethylene are available on the market¹⁰⁹ and are used to a limited extent in some commercial storage facilities.

The claimed advantage of the system is that the units are easy to install and to operate, and that they maintain a constant low ethylene concentration due to a stable conversion efficiency of 90–98%. The disadvantage of the system is that the catalyst bed is very expensive and is only warranted by the manufacturer for 2–3 years. Furthermore, the scrubber, even with an efficient heat exchanger, puts a significant heat load on the refrigeration system, which results in some dehumidification and additional energy use. Measurements on a commercial production unit

showed a significant decrease in the conversion efficiency at lower ethylene concentrations, which severely affected the economics of the system. Moreover, as reported by Lawton,³³ the degradation of chlorofluorocarbons (CFCs) leaking from refrigeration equipment can be a cause of catalyst deactivation and of damage to the scrubber.

4.2.7. Ethylene Adsorbents. Besides destructive techniques based on the removal of ethylene by oxidation (often labeled as ethylene scrubbers), the recuperative techniques operate on the principle of adsorption. Adsorption phenomena can be efficiently used to achieve a very selective separation process for removing a small quantity of an adsorbate from a fluid stream. Adsorption of any molecule depends on several parameters, such as temperature, its concentration or partial pressure, and the gas composition. In particular, the presence in the gas stream of other molecules such as H₂O or CO₂ that can compete for adsorption sites with the target molecule will greatly influence the choice of adsorbent material.

Flowers and vegetables are generally stored/transported under high humidity conditions—usually with a relative humidity greater than 80% (see Table 3)—and an effective ethylene adsorbent should thus be able to work under high humidity conditions. Surprisingly, despite the wide and considerable interest in food technology processes, published results on ethylene adsorption under horticultural product storage conditions (i.e., low ethylene concentrations, high relative humidity, low temperature, presence of other molecules) remain very scarce. Most studies have only evaluated the impact of an adsorbent on a single product, without discussing the adsorption mechanism itself. In addition, only seldom papers report the ethylene adsorption isotherm or even the adsorption capacity of the adsorbent under the studied conditions. This lack of systematic quantitative and comparative studies of different ethylene adsorbents has hindered significantly the wide use of adsorbent scrubbers with horticultural commodities. The two main groups of adsorbents used for this purpose are zeolites and carbon-based adsorbents.

Table 10. Examples of Adsorbents and Their Ethylene Adsorption Capacities^a

adsorbent	BET (m ² g ⁻¹)	temp (°C)	ethylene adsorption capacity (mmol kg ⁻¹)	ethylene content (ppm)	water content	hydrophobicity index (HI)	ref
mordenite Na	320	30	19.6	50		2.4×10^{-4c}	114
mordenite Na	320	30	1.3 ^b	50	4200 ppm	2.4×10^{-4c}	114
chabazite	25		~ 0.15	~ 3.5			115
KMnO ₄ based “adsorbents” ^e	25		34 – 41				76
saponite-TiO ₂	368	20	~ 10	120	20–30% RH	11 ^d	120
montmorillonite-TiO ₂	301	20	~ 15	120	20–30% RH	21 ^d	120
fluorine mica-TiO ₂	402	20	~ 10	120	20–30% RH	33 ^d	120
TiO ₂ -P-25	49	20	~ 10	120	20–30% RH	20 ^d	120
activated carbon (AC)	1120	30	~ 11–78	64–1000			119
carbon nanoballs (CNB)	1431	30	~ 7–11	64–400			119
Pd/AC	1109	30	~ 7–71	64–1000			119
Pd/CNB	827	30	~ 14–71	64–1000			119

^aData taken from refs 76, 114, 115, 119, and 120. ^bAdsorption equilibrium data in the case of a binary mixture of ethylene and H₂O. The equilibrium adsorption capacity for H₂O was 5.4 mol kg⁻¹. ^cHI was expressed as $(q_{C_2H_4})/(q_{H_2O})$, where q represents the adsorbed quantity at equilibrium. ^dHI (%) was expressed as $((1 - BET\text{ surface area in water adsorption})/(BET\text{ surface area in N}_2\text{ adsorption}) \times 100$. ^eThe “adsorption capacity” for KMnO₄ is in fact the oxidation capacity and, for a given KMnO₄ content, is a constant value not depending on the ethylene concentration. On the other hand, the adsorption capacity of any adsorbent is strongly decreasing with increasing ethylene concentration.

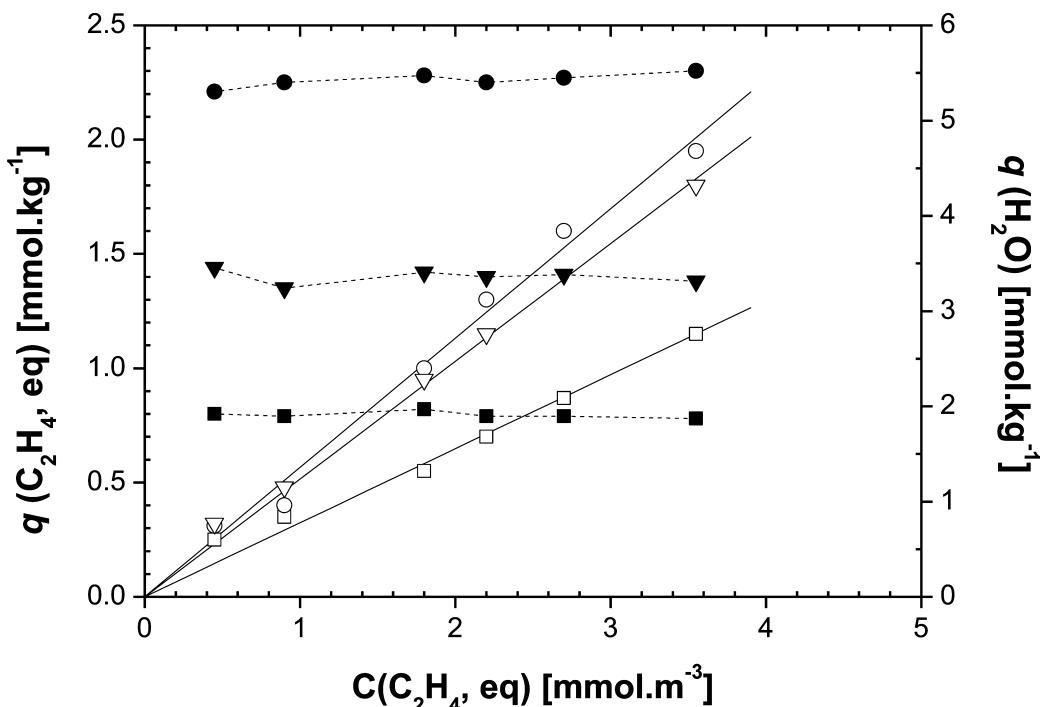


Figure 9. Amounts of adsorbed ethylene (open symbols) and water (solid symbols) for (○, ●) Na-mordenite SiO₂/Al₂O₃ = 18.3, (▽, ▼) H-mordenite SiO₂/Al₂O₃ = 18.9, and (□, ■) H-mordenite SiO₂/Al₂O₃ = 240 in a binary mixture system at 308 K. Redrawn and reprinted with permission from ref 114. Copyright 2005 Elsevier.

Table 10 compares different ethylene adsorbents and their properties.

Zeolites. Zeolites are aluminosilicate minerals displaying a three-dimensional framework structure with interconnected cages and channels. They have a high ability for adsorption of VOCs at concentrations below parts per million. The hydrophobic property of zeolite is an important factor for the removal of nonpolar VOCs, such as ethylene, because such VOCs are usually accompanied by water vapor at higher concentration (over 5000 ppmv) in air. However, it is known that the affinity of zeolite surfaces to water is reduced by dealumination.^{112,113}

A comprehensive study of a zeolite adsorbent has been published by Kim et al. and deals with the binary adsorption of a very low concentration of ethylene (10–100 ppm) and water vapor (4200 ppm) on mordenites and their desorption by microwave heating (Figures 9–11).¹¹⁴ In single-component experiments, the Na form of mordenite (NaMOR) adsorbed much greater amounts of ethylene than its exchanged H-form (HMOR) analogue with the same SiO₂/Al₂O₃ molar ratio (~18–19) (Figure 11). In the case of adsorption on HMORs, the amount of adsorbed ethylene was slightly higher for a SiO₂/Al₂O₃ ratio of 240 than for 18.9 at low ethylene concentrations,

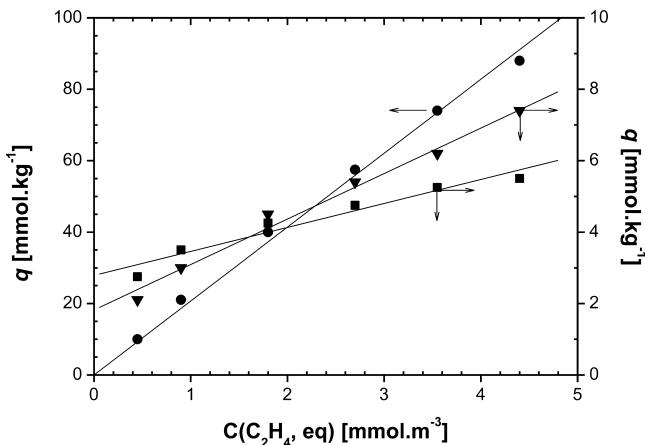


Figure 10. Adsorption isotherm of ethylene at very low concentration levels on (●) Na-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 18.3$, (▼) H-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 18.9$, and (■) H-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 240$. Redrawn and reprinted with permission from ref 114. Copyright 2005 Elsevier.

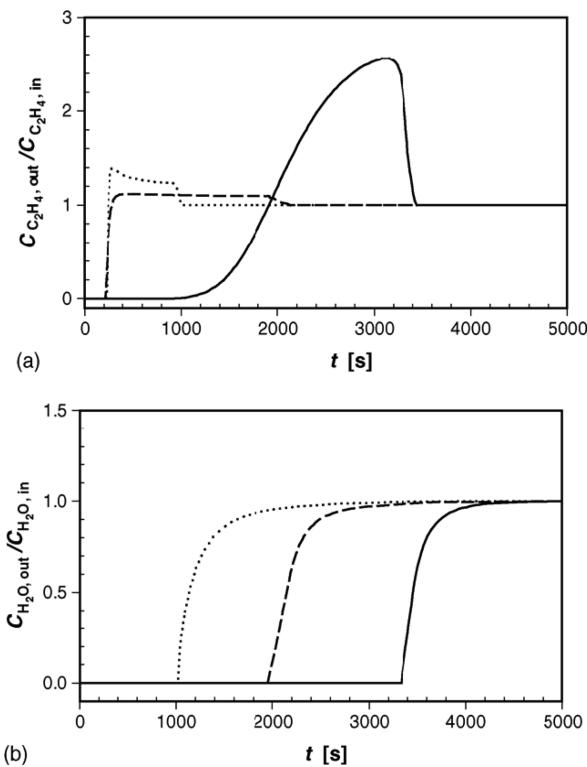


Figure 11. Breakthrough curves of (a) ethylene and (b) water in a binary mixture system of ethylene (2.23 mmol m^{-3}) and water vapor ($187.5 \text{ mmol m}^{-3}$) on (—) Na-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 18.3$, (---) H-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 18.9$, and (...) H-mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 240$ at 308 K . Reprinted with permission from ref 114. Copyright 2005 Elsevier.

while, by contrast, the contrary was observed for concentrations greater than 34 ppm.

The authors showed that, by microwave heating of Na-mordenite after preadsorption of ethylene and water, desorbed ethylene was concentrated maximally about nine times higher than in the initial inlet feed. The energy necessary for desorption was supplied by microwave-heated water, giving rise to a sharp ethylene desorption peak. The authors

considered Na-mordenite as the most favorable adsorbent for a cyclic adsorption–catalytic process. Such a process consists of consecutive adsorption, desorption, and catalytic oxidation steps with temperature swings in order to remove very low concentrations of ethylene. The ethylene preconcentration by subsequent adsorption–desorption will give rise to a higher rate of ethylene removal, since the catalytic oxidation of ethylene has always positive order with respect to its concentration.

Peiser and Suslow reported much lower ethylene adsorption capacities¹¹⁵ and showed that Chabazite zeolite adsorbed ethylene ($3.3 \mu\text{L g}^{-1}$) only if it was previously heat-treated at 150°C for 15 h and at 635 mmHg vacuum. In contrast, Clinoptilolite zeolite did not adsorb ethylene, with or without heat treatment. When 1.0 g of Chabazite with $3.3 \mu\text{L}$ of ethylene adsorbed and was subsequently exposed to an atmosphere with relative humidity close to 100%, more than 95% of the ethylene was released after 3 h. In contrast, heat-treated Chabazite placed in an atmosphere with relative humidity close to 100% for 1.5 h before ethylene application essentially lost all of its ethylene adsorption ability. In the investigated ethylene concentration range from 0.13 to 7.4 ppm, chabazite was able to adsorb about 94% of the ethylene added to a 1 L jar. In comparison, the commercially available Ethylene Control packet (a potassium permanganate-based product) removed all of the applied ethylene within 1 h and had an ethylene removal capability of about $929 \mu\text{L g}^{-1}$ ($\sim 41 \text{ mmol kg}^{-1}$).

Carbon-Based Materials. Bailen et al. showed an interesting combination of modified atmosphere packaging (MAP) ($\sim 4 \text{ kPa O}_2$, $\sim 10 \text{ kPa CO}_2$) with the use of granular-activated carbon (GAC) alone or impregnated with palladium as a catalyst (Pd/GAC), added to packages stored at 8°C and with 90% relative humidity in darkness.¹¹⁶ Palladium was introduced in the form of acetate (1 wt %). The addition of GAC or Pd/GAC led to a lower accumulation of ethylene (Figure 12a) in the MAP packages of tomatoes, to an improvement in fruit quality (in terms of sweetness, juiciness, odor, and flavor) after 14 days of storage, and to significantly delayed decay (Figure 12b). After longer storage periods, Pd/GAC showed better efficiency in fruit decay limitation than GAC alone.

Abe and Watada used charcoal impregnated with palladium chloride as an ethylene absorbent.¹¹⁷ It prevented the accumulation of ethylene in the surrounding atmosphere and was effective at 20°C in reducing the rate of softening in kiwi fruits and bananas and of chlorophyll loss in spinach leaves.

Another attractive ethylene adsorbing material, recently reported, is hollow, nanosized carbon spheres, called also carbon nanosized balls (CNBs),¹¹⁸ displaying large surface area and good porosity with inherent organophilicity. Liu et al. studied the ethylene adsorption capacities of hollow, CNBs, active carbon (AC), and PdCl_2 impregnated CNBs or AC (Pd/CNB, Pd/AC).¹¹⁹ The adsorbents were heat-treated under various conditions and evaluated at ethylene concentrations from 64 to 1060 ppm . At lower ethylene concentrations, both CNB and AC adsorbed ethylene with similar efficiency, while AC showed a better adsorption capacity at higher ethylene concentrations. By contrast, the reverse behavior was observed on the Pd impregnated carbon adsorbents, with Pd/CNB being more efficient than Pd/AC at lower concentrations.

Clays. Ooka studied the influence of the surface hydrophobicity of TiO_2 -pillared clays on the adsorption of different gaseous molecules in air.¹²⁰ Three kinds of TiO_2 -pillared clays

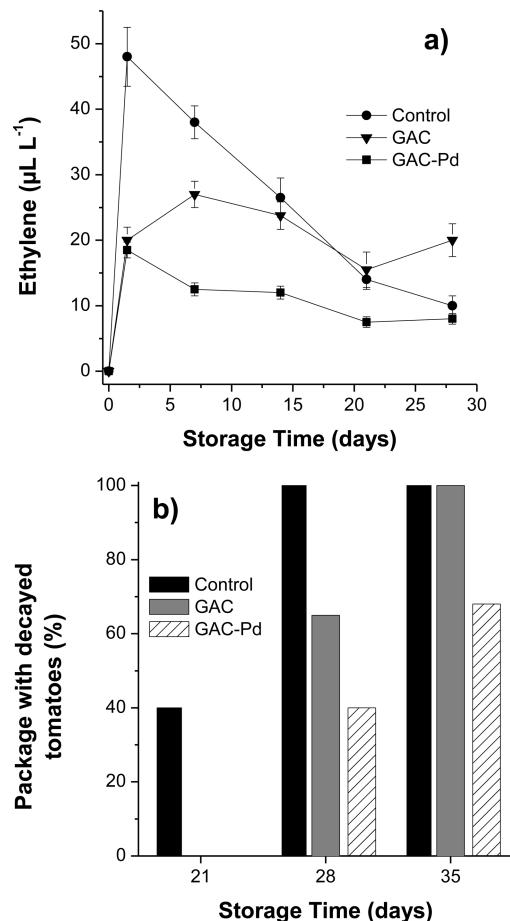


Figure 12. (a) Ethylene concentration in the MAP and (b) percentage of bags that showed some decayed fruit as a function of the storage time for MAP-packaged tomatoes. Redrawn and reprinted with permission from ref 116. Copyright 2006 American Chemical Society.

(Saponite-Ti, Montmorillonite-Ti, and Fluorine-mica-Ti) were prepared using the corresponding raw clays. However, all of them showed amounts of adsorbed ethylene similar to that obtained on TiO₂ P-25 (see Table 10) and no correlation between the amount of ethylene and the hydrophobicity index of the pillared clay could be drawn, so that the authors concluded that the surface hydrophobicity of the clays did not influence the ethylene adsorption.

Remarks. The comparison of adsorbents remains highly difficult and only qualitative, since the available data are scarce and strongly asystematic. The adsorbents display low ethylene removal capacity when compared with oxidative removal techniques, and the possibility of regeneration remains only a minor advantage if this regenerative step is not coupled to an oxidative ethylene removal process. Future development of a high performance ethylene adsorbent will require further investigation with implementation of various strategies. One could cite the understanding of the adsorption mechanism for multicomponent systems for which the literature lacks of data (i.e., study of the competitive adsorption of ethylene in the presence of additional gases and simulation of different atmospheres depending on the produce and storage parameters such as temperature, relative humidity, oxygen and CO₂ partial pressures, and presence of other molecules), the development of hydrophobic adsorbents selective in high relative humidity atmospheres, the ability of supporting different metals for

improving adsorption by π -complexation, the development of an appropriate desorption mode (temperature or pressure swing), as well as the coupling with an oxidative ethylene removal method. Among different coupling strategies, coupling adsorption and photocatalytic oxidation will be presented in section 5.6.

We have to point out that KMnO₄-based products which are the most widely used in practice are often referenced by manufacturers as *adsorbent* scrubbers for ethylene, although the efficiency of such materials only results from an oxidation capacity as previously detailed in section 4.2.6. and, thus, from the stoichiometry of the reaction with permanganate. This capacity remains constant whatever the ethylene concentration, contrary to the adsorption capacity of any adsorbent, which strongly decreases with decreasing the ethylene concentration. This highlights a strong discrepancy between the scientific terminology and that used by manufacturers, which often leads to misunderstandings. However, due to its wide use, the ethylene removal capacity for KMnO₄-based products (containing usually 4–6 wt % of KMnO₄), can serve as a reference for comparison with other adsorbents. Keeping in mind the crucial restrictions mentioned above, Table 10 shows a similar order of magnitude for carbon-based adsorbents.

4.2.8. Active Packaging. Active packaging (AP) is an innovative concept which, by changing the condition of packaging, extends shelf life or improves safety or sensory properties while maintaining the quality of the food.¹²¹ The main active packaging techniques are concerned with substances that absorb oxygen, ethylene, moisture, carbon dioxide, and flavors/odors and with those releasing carbon dioxide, antimicrobial agents, antioxidants, and flavors (Figure 13). Oxidants (such as KMnO₄) as well as ethylene adsorbents (mostly based on activated carbon) can be used in active packaging technology.

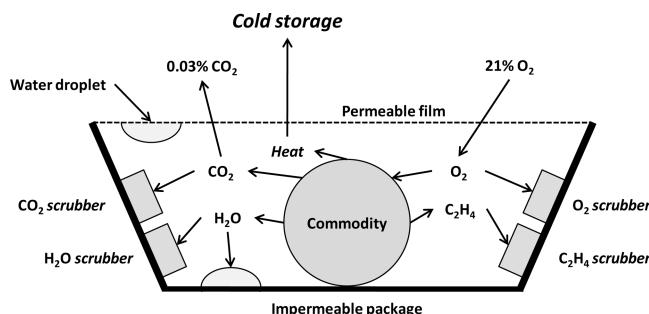


Figure 13. Active packaging.

Other ethylene-adsorbing technologies are based on the inclusion of finely dispersed minerals such as zeolites, clays, and Japanese oya into packaging films.⁷⁵ Most of these packaging films, however, are opaque and not capable of adsorbing sufficient amounts of ethylene. Although the incorporated minerals may adsorb ethylene, they also alter the permeability of the films: ethylene and CO₂ diffuse much more rapidly, and oxygen enters more readily than through pure polyethylene (PE) films. These effects can improve shelf life and reduce headspace ethylene concentrations independently of any ethylene adsorption. In fact, any powdered material can be used to achieve such effects. Furthermore, the adsorbing capacity of minerals is often lost when incorporating these minerals into a polymer matrix.⁶³ It is worth mentioning here

that, although not yet applied, there is great potential for the successful application of photocatalysts in modified atmosphere packaging. Indeed, Maneerat studied at the laboratory scale a TiO₂-coated plastic film for the photocatalytic decomposition of ethylene gas in fruit packaging.¹²² It is worth noting that such photocatalytic films can be used to remove not only ethylene but also other volatile compounds that can have a negative impact on produce.

4.3. Additional Operating Parameters of Interest in the Frame of the Strategy Aiming at Removing Ethylene from the Plant Environment

Whatever the nature of the technique used for removing ethylene from the plant environment, destructive *via* oxidation or recuperative *via* adsorption, additional impacting parameters, such as the heat input from the external scrubbing systems and both air-flow pattern and temperature distribution, are of high interest to take into account. Indeed, such unusual additional parameters enable strongly influencing the efficiency of the technology.

4.3.1. Heat Input from External Scrubbing Systems. A parameter that is very scarcely taken into account—although it is of high importance—is the heat input resulting from external scrubbing systems such as oxidation-based ethylene scrubbers. The inevitable addition of an extra heat load on the store's refrigeration plant is the main limitation of the use of such systems.²² Even with an efficient heat exchanger, the gas feeds back to the store at a higher temperature than the gas in the store. This may still be the case for a system operating at essentially ambient temperatures as a result of the heat input from the circulation fan, and that ambient may be above storage temperature for many commodities. Table 11 shows the increase in refrigeration requirement resulting from this heat input for a typical apple store of 100 t capacity.

Table 11. Increase in Refrigeration Plant Running Time for a Typical 100 t Apple Store as a Result of the Heat Input from an External Scrubbing System

heat input (kW)	mean total heat load (kW)	increase in refrigeration plant operation (%)
0	2.8	0
0.2	3.0	8
0.4	3.2	16
0.6	3.2	23
0.8	3.6	31
1.0	3.8	39

Moisture loss from the stored produce is a function of the plant operation, and thus additional heat loads should be kept to a strict minimum. The heat input is determined by both gas temperature and flow rate. The flow through the removal system is defined by the ethylene production rate of the commodity, the desired concentration, and the removal efficiency of the system (Table 12). A high production rate together with a low concentration requirement will result in a high flow and large heat input, which may be prohibitive in terms of capital and running costs and in moisture loss.

4.3.2. Air-Flow Patterns and Temperature Distribution. Since it was reported that temperature and humidity control during cooling, storage, transportation, and display were essential to the maintenance of product quality, it is of great importance to also work at the container level during the storage and transportation steps of perishable fresh product life.

Table 12. Store Gas Flow through an External Scrubbing System as a Function of Both Ethylene Concentration and Production Rate^a

desired ethylene conc (ppm)	flow (m ³ h ⁻¹) for 100 t of produce at the following production rates (μL kg ⁻¹ h ⁻¹)		
	0.01	0.1	1.0
0.01	110	1100	11000
0.1	11	110	1100
1.0	1.1	11	110

^aA removal efficiency of 90% is assumed.

In the majority of food refrigeration systems, heat is transferred primarily by convection. Therefore, air-flow patterns directly govern the temperature and its homogeneity. Recently, significant spatial temperature variability has been observed in different food refrigeration systems, mainly caused by nonuniform air flows.^{123–125} In the case of sensitive products, this temperature variability may strongly impact on food quality and safety. The design of the air-distribution system should allow heat fluxes exchanged through the insulated walls or generated by the products to be compensated for by the air flows. This compensation process is absolutely essential in order to decrease temperature differences throughout the cargo.¹²⁶ The air is usually supplied at relatively high velocity from a small inlet section located close to or near the ceiling, and via the coanda effect, the confined wall jet produced can directly remove the heat fluxes exchanged by the walls, at least as far as possible.^{127–129}

Understanding the different phenomena controlling, associated to, and impacting on air flows and product temperatures remains a highly difficult task due to a large number of interdependent parameters acting simultaneously.¹²⁶ It is admitted that these factors are usually dependent on operating and/or ambient conditions, so that even partially optimizing some of the factors usually requires extensive practical experimentation. Therefore, numerical modeling has attracted growing interest as an economic alternative to experimentation, although obviously it is well established that the reliability of the models is established from their validation against experimental figures. Air-flow models for refrigeration systems have been developed for over 30 years.¹³⁰ Since the beginning of the 1990s, first-principles computational fluid dynamics (CFD) has become a methodology of choice for developing air-flow models, obviously helped by the proliferation of powerful computers and driven by the current growing emphasis on the power consumption of refrigeration systems and by the sudden awareness of the impact of temperature heterogeneity on food quality and safety.

The reader is likely referred to the excellent recent review of Smale et al. dealing with numerical modeling approaches—including the application of CFD—of air flow in refrigerated food applications, such as, e.g., cool stores, transport equipments and retail display cabinets.¹²⁶ In most food refrigeration systems, the air-flow patterns in the system directly governs the temperature homogeneity, and numerical modeling of air flow provides an opportunity to develop an improved understanding of the underlying phenomena influencing system performance, which can lead to reduced temperature heterogeneity and increased effectiveness and efficiency of refrigeration systems. The authors highlighted the interest of dynamic CFD simulations, with the integration of more sophisticated turbulence models than the widely used k–var. epsilon

model, that has been shown not to be sufficiently accurate for use in many applications. However, one should note that this review also envisaged network models for providing an alternative approach to the CFD modeling methodology for transport systems and predicting air flow in refrigerated food applications. The authors have pointed out that these models would also benefit from a multiscale approach in which CFD could be used to develop correlations for important geometries in transport systems.

4.4. Comparison of Ethylene Removal Systems

The general approaches used to modulate ethylene activity involve controlling exposure (environmental modifications), as well as altering perception or varying the response of the tissue (plant level modifications). In spite of the high importance of ethylene removal in the horticulture produce distribution chain, there is surprisingly very little comparison of different methods in the literature (and none comparing both plant receptor level and plant environment level strategies), although practical uses for ethylene and treatments to minimize its adverse effects have slowly accumulated over almost a century of study.

Lawton has examined four methods (ventilation, catalytic oxidation, photochemistry under UV-C light, and KMnO_4) of ethylene removal.³³ Each of the ethylene removal systems was installed in a 20 ft integral refrigerated container (i.e., 33 m³ of useful volume), and the ethylene concentration was monitored as a function of time for each ethylene removal method, with 17–19 ppm as the starting ethylene concentration. The experimental results are shown in Figure 14. Unfortunately, this interesting study from 1991 did not exploit all the data for drawing conclusive remarks on the relative efficiencies.

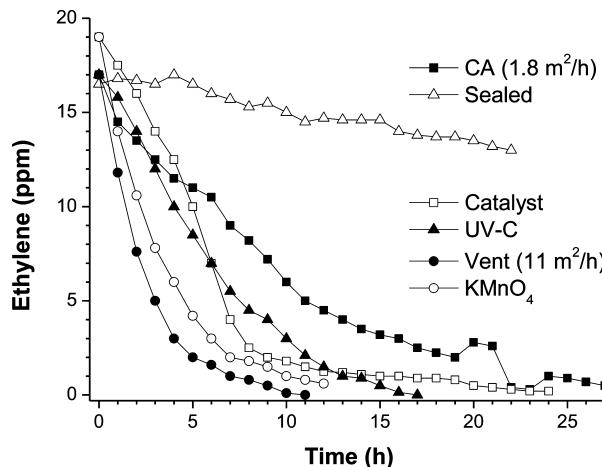


Figure 14. Comparison of ethylene removal with different systems. Lawton reported in his testing report that the catalytic system used here was designed for a 300 t store and, therefore, that a correction for a 12 t store has been made, without mentioning the correction relationship. Data redrawn and reprinted with permission from ref 33. Copyright 1991 International Institute of Refrigeration (www.iifir.org).

In conditions for sea shipment, it was determined that, under normal refrigerated air storage, ethylene can be removed efficiently by ventilating with ambient air, which is seldom sufficiently polluted to cause any injury even to very sensitive products. Ambient levels in the sea transport environment rarely exceed 10 ppb (measured at pack houses, container terminals, and ports in Australia, New Zealand, and over the

Pacific and Atlantic oceans). Overall, it was concluded that ventilation with air is still, up to now, the best available method for the removal of ethylene gas. For air storage, an economic appraisal of ventilation against a scrubbing system would need to include the external ethylene concentration as well as the effect and management of heat load on the store produced by different methods of ethylene removal.⁴¹

Palou and Crisosto evaluated the effects of postharvest treatments with AVG, 1-MCP, and potassium permanganate sachets on postharvest quality attributes of apricots.¹³¹ They concluded that all three treatments could be used to satisfactorily delay fruit softening and prolong postharvest life. However, the response to these treatments may vary with cultivar and maturity stage, treatment timing and characteristics, and storage conditions after treatment. In particular, the presence of exogenous ethylene during storage or shipment could counteract the effect of these treatments.

Leventisz-Huszár et al.¹³² compared three methods (active carbon adsorption, catalytic combustion, and KMnO_4). The investigations were carried out in a gastight polyethylene foil tent of 10 m³ volume at room temperature in a model atmosphere (in the absence of fruits), the same as in industrial storage chambers with reduced oxygen content and saturated with water vapor. The most effective method was catalytic combustion (Swingtherm) with 20 m³ h⁻¹ capacity and 170 W electrical output, which required 1.5 h to reduce by half the initial 800–900 ppm of ethylene. However, the efficiency of the catalyst was significantly reduced at lower ethylene concentrations, with the halving time at 30 ppm increasing to 3 h, and this strongly limits the interest of such a device. By contrast, no suitable carbon-based adsorbent was found.

Finally, one can also put forward that simple methods, such as ventilation and temperature management, can be combined with more sophisticated treatments, such as controlled atmospheres, modified atmosphere packaging, inhibitors of specific induced enzymes, or ethylene scrubbers, to provide conditions that optimize both storage life and product quality.

Although the positive effects of ethylene removal from the atmosphere surrounding crops have been widely described and the effects of ethylene are known to be related to multi-parameter interactions, including temperature, storage conditions, exposure time, and susceptibility of the product to damage, there is, however, little information on the comparison of different ethylene removal methods, and especially on their use in large commercial storage facilities and on the financial advantages gained by their application. Indeed, beyond laboratory scale experiments, the efficiency of different ethylene removal methods should be compared in different commercial storage facilities for a more precise determination of the benefits and costs emerging from storing horticultural crops at low ethylene levels (or no ethylene). Total removal or maintenance of ethylene at very low levels can be expensive in terms of both equipment requirements and running costs. Thus, additional information on the costs and benefits of ethylene removal for products stored under commercial conditions would be of considerable interest to many industries. Unfortunately, there is a strong lack of data recorded during on-site measurement series, and even of data obtained at the laboratory scale in postharvest chambers.

So, it is our sincere hope that this review will encourage academics and industrialists to conduct cooperative projects for extending lab-scale reactor tests to lab-scale postharvest chamber tests and finally to real on-site measurements. Also,

we wish that this review will stimulate the achievement of more numerous comparative studies and that, among different ethylene removal methods, photocatalytic oxidation (detailed in section 5) can be considered as an interesting alternative to stoichiometric ethylene oxidation or catalytic oxidation and also to plant level modifications such as genetical or chemical blocking of ethylene synthesis and action.

5. PHOTOCATALYTIC OXIDATION OF ETHYLENE

5.1. Introduction

Within the advanced oxidation processes developed to meet ever stricter antipollution legislation and driven by the pressure for environmental protection, heterogeneous photocatalysis attracted worldwide a growing interest and appeared in the middle of the 1980s to be promising for the purification of contaminated wastewater containing organic pollutants and the removal of air contaminants. It requires the use of semiconductor materials with suitable band gaps as catalysts, with energy being supplied by the direct absorption of light rather than by thermal heating as in conventional catalysis (photonic vs thermal activation). Among the semiconductors used that are activated by UV light, titanium dioxide (TiO_2) is currently the most attractive and efficient, with a high photocatalytic efficiency due to its high quantum yield, stability toward photocorrosion and chemicals, insolubility in water, low toxicity, and low cost. Its band gap energy of 3.2 eV leads to photoexcitation requiring wavelengths less than ca. 385 nm, corresponding to a UV irradiance. Similarly to classical heterogeneous catalysis, the photocatalytic process can be decomposed into independent steps: transfer of reactants to the catalyst surface, adsorption, reaction in the adsorbed phase, product desorption, and transfer to the gas or liquid media. The reader is encouraged to refer to the many well-documented reviews and books devoted to both fundamentals and applications of photocatalysis.^{133–143}

Photocatalysis is an emerging and promising technology. Considered as a laboratory process for many years, it is now enjoying unprecedented development resulting from simultaneous efforts by research laboratories and industrials in the search for innovative solutions to the environmental treatment of liquid and gaseous effluents, and surfaces. This has resulted from the advantages that photocatalysis can offer to the targeted application fields foreseen by both academic and industrial partners.

The state of the art on photocatalytic oxidation of ethylene is reviewed, including the reaction mechanism and the influence of reaction parameters as well as the photocatalytic materials investigated. Focus has been made on the research efforts aiming at an increase in the efficiency of the ethylene removal photocatalytic process, notably by associating photocatalysis to other technologies, and advantages of implementing photocatalysis are reported in view of the application of the technology to the storage of fresh products storage.

5.2. Unexpected Fruit Storage Applications as Driving Force for New Ethylene Removal Technologies

The search for the development and implementation of new technologies has been a driving force in reaching breakthroughs in ethylene removal from air for many decades. Surprisingly, two unexpected applications of fruit storage acted as one of the driving forces for the development of a technology for removing ethylene, that is the removal of ethylene in military food supply and in space flights.

Indeed, supplying military forces with high quality fresh fruits and vegetables in foreign bases has always been a major challenge.¹⁴⁴ Taking as an example U.S. troops, the majority of the fresh products consumed in the Pacific and Far East come from a long, sometimes more than three week, supply line over the ocean from the US West Coast. Although ships in the Mediterranean Sea are supplied with produce from local countries, they only take on board a quantity that can be consumed before spoilage occurs and, therefore, require frequent resupply. Therefore, removing ethylene by a low energy-consuming technology could be of high interest for such applications. Submarines, which are sometimes at sea for months without contact or resupply, could also benefit from the design of such an ethylene removal technology (Reports from Defense Supply indicated that spoilage could be as high as 30% or more for individual products).

Also, spaceflight plant growth for bioregenerative life support (BLS) represents another important challenge for ethylene removal, especially due to small confined spaces and the impossibility of ventilation.^{145,146} BLS systems are considered as the best strategy for supporting long-duration space missions. An integral part of a BLS system is a chamber supporting the growth of higher plants that would provide food, water, and atmosphere regeneration for a human crew. Ethylene production by 20 m² stands of wheat, soybean, lettuce, and potato was monitored throughout growth and development in NASA's Controlled Ecological Life Support System (CELSS) Biomass Production Chamber. Ethylene can accumulate in closed growth chambers at levels well above those to which crop plants are normally adapted; for example, studies indicate that ethylene levels as low as 50 ppb result in a 25% yield reduction in wheat. Building and testing a photocatalytic device at the Wisconsin Center for Space Automation and Robotics (WCSAR) have pointed out that major implications for using photocatalysis to eliminate pollutants from confined spaces could be derived for NASA applications (such as long-term spaceflights dealing with both Space Shuttle and International Space Station) as well as for the general use of photocatalysis in non-NASA applications.¹⁴⁷

Compared with the different ethylene oxidation methods, the photocatalytic oxidation process can be considered as a highly promising and reliable technology, combining the efficiency of the catalytic oxidation with both low energy consumption and low heat load resulting from the UV irradiance. It has proven to be an efficient method for removing ethylene from horticultural storage facilities in order to extend the postharvest storability of produce¹⁴⁸ and can further be used in combination with other means such as the cold storage, controlled atmospheres, or modified atmosphere packaging. Photocatalytic processes chemically oxidize (or convert) organic compounds into carbon dioxide and water at near-ambient temperatures to complete mineralization. Since the photocatalytic material is not consumed during the oxidation process, there is no need for the replacement and disposal of depleted treatment units. It can be applied to both large and small scale storage units and used for low and high ethylene concentrations.

Only very few studies have been performed to investigate the efficiency of ethylene removal by photocatalysis during the storage of fresh products. Maneerat et al. chose mature green tomato fruit (*Lycopersicon esculentum* cv. House Momotaro) for fruit ripening tests due to its high sensitivity to ethylene and because its principal reaction with ethylene can easily be observed as ripening from a green to a red fruit.^{148,149} The

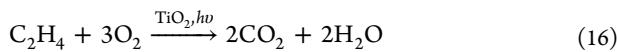
authors have observed that tomato fruit stored without TiO_2 photocatalytic reaction showed a ripening response (red fruit) after two weeks of storage at 25 °C, whereas those stored in the presence of TiO_2 photocatalytic reaction for removing ethylene showed no ripening response (green fruit). The color development, fruit softening, and ethylene climacteric peak of tomato fruits were strongly delayed under TiO_2 photocatalytic reaction storage, while tomato fruit without TiO_2 photocatalytic reaction storage ripened after four weeks of storage. It is worth noting that no differences in terms of the nutritional content (lycopene, vitamin A, and vitamin C) and of pH and total soluble solids (TSS) of ripe fruit were observed between fruits stored with and without TiO_2 photocatalytic reaction, and none of the tomato fruits stored in the presence of the TiO_2 photocatalytic reaction showed any symptoms of disorder when they ripened.¹⁴⁸

Since the accumulation of acetaldehyde and ethanol in the storage atmosphere is thought to be a problem during the fruit storage, both being responsible for the development of off-flavors,^{150,151} the photocatalytic process was also efficient at removing off-flavors from the storage atmosphere of red tomatoes (*Lycopersicon esculentum* Mill. cv. House Momotaro) over 10 days of storage.¹⁴⁹ Indeed, off-flavors were not present in the storage atmosphere of the TiO_2 treatment from days 0 to 8, with only a score of 1.0 after 10 days, while in the absence of TiO_2 treatment, the off-flavors were scored at 1.0, 3.0, and finally 4.0 for a storage of 4, 8, and 10 days, respectively (with “off-flavors” scores of 0 and 4.0 meaning no and very strong fermented or alcoholic odor, respectively). Both precursor studies were performed using a photoreactor based on a UV-A irradiated TiO_2 slurry located inside the fruit storage chamber, and not with one based on immobilized TiO_2 for running a pure gas-phase reaction. Unfortunately, such studies remain up to now very scarce.

However, although some commercial photocatalytic devices are already available and are claimed to have been designed for fruit storage chambers,^{109,152} its widespread industrial adoption will still require a significant research effort at both laboratory and industrial scales, demonstrating its performance in different storage/transport conditions, taking into account critical variables such as the type and amount of commodity, the storage duration, and the atmospheric composition.

5.3. Reaction Mechanism and Influence of Reaction Parameters

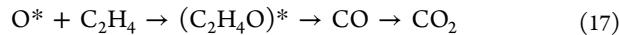
5.3.1. Reaction Mechanisms. Several studies dealing with the photocatalytic degradation of ethylene under UV irradiance have been reported in the literature.^{153–174} They basically showed that ethylene can be mineralized completely to CO_2 following a Langmuir–Hinshelwood type kinetic. The photocatalytic oxidation of ethylene is based on eq 16:



However, there is still uncertainty about the reaction pathway, and the molecular mechanism still needs to be unraveled. Initially it was difficult to establish a mechanism of ethylene degradation from experimental results collected from the literature, since the majority of the studies claimed that no organic product other than ethylene could be detected at the outlet of the photoreactor.^{154,157,162} Yamazaki et al. reported an increase in ethylene photocatalytic degradation rate with increasing ethylene concentration, at least in their experimental conditions, between 53 and 346 ppmv of ethylene.¹⁵⁷ This

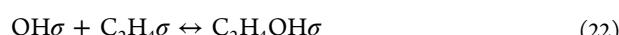
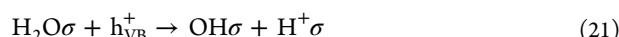
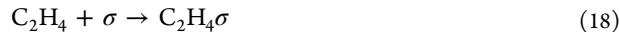
indicated that the reaction apparently seems to follow the Langmuir–Hinshelwood kinetic model with respect to ethylene concentration. They confirmed the results obtained a few years ago by Obee and Hay¹⁵⁵ and Tibbitts et al.¹⁵⁶ with lower ethylene concentrations. According to Fu et al.,¹⁵⁴ the rate of the oxidation of intermediates is probably faster than their rate of formation.

Park et al. have reported that the photocatalytic oxidation of ethylene at room temperature formed CO_2 , CO , and H_2O .¹⁵⁸ They proposed that ethylene was first oxidized to CO through the formation of a $\text{C}_2\text{H}_4\text{O}$ radical, which in turn was then oxidized into CO_2 following the sequence of reactions in eq 17:



The authors have proposed that the key active species playing a significant role in the reaction sequence could be OH° radicals as well as O_2° and O_3° anion radicals. They mentioned that OH° radicals are obtained by reaction of adsorbed water with photoholes, whereas O_2° and O_3° anion radicals are formed by reduction of molecular oxygen by a photoelectron and by reaction of molecular oxygen with the hole-trapping O_1^- center, respectively. The oxygen rate in the reaction system was reported to be responsible for the product distribution of CO and CO_2 , and only when there is excessive oxygen in the feed is it possible that ethylene is completely oxidized into CO_2 with no CO release.

By contrast, Yamazaki et al. suggested that adsorbed ethylene reacts with OH° radicals to form $\text{C}_2\text{H}_4\text{OH}^\circ$ intermediate radicals, that can subsequently react with adsorbed oxygen to reach mineralization into CO_2 according to their reaction formalism (eqs 18–23):¹⁵⁷



where σ and σ' indicate different types of active sites at the surface of TiO_2 and eqs 18–20 imply the adsorption–desorption equilibrium for the reactants. The authors mentioned that the equilibrium processes for reaction intermediates or products have not been taken into account, since the kinetic experiments have been carried out under reaction conditions for which the catalyst operated at a conversion lower than 10%. They reported that the rate determining step was found to be the oxidation of $\text{C}_2\text{H}_4\text{OH}^\circ$ radicals by oxygen on the catalyst surface and that the rate law conformed to a Langmuir–Hinshelwood type kinetic. They suggested that the adsorption sites of water and ethylene are the same, so that water adsorption is in competition with that of ethylene, whereas the oxygen molecules adsorb separately on other surface sites. In their formalism, σ and σ' surface active sites correspond respectively to Ti^{4+} and Ti^{3+} surface sites (eqs 24 and 25), on which water and ethylene, and oxygen, adsorb and react, respectively.



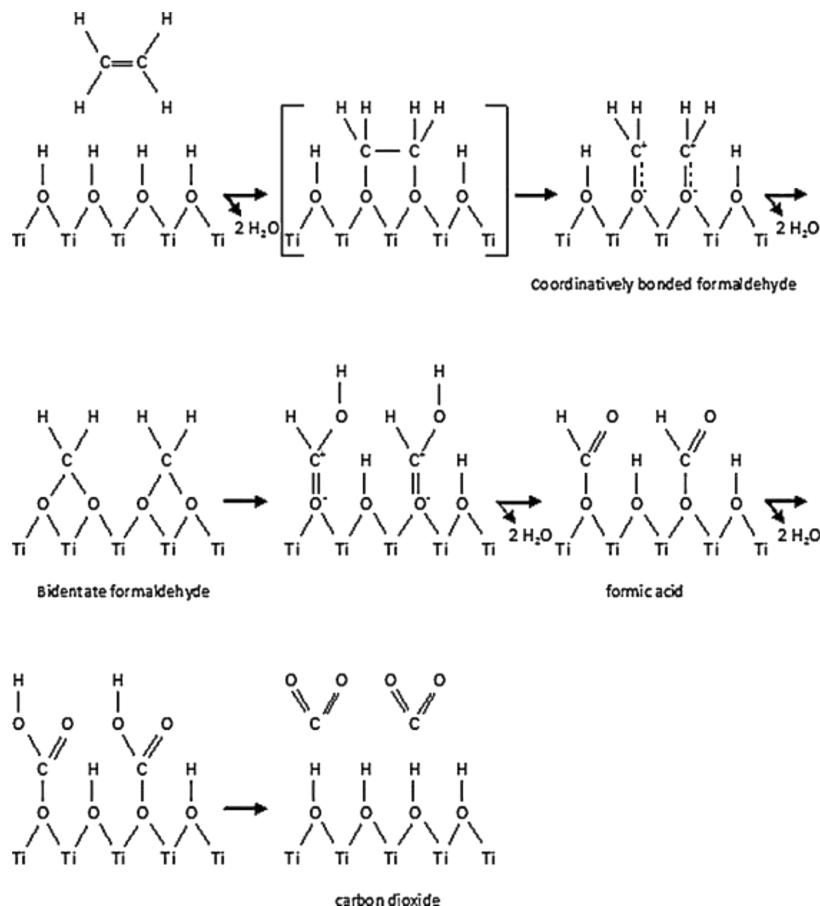


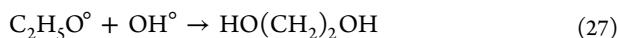
Figure 15. Reaction pathway of the photocatalytic oxidation of ethylene proposed by Hauchecorne et al. The electron flows and the OH° radicals have not been indicated for clarity purposes. Reprinted with permission from ref 169. Copyright 2011 Elsevier.



Hence, the reaction rate decreases with an increase in the water vapor molar fraction.

More recently, over zeolite- and silica-incorporated TiO_2 films, Tanaka et al. observed under recirculation the presence of three intermediates, i.e. formic acid, formaldehyde, and carbonate ion, with a production of formic acid and formaldehyde of about 0.1 and 0.08 mol {[mol of ethylene] $^{-1}$ }, respectively.¹⁶⁵ This led the authors to suggest the following possible degradation pathway starting from ethylene: $\text{C}_2\text{H}_4 \rightarrow \text{HCHO} \rightarrow \text{HCOOH} \rightarrow \text{CO}_2$. This mechanism was supported by work reporting the fission of the $\text{C}=\text{C}$ bond during the photocatalytic degradation of ethylene.¹⁷⁵

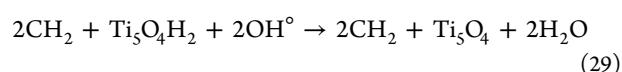
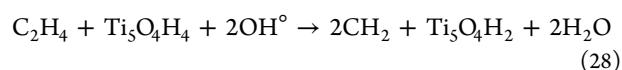
Recent *in situ* FTIR investigation reported by Hauchecorne et al. provided new insights on the way for elucidating the reaction mechanism.¹⁶⁹ The authors first ruled out the formation of $\text{HO}(\text{CH}_2)_2\text{OH}$ ethane-1,2-diol as reaction intermediate that could result from the breaking of the double bond of ethylene through OH° radicals (eqs 26 and 27), which is assumed to be the first reaction step.

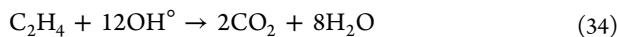
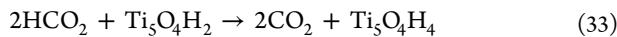
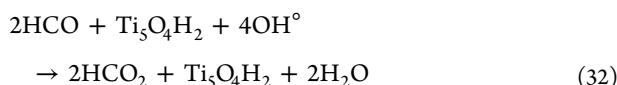
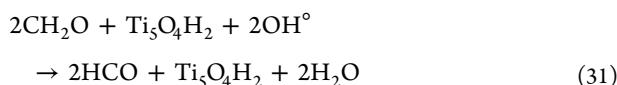
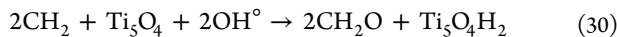


By contrast, the authors have proposed that there is a change in dipole moment of the ethylene molecule when it is brought in the neighborhood of the TiO_2 photocatalyst, and they preferred to put forward a new hypothesis on how the breaking of the

double bond of ethylene could occur. They proposed that an interaction between the negatively charged π -system of the ethylene molecule and the partially positively charged hydrogen atoms at the surface of TiO_2 occurs. The hydrogen atoms can then be split from the surface to form water molecules together with OH° radicals. Then, the lowest unoccupied molecular orbital (LUMO) of the ethylene molecule—the $2\pi^*$ orbital—can accept electrons from the photocatalyst following a backdonation process, till the complete filling of the $2\pi^*$ orbital with electrons, that causes consequently the breaking of the CC double bond of ethylene. This results in the formation of two coordinatively bonded formaldehyde molecules.

In a second step, they proposed that the coordinatively bonded formaldehyde could be oxidized to bidentate formaldehyde, following the hypothesis also formulated by Popova et al.¹⁷⁶ The authors also evidenced by *in situ* FTIR the presence of formic acid, as usually observed during the known photocatalytic oxidation of adsorbed formaldehyde molecules that leads to complete mineralization into CO_2 . According to their simplified formalism, Hauchecorne et al. could propose the following reaction pathway (eqs 28–33) with the overall eq 34, as schematized in Figure 15.





Regarding the well-known photocatalytic oxidation of formaldehyde, the reader is encouraged to refer to the detailed mechanism reported by Herrmann,¹⁴³ that includes all the dotted unpaired electrons which have to be considered as reactant intermediates belonging to stoichiometry. So, meeting the necessary requirement of mass balance in agreement with Lavoisier's principle, the establishment of the overall final mass balance equation revealed that two photons were required for mineralizing a single formaldehyde molecule, and the complete molecular mechanism detailed by Herrmann involves 14 elementary steps and includes 5 different radicals (OH° , O_2^- , $\text{H}-\text{C}=\text{O}$, $\text{H}-\text{COO}^\circ$, and HO_2°).

5.3.2. Influence of Reaction Parameters. Influence of Relative Humidity and Temperature. Determining the influence of relative humidity on photocatalytic behavior is usually of high importance, since, as for many catalytic reactions, heterogeneous photocatalysis of ethylene is a surface reaction with surface redox reaction and interfacial electron transfer. Ethylene is a nonpolar molecule, which would therefore weakly physisorb on the polar surface of titanium dioxide. As a result, the oxidation of ethylene should exhibit a strong dependence on the water vapor content. Consequently, the reaction kinetic is dominated by competitive adsorption between water and ethylene molecules especially. The influence of the content of water vapor in the feed stream on gas–solid photocatalytic oxidation has been well described by Fu et al.¹⁵⁴ and Obee and Hay¹⁵⁵ in the case of ethylene. The authors also mentioned that other studies have shown that the effect of water vapor depends strongly on the targeted reactant and on the concentration of the water vapor itself (Figure 16). Obee and Hay used the bimolecular form of the Langmuir–Hinshelwood rate equation, assuming the simplification that possible reaction intermediates and reaction products did not influence the observed oxidation rates and that only ethylene and water vapor were important. Taking that into account, the Langmuir–Hinshelwood rate was given by eq 35, and the L–H parameters derived can be found in Table 13.

$$r = k_0 \frac{K_e X_e}{(1 + K_e X_e + K_w X_w)} \quad (35)$$

where k_0 ($\mu\text{mol}/(\text{cm}^2 \text{ h})$) is the rate constant for a given UV intensity, K_e and K_w (ppmv^{-1}) are the Langmuir adsorption equilibrium constants, and X_e (ppmv) and X_w (ppmv) are the gas-phase concentrations of ethylene and water vapor, respectively. The ratio on the right-hand side represents competitive adsorption between ethylene and water for the same adsorption site.¹⁷⁷

The literature shows that the impact of humidity level depended on the temperature during the photocatalytic degradation. The experimental results indicated that the rate

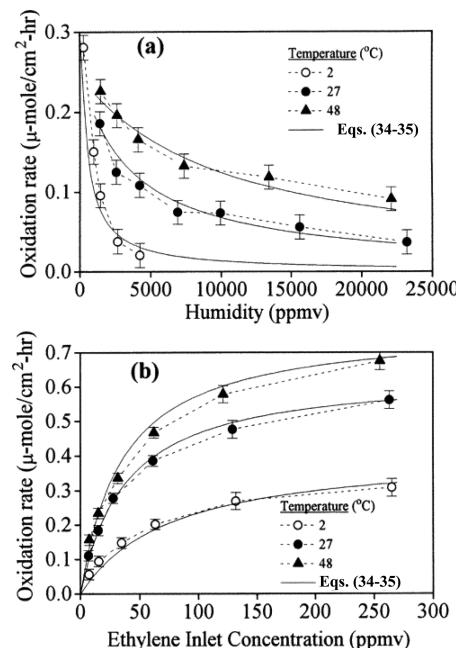


Figure 16. Ethylene photooxidation dependence: (a) influence of humidity level, 15 ppmv; and (b) influence of ethylene concentration, 1500 ppmv humidity. Reprinted with permission from ref 155. Copyright 1997 American Chemical Society.

Table 13. Langmuir–Hinshelwood Parameters for Eq 35^a

parameter	units	temp (°C)		
		2	27	48
k_0	$\mu\text{mol cm}^{-2} \text{ h}^{-1}$	0.41	0.63	0.75
K_e	ppmv^{-1}	0.077	0.045	0.035
K_w	ppmv^{-1}	0.00330	0.00045	0.00015

^aData taken from ref 155.

of ethylene photocatalytic oxidation increased with increasing temperature,^{154,155,157,158,160} although, by contrast, operating at higher humidity significantly decreased the rate of ethylene photooxidation (Figure 16a). Increasing the temperature led to a decrease in the adsorption of water, thus resulting in an increase in the rate of ethylene oxidation. Figure 17 shows this behavior, with the authors having observed a strong increase in the reaction rate between 30 and 65 °C, attributed to a significant decrease in the adsorption of water molecules which compete with ethylene adsorption.

Therefore, an explicit temperature dependence was further included by Obee and Hay in the L–H rate equation, given the following assumptions: (i) the temperature-dependence form of the Langmuir adsorption constants¹⁷⁸ for monolayer adsorption on a homogeneous surface can be applied to both ethylene and water molecules, and (ii) the k_0 rate constant follows an Arrhenius temperature dependence. Taking that into account led to proposal of the temperature-dependent rate law of eq 36, and the derived parameters can be found in Table 14.

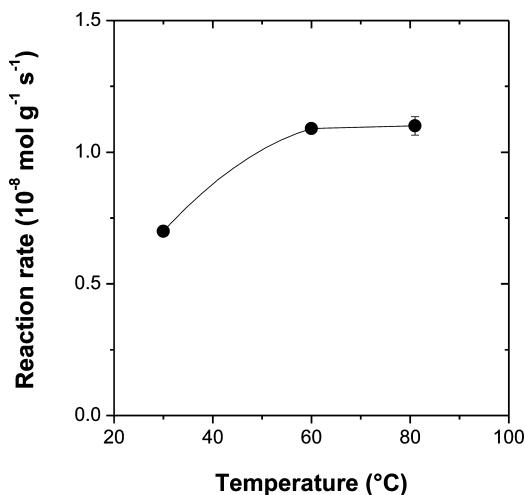


Figure 17. Influence of the temperature on the reaction rate. The molar fractions of ethylene, oxygen, and water vapor were 2.4×10^{-4} , 0.19, and 1.0×10^{-3} , respectively. Redrawn and reprinted with permission from ref 157. Copyright 1999 Elsevier.

$$r = \left[k'_0 \exp\left(-\frac{E}{RT}\right) K'_e \frac{\exp(-\Delta H_e/RT)}{\sqrt{T}} X_e \right] \left[1 + K'_e \frac{\exp(-\Delta H_e/RT)}{\sqrt{T}} X_e + K'_w \frac{\exp(-\Delta H_w/RT)}{\sqrt{T}} X_w \right] \quad (36)$$

Table 14. Parameters for Eq 36^a

parameter	units	1 ^b	2 ^c
k'_0	$\mu\text{mol cm}^{-2} \text{ h}^{-1}$	10.4	10.9
K'_e	$K^{1/2} \text{ ppmv}^{-1}$	0.0098	0.0089
K'_w	$K^{1/2} \text{ ppmv}^{-1}$	1.04×10^{-11}	2.3510^{-12}
E	kcal/mol	1.67	1.70
ΔH_e	kcal/mol	-2.61	-2.67
ΔH_w	kcal/mol	-12.2	-13.0

^aData taken from ref 155. ^b(1) ΔH_w constrained to -12.2 kcal/mol. ^c(2) ΔH_w unconstrained.

where k'_0 ($\mu\text{mol}/(\text{cm}^2 \text{ h})$) is the (temperature-independent) rate constant for a given UV intensity, K'_e and K'_w ($K^{1/2} \text{ ppmv}^{-1}$) are the (temperature-independent) Langmuir adsorption equilibrium constants, E (kcal/mol) is an apparent activation energy, ΔH_e and ΔH_w (kcal/mol) are the change in enthalpy accompanying adsorption for ethylene and water, respectively, X_e (ppmv) and X_w (ppmv) are the gas-phase concentrations of ethylene and water vapor, respectively, T (K) is the TiO_2 temperature, and R (1.99×10^{-3} kcal mol $^{-1}$ K $^{-1}$) is the gas constant.

Following this model, the unknown constants in eq 36 were determined either by setting the ΔH_w adsorption enthalpy for physisorbed water at -12.2 kcal/mol,¹⁷⁹ or through the optimization process. This led to calculate the ΔH_e adsorption enthalpy for physisorbed ethylene at -2.6 kcal/mol. In both cases, the rates derived from eq 36 did not significantly differ from eq 35 and was in good agreement with the measured data shown in Figure 16. Obee and Hay explained the observed behavior by the relative adsorption affinity of water and the

contaminant.¹⁵⁵ Physisorbed water is hydrogen-bonded to titanium dioxide with an adsorption energy of 12.2 kcal/mol, while the adsorption enthalpy of ethylene on titanium dioxide is close to -3 kcal/mol (-2.6 kcal/mol for Obee and Hay¹⁵⁵ and between -3.2 and -3.8 kcal/mol for Fu et al.¹⁵⁴). The reaction rate is thus probably limited by the low adsorption of ethylene due to its low adsorption affinity compared to water.

However, one should add that constraining the E apparent activation energy to a value of zero—as it is expected to be near zero for a photocatalytic reaction with only the adsorption enthalpy for each species of interest appearing in the rate equation—did not lead to matching of the fit of eq 36 with the recorded data. By contrast, this match was obtained using the E apparent activation energy determined through the optimization process.

In addition, the predicted oxidation rate dependence on temperature, ethylene, and humidity concentrations derived from eq 36 by Obee and Haye is shown in Figure 18.¹⁵⁵ The

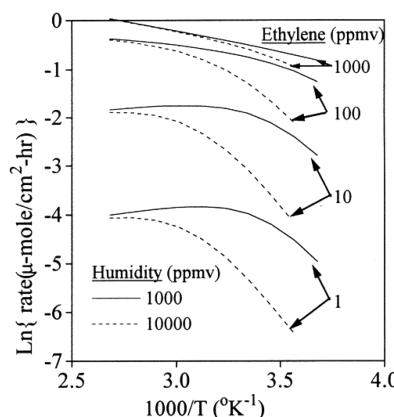


Figure 18. Predicted oxidation rate dependence on temperature, ethylene (1–1000 ppmv) and humidity (1000–10000 ppmv) concentrations, derived from eq 36. Reprinted with permission from ref 155. Copyright 1997 American Chemical Society.

rate increased with increasing the temperature or decreasing the water vapor concentration, till a plateau of zero-order temperature dependence was reached, and the temperature location of this plateau was switched to higher temperatures with increasing either the ethylene or the water vapor concentrations

Even if the model derived an adsorption enthalpy of ethylene on TiO_2 (-2.6 kcal/mol) only slightly differing from that found by Fu et al. (in the -3.2 to -3.8 kcal/mol range)—this mismatch being largely acceptable in catalysis—Obee and Hay very fairly pointed out the limitations of the model.¹⁵⁵ They considered first that the apparent activation energy should be interpreted by some method similar to the temperature-dependent L-H rate law equation (eq 36), rather than being only attributable to the adsorption of ethylene on TiO_2 . Also, the fact that $K'_e \gg K'_w$ in their study, even if fully consistent with the literature,^{180,181} seems to contradict the fact that water molecules are expected to bind more strongly to the TiO_2 surface than ethylene molecules. At the TiO_2 surface, the reaction kinetics at low ethylene concentration are dominated by competitive adsorption between ethylene and water molecules, so that the model should in fact also take into account other key species such as molecular oxygen as well as byproducts and reaction products such as CO_2 , that adsorb at

the photocatalyst surface and are directly involved in the reaction scheme. However, the excellent fit of the L–H kinetic model to the recorded data with only slight deviations observed from the L–H behavior highlights that no significant errors accrue from the model simplifications.

High Temperature Aspects. Recently, Westrich et al. investigated the influence of high temperatures on the photocatalytic oxidation rates over TiO_2 photocatalysts, i.e. in the 100–500 °C range,¹⁷⁰ taking ethylene as gaseous probe molecule. They aimed at evidencing that the number of charge carriers present at the photocatalyst surface should be dramatically limited at high temperatures by charge carrier recombination dynamics, since nonradiative, multiphonon recombination of photogenerated charge carriers becomes significant at photocatalyst temperatures equivalent to and larger than the Debye temperature of the photocatalyst,^{182,183} known to be 247 and 327 °C for the anatase and the rutile phases, respectively.¹⁸⁴ However, they mentioned that the available literature only concerned test temperatures too low to fully observe the effects of such recombination dynamics, i.e. at operating temperatures lower than 110 °C. By discriminating the photocatalytic oxidation rates from the thermal oxidation rates (that become equivalent to or greater than the measured photocatalytic rates with increasing the temperature), they showed that maximum photocatalytic ethylene oxidation rates were obtained between 100 and 200 °C whatever the TiO_2 photocatalyst tested, i.e. above the usually reported 50–110 °C temperature range. Besides the increased oxidation rates at temperatures lower than 200 °C logically attributed to differences in ethylene and water adsorption energies on the polar Ti–OH surface, they have attributed the decrease in photocatalytic activity above 200 °C to the loss of photo-generated charge carriers, resulting from the nonradiative, multiphonon recombination of charge carriers. They modeled this latter by an exponential function of the temperature and of two bulk TiO_2 parameters, namely phonon energy and phonon participation number, so that they proposed that materials with increased photocatalytic efficiency at elevated temperatures could thus be obtained by engineering photocatalysts with designed specific phonon energy, phonon number, band gap energy, and electronic trap states.

Influence of the Atmosphere Composition (Ethylene and Oxygen). The relationship between the oxygen molar fraction and the ethylene conversion rate was detailed by Yamazaki and co-workers,¹⁵⁷ who reported that this rate classically increased with an increase in the oxygen molar fraction. The authors explained this trend by the fact that the dioxygen molecules are electron acceptors that limit the recombination of photo-generated charges at the titanium dioxide surface. By contrast, they reported that, under their experimental conditions, the reaction rate approached a plateau with increasing oxygen molar fraction higher than 0.2 (Figure 19). Therefore, with the photocatalytic oxidation of ethylene being usually performed in air, the large excess of dioxygen molecules led them to consider the reaction rate as being at its maximum, obviously at least relative to the oxygen molar fraction.

Studies investigating the influence of ethylene concentration on its photooxidation in the presence of TiO_2 ,^{155–157} indicated that the reaction seemed to follow a Langmuir–Hinshelwood kinetic model, with a linear relationship being observed between the reciprocal of the reaction rate and that of the initial ethylene molar fraction (Figure 16b).¹⁵⁷

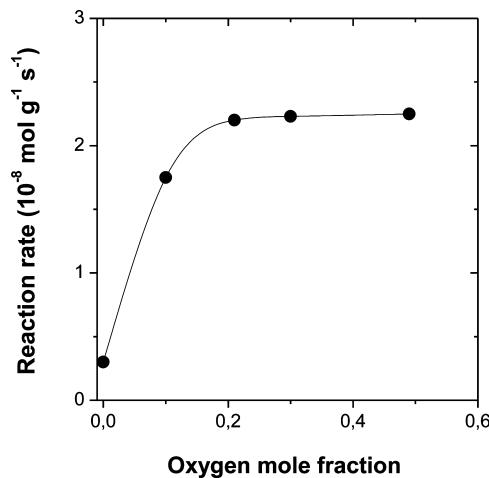


Figure 19. Influence of the oxygen molar fraction on the reaction rate. Redrawn and reprinted with permission from ref 157. Copyright 1999 Elsevier.

Influence of the Radiant Flux. Experimentally, many reports have shown that the rates of the photocatalytic reactions are proportional to the radiant flux Φ .¹⁸⁵ However, above a certain value depending on the experimental reaction conditions (photocatalyst, targeted compounds, photoreactor design, etc.), the reaction rate becomes proportional to $\Phi^{1/2}$. No specific studies devoted to the influence of the radiant flux on the ethylene photocatalytic oxidation could be found in the literature, although Yamazaki et al.¹⁵⁷ studied the effect of the number of lamps (in the case of 4 W fluorescent black light bulbs) on the ethylene conversion reaction rate. Their results confirmed that the reaction rate was first-order with respect to the radiant flux.

5.4. Photocatalytic Materials

5.4.1. Under UV Light. Various TiO_2 or TiO_2 -based photocatalysts have been reported for ethylene photodegradation under UV light (Table 15), either as powder or deposited on different supports. For example, the commercially available TiO_2 P25 photocatalyst produced by Degussa (now Evonik) has been used for the so-called “PCO” of ethylene under UV light, and used as a standard reference compared to other titanium dioxide materials prepared by sol-gel methods.^{153,157,163} Fu et al. showed the influence of platinizing the TiO_2 photocatalyst on the oxidation of a dry stream of ethylene.¹⁵³ The reactivity shown by a sol-gel prepared Pt/ TiO_2 photocatalyst was greatly enhanced compared to that obtained for pure TiO_2 . Obviously, this beneficial effect is highly dependent on the preparation process and on the metallic platinum weight content, both influencing strongly the average platinum nanoparticle size distribution and their interfacial physicochemical properties, with, as a result, a strong impact on the oxidative photocatalytic properties.

More recently, Belapurkar et al. have evaluated in a closed concentric quartz tubular reactor the efficiency of hydrothermally prepared 0.3–7.5 wt % Au/ TiO_2 sol-photocatalysts toward the photooxidation of ethylene in gas phase,¹⁸⁶ aiming at benefiting from the usually reported metal– TiO_2 synergistic effect. Indeed, as far as volatile organic compound photo-oxidation is concerned, adding metallic nanoparticles in optimized amounts to TiO_2 has been usually reported to enhance the photocatalytic activity by comparison to bare TiO_2 , at least in most cases. Especially, gold has been studied in the

Table 15. Studies Conducted on the Photocatalytic Oxidation of Ethylene^a

photocatalyst used	light source	parameters studied	temp (°C)	ethylene conc (ppm)	water content	ethylene conversion (%)	ref
TiO ₂ -P25	4-W UV ($\lambda = 365$ nm)	photocatalyst parameters	107	140 ppm	0.02 mol fraction		153
TiO ₂ /SiO ₂ TiO ₃ /ZrO ₂	4-W UV ($\lambda = 365$ nm)	temp	30–110	502 ppm	5–1500 ppmv	10–100	154
TiO ₂ sol-gel	water vapor	temp	2–48	5–260 ppm	5–24000 ppmv		155
TiO ₂ /Pt (0.3 wt %)	black-light lamp ($\lambda = 352$ nm)	water vapor					
TiO ₂ -P25 coated on glass plate	C ₂ H ₄ conc	water vapor	20–80	40–2000 ppb	relative humidity 2–37%	0–98	156
TiO ₂ /ZrO ₂	C ₂ H ₄ conc	water vapor					
TiO ₂ /ZrO ₂ /Pt	temp	flow rate					
TiO ₂ sol-gel	4-W UV	C ₂ H ₄ conc	30–81	50–500 ppmv	0–0.008 mol	95	157
TiO ₂ -P25	light intensity	TiO ₂ conc					
ultrafine powdered TiO ₂	C ₂ H ₄ conc	water vapor temp	22	2 Torr	1–16 Torr		158
TiO ₂ supported on glass ring	100 W high pressure Hg lamp ($\lambda > 280$ nm)	TiO ₂ particle size					
TiO ₂ and TiO ₂ /ZrO ₂ supported on glass ring	8 black light blue 8 W	water vapor	30–40 and 90–110	50–1000 ppmv	40–100	159	
	4-W UV ($\lambda = 365$ nm)	no. of coats of TiO ₂	30	1055 ppm			160
		temp	70				
TiO ₂ sol-gel	4-W UV ($\lambda = 365$ nm)	107					161
TiO ₂ /ZrO ₂ supported on glass ring or circular glass slides	fluorescent bulb or 200 W medium pressure Hg vapor lamp	parameters of TiO ₂ synthesis	50 or 60	160 ppmv	1900 ppmv		162
P25 synthetic macro-/mesoporous TiO ₂	four 8 W UV bulbs	- light irradiance		404 ppm			
TiO _{2-x} N _x coated on quartz tubes	- 100 W UV lamp	- microwave irradiation		640 ppm			163
zeolite and silica incorporated TiO ₂ film	- ordinary 15 and 100 W visible light incandescent lamps	parameters of TiO ₂ synthesis	110				4–42
TiO _{2-x} N _x	6 W black lamp	- light irradiance	25	1.75 mL/min			164
HZSM-5 zeolite with iron impurities	500 W Xe-lamp	- humidity	19	1.35 × 10 ⁻⁶ mol/L	28–63%	10–95	165
HZSM-5 zeolite with iron impurities	four UV light lamps (4 W) $\lambda = 254$ nm	- photocatalyst	27	700 ppm		10	166
	four UV light lamps (4 W) $\lambda = 254$ nm	- wavelength of irradiation					
		Fe and Al content	20	1000 ppm	dry air	10–48	167
		Si/Al ratio	20	1000 ppm	dry air	5–52	168

^aData taken from refs 153–168.

context of the photocatalytic degradation of organic compounds in water.¹⁸⁷ Figure 20 shows the influence of gold

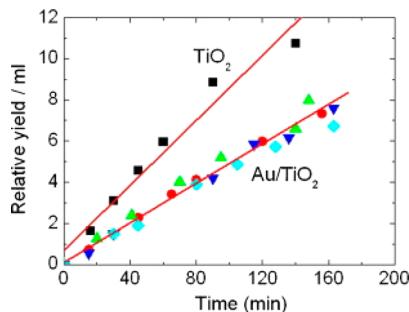


Figure 20. Relative yields to CO_2 (i.e., mineralization yield) obtained as a function of time under UV irradiation time over bare TiO_2 (squares) and Au-modified TiO_2 with Au contents of (green up triangles) 0.5%, (circles) 1%, (blue diamonds) 2%, and (green down triangles) 5%. Ethylene (5 mL) in 160 mL capacity quartz cell, corresponding to an initial ethylene concentration of 1.4 mM in air. Reprinted with permission from ref 186. Copyright 2010 Elsevier.

(which is dangerously named by the authors as “gold doping”) on the ethylene mineralization yield obtained as a function of time under UV light over Au-modified and bare TiO_2 . The so-called Au doped TiO_2 materials have been prepared by UV photolysis of a mixture of AuCl_3 and an aqueous TiO_2 sol, first hydrothermally prepared at 225 °C in water and acetic acid.¹⁸⁶ By contrast to the results obtained by the authors in the photocatalytic degradation of methanol and formic acid in aqueous phase, evidencing an enhancement of the mineralization rate of 1.8–1.5 by gold doping compared to bare TiO_2 , a strong decrease of the ethylene mineralization rate was observed compared to the TiO_2 reference, whatever the gold weight content. According to the authors, photoholes formed during the irradiation of TiO_2 are trapped by gold nanoparticles. Since gold nanoparticles located at the surface of TiO_2 are in metallic form, they reported that positive charge is distributed over the entire particle and finally neutralized with photogenerated electrons, performing a recombination center, which in turn decreased ethylene oxidation rate. They reported that a significant role of water in the oxidation process was demonstrated over the Au/TiO_2 photocatalysts.

Besides the association of TiO_2 with metallic nanoparticles, one should also report that the photocatalytic performances of titanium dioxide-based binary metal oxide photocatalysts such as $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{ZrO}_2$ were investigated in refs 153, 156, 160, and 162, with a higher photocatalytic activity being achieved for the $\text{TiO}_2/\text{ZrO}_2$ binary photocatalyst, attributed by the authors to an increased specific surface area and also to a change in the photocatalyst surface chemistry, particularly in terms of surface acidity. These two binary photocatalysts were prepared using classical sol-gel methods by acid hydrolysis of their appropriate metal oxide precursors.¹⁵³ The separate sols were stirred before being mixed to the desired composition. After dialysis of the mixed sols and drying for removing water, the resulting solids were sintered at 300 and 400 °C, for silica-titania and zirconia-titania, respectively. Fu et al. reported that optimum mixture concentrations were found at 12 wt % zirconia and 16 wt % silica in titania, with both catalyst types exhibiting activity maxima with respect to sintering temperature.¹⁵³ The authors suggested that the maxima arose from opposing effects of densification and phase transformation

versus beneficial sintering. In the case of a zirconia-titania photocatalytic system, the photocatalytic performance toward ethylene oxidation was affected by several factors, such as the temperature, the humidity, the flow rate, and the type of catalysts. Tibbits et al. demonstrated the close correlation between the photocatalytic activity and the relative humidity, with a decreasing photocatalytic activity for increasing humidity (e.g., above 15% relative humidity, the activity of the catalyst is half-reduced when compared to that at a low 2% relative humidity).¹⁵⁶ This behavior is a major problem because the reactors, and therefore the catalytic materials, used in refrigerated storage areas with fruits and vegetables should be able to efficiently operate at low temperature and under high relative humidity.

5.4.2. Under Visible Light. The development of photocatalysts active under visible light, either directly through solar irradiation (solar spectrum) or even through interior room lighting, was studied by Kumar et al.¹⁶⁴ The authors demonstrated that nitrided TiO_2 -based samples were of interest, and they ranked the photocatalytic activity of such nanostructures toward the photocatalytic oxidation of ethylene under visible light in the following order: $\text{TiO}_{2-x}\text{N}_x + \text{Pd}(\text{NO}_3)_2 > \text{TiO}_{2-x}\text{N}_x + \text{PdCl}_2 > \text{TiO}_{2-x}\text{N}_x >$ colloidal TiO_2 . More recently, a new nitrogen-doped TiO_2 was successfully prepared by a simple wet impregnation method at low temperature by dipping the amorphous TiO_2 powder in hydrazine hydrate (80%).¹⁶⁶ The results indicated that the photocatalytic conversion of ethylene was possible at wavelengths higher than 450 nm. Chen et al. also evidenced that the photocatalytic activity of N-doped TiO_2 samples for decomposing ethylene under visible light ($\lambda > 420$ nm) was strongly influenced by the sol-gel postcalcination temperature.¹⁸⁸ In their works, the authors synthesized N-doped TiO_2 photocatalysts by annealing at 200–600 °C in static air for 2 h TiO_2 xerogels previously treated at 400 °C for 3 h in flowing NH_3 . Figure 21 represents the influence of the annealing temperature on the amount of carbon dioxide produced by the photocatalytic degradation of C_2H_4 over N-doped TiO_2 . As a function of the annealing temperature, the activity curves showed a volcano-like behavior, with a maximum at 400 °C. The authors explained that increasing the final calcination

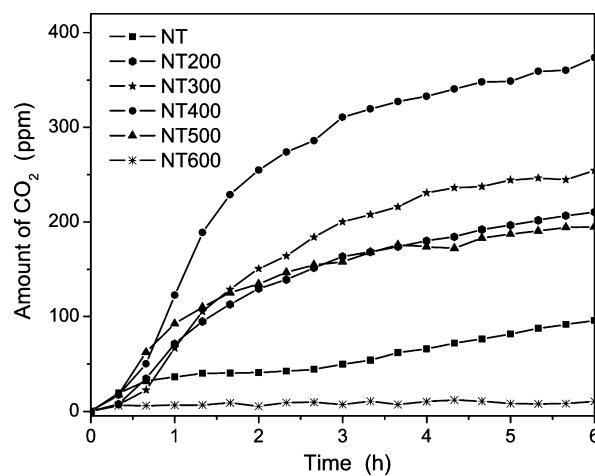


Figure 21. Influence of the annealing temperature in static air on the amount of CO_2 produced by the photocatalytic degradation of ethylene over N-doped TiO_2 . Reprinted with permission from ref 188. Copyright 2008 Elsevier.

temperature within the 200–400 °C range resulted only in a moderate increase in the crystal size and in a slight decrease in the specific surface area of the samples, simultaneously with a strong increase in the photocatalytic activity. By contrast, thermal annealing of N-doped TiO₂ at temperatures above 400 °C caused the phase transformation from anatase to rutile, together with a loss of specific surface area.

5.4.3. Immobilized Supported Photocatalyst. In parallel to the search for improved materials, the need of depositing the active photocatalyst on a suitable support for targeting the practical photocatalytic removal of ethylene is of importance. In the case of the ethylene PCO treatment, glass rings are to date the support mainly investigated.^{159,160,162} According to Sirisuk et al.,¹⁵⁹ titanium dioxide supported on borosilicate glass rings exhibited a higher photocatalytic activity for the oxidation of ethylene than unsupported TiO₂ pellets. Borosilicate glass rings were coated with a titanium dioxide sol, generated by the controlled hydrolysis of a titanium isopropoxide precursor. The authors have also studied the influence of reaction temperature on the photocatalytic oxidation of ethylene on unplatinized and platinized TiO₂/ZrO₂ mixed-oxide thin film photocatalysts.¹⁵⁹ One can also mention that following works on conventional optical fiber reactors (see, e.g., works of Marinangeli and Ollis,¹⁸⁹ Peil and Hoffmann,¹⁹⁰ Choi et al.,¹⁹¹ Wang and Ku,¹⁹² Lin and Valsaraj,¹⁹³ or Carneiro et al.,¹⁹⁴ for which TiO₂ is coated on optical fibers or more recently for which TiO₂ is also coated on the surrounding internal walls of monolith channels inside each of which is radially distributed a single optical fiber), Denny et al. have developed a channeled optical fiber photoreactor, taking ethylene molecule as model target in the gas phase.¹⁷¹ This channeled optical fiber reactor comprises 30 600 μm diameter hexagonal channels—with TiO₂ coated on the channel walls—located radially inside a 6 mm diameter optical fiber core. Prior to the TiO₂ coating, the channeled optical fiber was immersed in a diluted nitric acid solution, ultrasonically cleaned and subsequently rinsed with deionized water, and finally dried in an oven at 120 °C for 24 h. TiO₂ P25 was then coated onto the channel walls by vacuum coating, using a TiO₂-based suspension made from TiO₂ particles suspended in a 2.6 wt % SiO₂ sol,¹⁷² added for assisting the adhesion of TiO₂ particles to the channel walls. After alternative cycles of coating and air-drying, final calcination at 450 °C was performed. The authors observed the independence of quantum yield on the rate of incident photons and on the incidental light angle in the reactor. They claimed that this addresses two limitations of conventional optical fiber reactors, first by allowing the use of a high incident photon rate for increasing the photocatalytic rate without compromising the quantum yield, and second by allowing more flexibility in the type of light source available for the channeled optical fiber reactor (e.g., for facilitating the coupling of the reactor with a solar concentrator for improving the sustainability of the system). More classically, one notes also the use of glass and pyrex plates,^{155,162,163} quartz tubes,¹⁶⁴ or glass beads¹⁷³ as photocatalyst supports for removing ethylene. For instance, Verbruggen et al. have reported that using 2 mm glass beads as support offers a convenient and versatile tool for increasing the irradiated photocatalyst surface (i.e., for increasing the irradiated specific surface of the reactor, expressed in m⁻¹).¹⁷³ They have reported that a gain in TiO₂ loading inside the reactor of 25 was achieved by coating them with a thin layer of a commercial TiO₂ nanopowder (1 wt % of TiO₂ relative to glass bead mass), when compared to the same

TiO₂ catalyst but commercially shaped as bulk pellets. They claimed that an efficient coating was obtained using an ethanolic suspension, with ultrasonication prior to the coating, with no additional heat treatment after the drying step in an oven.

5.4.4. Zeolithe as TiO₂-Free Photocatalyst. Few studies have been performed investigating TiO₂-free photocatalyst for the photooxidation of ethylene, with TiO₂ largely remaining the material most studied. It is noteworthy that, according to Yan and co-workers, commercially available HZSM-5 zeolite with different Si/Al ratios and iron impurities has shown good photocatalytic activity for ethylene oxidation.^{167,168} The authors observed that photocatalytic activity increased with an increase in the iron content within the zeolite. They concluded that two types of isolated iron species in the zeolite framework were responsible for the photocatalytic activity.

5.5. Photocatalysis and Fresh Product Storage Applications

5.5.1. Ethylene as a Single and Short Carbon Chain Chemical Target. Targeting a single molecule such as ethylene, rather than a large collection of highly variable and chemically different molecules, such as in indoor air treatment, is a crucial advantage for the implementation of the technology. Indeed, even if TiO₂ is currently the most attractive and efficient semiconductor material for photocatalysis,^{133–143} it would be of interest to further increase the photocatalytic activity of TiO₂- or TiO₂-based photocatalysts. One of the approaches is to work at the “material” level for overcoming or at least positively impacting on the two major drawbacks that limit photocatalytic process efficiency at the catalyst level (without considering photocatalytic chemical engineering): the recombination of the photogenerated charges and the adsorption–desorption aspects of both the reactants and the reaction products, since they are the first and the last step of the process, respectively.¹⁸⁵ Among approaches explored at the “material” level for modifying bulk and surface physicochemical properties of TiO₂ photocatalysts, one can cite the modification of TiO₂ material surface properties to adapt the photocatalyst to the chemical nature of the ethylene molecule but also, if possible, to that of the partially oxidized hydrocarbon intermediates and of the CO₂ final product. Surface modifications can be made in order to improve the ethylene adsorption capacity/property of the surface, to improve the ethylene adsorption enthalpy, and to decrease that toward the reaction products. This “material” design approach can be of more efficient benefit to the “single target” ethylene mineralization with very few reaction intermediates than to applications targeting the removal of “multipollutants and variable pollutants”, with also an exponentially growing number of possible intermediates, such as the purification of indoor air.

Photocatalysis is usually considered as a fully mineralizing and, therefore, destructive method without any oxidative additives, with no secondary byproduct release as well as no solid waste generation (such as for KMnO₄-based stoichiometric oxidation). This differs strongly from storage recuperative technologies, such as adsorption-based techniques based on active charcoal, zeolites, clays, aluminosilicates, or cristobalites. However, it remains worth pointing out that the true mineralizing nature of photocatalysis depends also on reaction and chemical parameters such as the residence time in the photoreactor, so that intermediate byproducts formed by the attack of oxidative species on the organic target can be detected at the reactor outlet before being further oxidized into

CO_2 and H_2O , if the residence time is not long enough. Reversible photocatalyst deactivation can also occur during the oxidation of heavy aromatic BTX compounds due to low kinetic rates. By contrast, the presence of heteroatom-containing molecules leads to irreversible photocatalyst deactivation due to the solid nature of the ultimate oxidation state of the heteroatom, such as phosphates and sulfates, that poison the TiO_2 surface by blocking the active surface sites, in contrast to CO_2 , which leaves the surface free of any carbon-containing deposit. More consecutive reaction steps are needed to form only CO_2 and H_2O , more time is needed to achieve full mineralization, and thus, more intermediate byproducts could be released at the reactor outlet if the reactor is not well designed. So, the very short carbon chain of ethylene with the absence of any heteroatoms and any aromatic functions is an advantage in favor of the technological implementation of photocatalysis.

Indeed, studying UV photocatalysis for indoor air cleaning applications, Hodgson et al. showed that the oxidation rates of different chemical classes of molecules could be ranked as follows: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic and alkane hydrocarbons > halogenated aliphatic hydrocarbons,¹⁹⁵ in agreement with the results obtained by Obee and Hay, who showed that oxidation rates for C4 organic molecules were ranked as follows: 1-butanol > 2-butanone > 1-butene > *n*-butane.¹⁹⁶ The authors attributed the relative rates obtained to the strength of the expected type of attractive force between each compound and the hydrated TiO_2 surface, which was hydrogen bonding for 1-butanol, dipole–dipole interaction for 1-butane, and weak dispersive forces for *n*-butane. Hodgson et al. showed that gas-phase byproducts were generated when photocatalysis operated with indoor air relevant mixtures of VOCs (i.e., 10 and 27 VOCs representative of office buildings and emitted by cleaning products) at realistic concentrations (i.e., low ppb range).¹⁹⁵ They observed that there was net production of formaldehyde, acetaldehyde, and acetone, and the production of some acetic acid and formic acid. Indeed, outlet concentrations of formaldehyde and acetaldehyde were between 2.4 and 7.2 times, and 2.3 and 8.6 times higher than the inlet concentrations, respectively. This is in agreement with reports on the release of aldehyde and with a lesser extent of acid intermediates during the photocatalytic oxidation of commonly encountered VOC mixtures.^{197–202}

Therefore, the challenge to target a single and short carbon chain molecule such as ethylene is an advantage for implementing viably the technology for ethylene removal and fresh product storage.

5.5.2. A Flexible Use. This flexible use of the UV photocatalysis allows the technology to be adapted to meet the highly restrictive and necessary requirements for use in the transfer and storage of fresh products. This flexibility strongly benefits the technology in order to look for its scaling-up and its transfer from the laboratory scale to a practical application for targeting a future commercial implementation. Indeed, this specific application requires dealing with subambient temperatures or even near-zero temperatures for specific products, and with a very high relative humidity, mainly within the 85–95% range and even higher. The high oxidizing potential developed by the illuminated photocatalytic materials is effective at low temperatures, even close to zero. In addition, the photo-generated holes react with adsorbed water molecules for producing the very active and highly oxidative hydroxyl OH[•]

radicals. The high relative humidity of the air to be treated is thus not a problem, obviously as long as adsorption competition between both water and ethylene molecules does not become too detrimental, in contrast to what is observed for many adsorption products and technologies. One can cite the zeolite-based adsorbent which comprises (or at least partly) the Profresh additives from EIA Warenhandels GmbH, Austria (approved by the FDA), that lose their efficiency in high relative humidity air atmospheres.³⁰

5.5.3. Global Nature of Photocatalysis toward Chemical and Airborne Pathogenic Biological Targets.

The globalization of fruit and vegetable markets, forcing growers to increase product shelf life, has also increased problems due to microbial spoilage and diseases caused by pathogens such as bacteria, viruses, and parasites. Average postharvest losses of fresh fruit and vegetables in developing countries are estimated at 5–30% and in the 60–80% range in emerging countries. These losses are mainly due to physiological disorders and microbial spoilage caused by fungi and bacteria and to premature ripening directly linked to ethylene release from produce during storage. The main fungal rots of fruits are caused by *Penicillium*, *Botrytis*, *Monilia*, *Alternaria*, *Aspergillus*, *Rhysopus*, and *Colletotrichum*. Decays of bacterial origin can be due to *Erwinia Pseudomonas* and *Bacillus*. Most postharvest infections are a consequence of mechanical wounds during harvest and handling and occur during storage, packing, and commercialization. As they are filamentous, fungi reproduction is by spores, and they can be disseminated in the atmosphere; it is the same for parts of mycelium.²⁰³ The most common spore types are *Alternaria*, *Penicillium*, *Fusarium monilia*, and *Aspergillus*. For example, *A. niger* is not responsible for as many human diseases as other species of *Aspergillus*, but at high concentrations, it can cause aspergillosis, which causes lung abnormalities, a disease that appears more frequently in horticulturists.²⁰⁴ Some spores can induce a human pathogenicity, because of their allergenic properties; for instance, the spores of *Alternaria* are allergenic and can induce an allergic response at a concentration to 100 spores in one cubic meter of air; for *Cladosporium* the concentration is 3000 spores per cubic meter. In general, conidia up to 5 μm in diameter are responsible for type 1 allergies, because they remain in the upper parts of the aerial tract (nostrils, sinuses, bronchial tubes). Conidia smaller than this can easily reach the alveoli and induce type III allergies.

Therefore, the global nature of photocatalysis is an advantage of the technology. Indeed, besides the possible mineralization of ethylene into CO_2 and H_2O , it is efficient for inactivating airborne pathogenic flora that can exist in the air during the transfer and storage of fresh products, such as highly resistant bacterial spores. Since Matsunaga et al. opened the door by reporting on the microbiocidal effects of TiO_2 in water,²⁰⁵ the crossover between photocatalysis and life science is a growing research area, first mainly for self-decontaminating surfaces or water purification using TiO_2 suspensions,^{206–210} and more recently—and also more scarcely—for disinfecting air contaminated by airborne microorganisms (bacteria, viruses, and bacterial spores).^{211–223} The analogy between chemical and biological targets results from the organic nature of the microorganism constituents—and especially those constituting the cell outer membrane, made of a complex assembly of high molecular weight organic compounds and considered simultaneously as the first target for photocatalysis and the first barrier maintaining the vital functions of the cell. They can be oxidized

by photocatalysis similarly to liquid and gas-phase organics. Details can be found elsewhere.²²⁴

Therefore, the possible presence inside the storage or transfer area of airborne microorganisms detrimental to the storage and the quality of fresh products, or even pathogenic to them, could be significantly decreased or even fully avoided by the continuous photocatalytic disinfection of flowing air simultaneously to the removal of ethylene. Recently, Maneerat et al. evidenced the antifungal activity of the illuminated TiO₂ photocatalyst against the pathogen *Penicillium expansum* fungus,²²⁵ an airborne fungus which is one of the most important fungal postharvest in fruits and vegetables.^{226,227} They have efficiently performed *in vitro* tests, by mixing aliquots of *P. expansum* conidial suspension to TiO₂ powder before adding the resulting mixture to potato dextrose agar (PDA) plates. More interesting *in vivo* tests were carried out by applying TiO₂ powder directly to the apple fruit surface. Other *in vivo* tests were performed by inoculating tomato fruits—selected as it is juicer and softer than apple—with *P. expansum* before directly applying TiO₂ powder. Both *in vivo* tests on apple and tomato were successful, with (i) the development of *Penicillium* rot in apple fruit being retarded by the TiO₂ photocatalytic reaction: lesions with a diameter larger than 20 mm (visible as soft spots and a light brown color) occurred after 7 days of inoculation in the control experiment without TiO₂, while they occurred after 14 days of inoculation in the presence of illuminated TiO₂; (ii) unlike apple fruit, wrinkle spot or other surface disorders were not observed with tomato fruits during 2 weeks of storage in the presence of the TiO₂ photocatalytic process, while, by contrast, all tomato fruits showed fungal spoilage within 7 days after inoculation. For practical use in fruit packaging, the authors have also tested the antifungal activity of TiO₂-coated plastic films to control fruit rot development in lemon fruit, with less severe postharvest rot of lemon fruit stored in TiO₂-coated films compared to lemon fruit stored in uncoated film.

Maneerat et al. have also reported, in the case of 8–10 days storage of tomatoes, that off-flavors could result from extended ripening delays obtained by the photocatalytic ethylene removal from the atmosphere of fermented and alcoholic odors, namely acetaldehyde and ethanol that could accumulate in the storage chamber.^{148,149} Therefore, the mineralization activity of photocatalysis toward molecules such as acetaldehyde and ethanol is positive for avoiding their accumulation in the storage atmosphere.^{228,229}

5.5.4. Low Operation Costs. The photocatalysis technology benefits globally from low operation costs, mainly consisting of investment, energy, running, and maintenance costs. In terms of energy, it uses low-cost, low electrical power and energy-saving UV light sources with ecotechnology or sustainable technology labeling. It remains difficult to present economic figures, since only qualitative evaluations have been made in the field of storage or transfer containers, and technical designers, providers, as well as end-users are not providing figures in terms of economical gain and extra-costs resulting from the implementation of the photocatalysis technology for this application.

In terms of economic data, the French National Institute for International Transport and Ports (ITIP) has evaluated the annual replacement cost of containers on a world basis at 30 billion US\$. They calculated daily costs (maintenance and depreciation) at between 1 US\$ and 3 US\$ and between 5 US\$ and 25 US\$ for 20 and 40 ft containers, respectively

(corresponding to respective useful volumes of 33 m³ and 66 m³).

Taking into account current implementation costs of UV photocatalysis technology for air treatment applications, the sales costs for a photocatalytic device have been very roughly estimated at 1800 € and 2200 € for a 20 ft and a 40 ft container, respectively (corresponding to respective air ventilation rates of 1000 m³ h⁻¹ and 2000 m³ h⁻¹). Such rough estimations correspond to an extra-cost of 30% and 20% for a 20 and 40 ft container, respectively, corresponding to respective sale costs of about 6000 € and 9000 €.

Rather, no maintenance is necessary for the photocatalysis technology. The only maintenance operation and consumables consist in the periodic replacement of the UV-A lighting system, which would represent a yearly operation extra-cost of about 5–6% compared to the investment. The running costs would be limited to the electrical supply to the lighting of the photocatalytic system, estimated around 65 Wh for a 1000 m³ h⁻¹ photocatalytic device, in addition to the energy consummation of the additional ventilation internal to the device, estimated at about 0.15 kWh. Taking into account the actual kWh cost for a container-holder vessel, estimated at 0.10 €/kWh, the daily running extra-cost resulting from the use of the photocatalytic device would reach 0.0036 €.

Making all due allowance, the Florida Solar Energy Center (FSEC, USA) compared the investment and running costs resulting from the photoreactor they have developed to perform the remediation of VOCs extracted from contaminated soils and groundwater, and the treatment of industrial process vent gases, to two established technologies (carbon adsorption and catalytic incineration).²³⁰ Cost comparisons between the FSEC process and two carbon adsorption and catalytic incineration established technologies are reported in Table 16

Table 16. Compared Costs between the FSEC's Photoreactor and Both Carbon Adsorption and Catalytical Incineration Well-Established Technologies, In Terms of Capital and Annual Operating Costs^a

technology	treatment costs	
	capital cost	annual operating cost
Soil Vapor Extraction Vent (100 ppmv trichloroethylene, 500 ACFM ^b air flow, i.e. 850 m ³ h ⁻¹)		
FSEC, 4 stage	25000–35000 US\$	4000–6000 US\$
carbon adsorption	15000–100000 US\$	75000–125000 US\$
catalytic incineration	75000–350000 US\$	10000–50000 US\$
Pharmaceutical Product Dryer Process Vent (3 ppmv nitroglycerin, 12000 ACFM ^b air flow, i.e. 20400 m ³ h ⁻¹)		
FSEC, 4 stage	150000–250000 US\$	40000–50000 US\$
carbon adsorption	100000–350000 US\$	125000–150000 US\$
catalytic incineration	200000–450000 US\$	80000–180000 US\$

^aData taken from ref 230. ^bACFM: actual cubic feet per minute.

for the treatment of 100 ppmv trichloroethylene from soil vapor extraction and for that of 3 ppmv nitroglycerin from a pharmaceutical product dryer process vent. Both capital cost and annual operating cost are clearly in favor of the photocatalytic technology.

In addition, the developers of the FSEC's photoprocess reported that the expendable items only include low-pressure mercury lamps (LPML) and photocatalytic cartridges, with typical costs and lifetime of a standard LPML being estimated at 45 US\$ and 8000 h. The nature of the photocatalytic media

was not described, but the developers claimed that the design of the photocatalytic media is simple and lends itself to low-cost mass production, with an estimated cost of 5–10 US\$ for single-stage and 15–35 US\$ for multistage cartridges.

5.6. Research Efforts and Photocatalysis Coupling

This section is devoted to the research efforts aiming at the increase of the process efficiency by associating photocatalysis to another technology. Photocatalysis/adsorption coupling, photoelectrocatalysis, microwave-coupled photocatalysis, as well as VUV/TiO₂ are reported here.

5.6.1. Coupling of Adsorption and Photocatalytic Oxidation.

An enhancement of the ethylene photooxidation process could possibly be obtained by coupling it with a prior adsorption step, similarly for other gas purification processes. The scheme in Figure 22 shows some integration possibilities of photocatalysis within existing technologies for improving ethylene control.

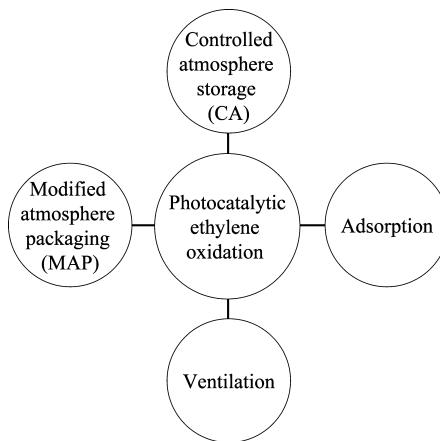


Figure 22. Potential coupling of the photocatalytic ethylene oxidation with other ethylene control methods.

Besides many advantages of photocatalysis, concentrating ethylene by adsorption could be an interesting method to increase the reaction rate of photocatalytic oxidation. Indeed, as for thermally activated catalysis, the reaction rate decreases at extremely low ethylene concentrations due to the positive reaction rate order with respect to the ethylene concentration. Therefore, ethylene in very low concentrations can be removed efficiently by a cyclic adsorption–catalysis process composed of three steps: a concentration step by adsorption at low temperature, followed by desorption, and a final photocatalytic oxidation step. An example are ethylene-decomposing devices used in chambers for vegetable and fruit storage, based on the combination of TiO₂ and zeolite.^{231,232} Another possibility of coupling deals with the controlled and progressive release of ethylene adsorbed on an adsorbent, through TiO₂ particles allowing ethylene mineralization to occur.

A second way of associating the adsorption to the photocatalysis functions in a process is the design of composite materials in which both materials are beneficially integrated. This advantage has been rationalized with the “adsorb and shuttle” and the “remote degradation” concepts.²³³ Both concepts derived from the presence inside the composite material of nonphotocatalytic and photocatalytic domains. First, the “adsorb and shuttle” concept is based on the presence of inert adsorptive domains allowing the adsorption of the target molecules, that would otherwise less adsorb on the TiO₂

photocatalytic sites. Those inert domains thus act as a tank for the molecules to degrade, that should be located close to the photocatalytic sites, and the adsorbed molecules can then further diffuse to the neighboring photocatalytic sites. It is worth noting that designing a composite material with intimate contact between both adsorptive and reactive phases is of high importance, which cannot generally be obtained by simple mechanical mixing. This concept was first evidenced with activated charcoal,^{234,235} before having been extended to oxide materials, such as mainly zeolites,^{236,237} silica,²³⁸ and alumina.²³⁷ This concept could be seen as a way of artificially increasing the residence time of the targeted molecules within the photocatalytic material and close to the photoactive TiO₂ particles.

By contrast to this mechanism, which implies the surface diffusion of molecules, the “remote degradation” concept is based on the surface diffusion of active species, from the TiO₂ particles where they are generated to the adsorption sites on which the targeted molecules and the reaction intermediates are preferentially adsorbed. This mechanism was first proposed in the liquid phase 6G rhodamine photodegradation on sol-gel composite particles associating TiO₂ and SiO₂ microdomains.²³⁹ It has been further put forward during the degradation kinetic of self-assembled monolayers chemisorbed on silicon,²⁴⁰ during which characteristic diffusion lengths of 80 μm were observed. The authors have concluded that this mechanism involved oxidative chemical species rather than directly the mobile charge carriers. This was confirmed separately by Lee and Choi during their works on soot degradation.²⁴¹ It should be pointed out that the stability of the oxidative species mainly depends on the nature of the inert substrate, as has been evidenced by studying the influence of the zeolite crystallinity on the photocatalytic activity of composites, that either affect the lifetime of oxidative radicals or impact on the adsorption of oxygen—known to act in the stripping of photogenerated electrons, at the surface of the zeolite. The role played by the inert substrate on the lifetime of mobile active species has also been reported, and the low “remote degradation” kinetic of aliphatic self-assembled molecules grafted on platinum or gold noble metals was evidenced, compared to the rapid kinetic obtained when anchored on silica.²⁴² Whereas the nature of the active species involved in the “remote degradation” mechanism remains under discussion, a laser induced fluorescence investigation led by Murakami et al. has already recorded the presence of hydroxyl radicals above the TiO₂ surface in the gas phase,²⁴³ proposing that they could move from the TiO₂ surface to the gas phase or that H₂O₂ formed at the TiO₂ surface could move to the gas phase before decomposing into hydroxyl radicals. Using the same very sensitive and selective detection method, Zahraa and collaborators have provided further insight on the nature of active oxidative radicals.²⁴⁴ They have recorded the time-resolved evolution of hydroxyl radical concentration at pressures between 4 and 600 Torr and at varying distances of the photocatalytic surface, while they did not evidence the formation and diffusion of any HO₂ radicals into the gas phase.²⁴⁵

5.6.2. Photoelectrocatalytic Degradation of Ethylene.

In parallel to strategies based on the coupling or the association of photocatalysis with methods such as adsorption, the investigation field dealing with the setting of two electron- and photon-assisted catalyses has recently received increasing interest: besides energy-related applications,^{246,247} photoelec-

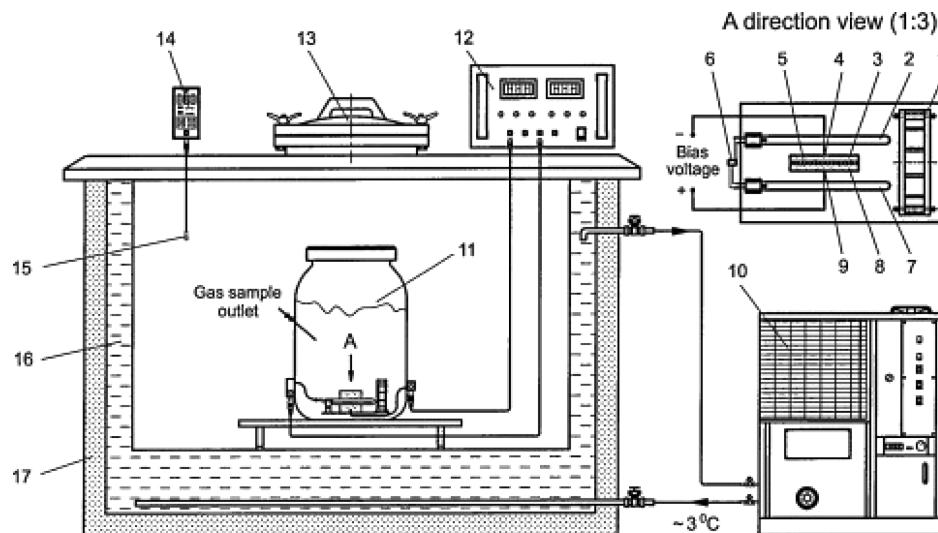


Figure 23. Schematic display of the experimental setup. (1) Direct current fan; (2, 7) double-tube UV lamp; (3, 8) TiO_2/ACF or $\text{TiO}_2/\text{ACF-Pt}$; (4) electrical conductive tape; (5) Nafion324; (6) pinboard to UV lamp; (10) refrigerator; (11) cylindrical vessel; (12) potentiostat; (13) airproof handhole; (14) control unit for temperature and relative humidity; (15) sensor; (16) coolant; (17) adiabatic layer. Reprinted with permission from ref 253. Copyright 2009 Elsevier.

trocatalysis could be an alternative to conventional heterogeneous photocatalysis for the degradation of organic pollutants.²⁴⁸ The principle is based on the further acceleration of the photocatalytic reaction rate by applying an external potential which moves the conduction band electrons away from the TiO_2 photoanode toward a counter electrode.²⁴⁹ Among many, photoelectrocatalysis takes a great advantage from preventing the recombination of h^+/e^- pairs and extending the life of the active holes. Although most studies remained focused on the use of photoelectrocatalysis for removing organic contaminants in water (dye, phenolic compounds, solvents, ...),^{250–252} a Chinese research team have recently successfully investigated the possibility of applying photoelectrocatalysis to gas-phase removal targeting the ethylene oxidation.²⁵³ The authors have synthesized active coke felts (ACF) supported TiO_2 photoelectrodes, modified or not by platinum deposition (labeled TiO_2/ACF and $\text{TiO}_2/\text{ACF-Pt}$). ACF are especially interesting as potential support materials due to their excellent characteristics and properties. The surface area of these activated carbon felts is very high, with a porous network mainly formed by deep pores in a narrow range of sizes, especially micropores.²⁵⁴ The experimental setup used for investigating the photoelectrocatalysis coupled process for oxidizing ethylene is shown in Figure 23, allowing the regulation of the temperature at 3 °C and of the relative humidity at 90%, i.e. close to some fresh product storage conditions. The results reported in Figure 24 show the benefit of using photoelectrocatalysis compared to single electrocatalysis and photocatalysis for removing ethylene. Especially, performing the electrochemical process in the presence of UV irradiation (test 3 PEC) led to a ethylene degradation kinetic about 10 times higher than when performing the electrochemical process in the dark (test 1 EC). According to Ye et al., the enhancement effect of the PEC process may be attributed to two factors.²⁵³ First, the external electric field could capture the photogenerated electrons, reducing the recombination rate of electrons and holes. Second, the external electric field could also cause electrochemical oxidation of ethylene in addition to the PEC

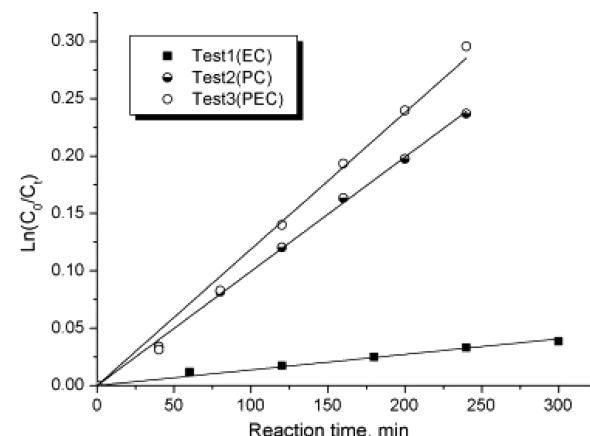


Figure 24. Ethylene degradation kinetic curves in the three processes (EC, electrochemical; PC, photocatalysis; and PEC: photoelectrocatalysis). Reprinted with permission from ref 253. Copyright 2009 Elsevier.

synergetic effect. In this case, Vayenas et al. explained that the key finding in the interpretation of the electrochemical promotion effect is the variation in the surface coverage and the work function of the electrode upon polarization, with concomitant changes in the binding strength of chemisorbed species and reaction intermediates.²⁵⁵

5.6.3. Microwave-Coupled Photocatalysis. Microwaves can be associated with heterogeneous photocatalysis oxidation for the degradation of pollutant, usually abbreviated as MWPCO for MicroWave PhotoCatalytic Oxidation. Although there have been few studies concerned with the effect of microwave on photocatalytic reactions, the investigation in this field remained mainly conducted in the liquid phase, leading to the conclusion that OH radicals are formed by microwaves, while the reactant diffusion is unfortunately disturbed by the microwave irradiation.^{256,257} Works by Kataoka et al. remain a scarce study investigating the influence of microwave irradiation on the photocatalytic oxidation of ethylene and on the behavior of water at the surface of the $\text{TiO}_2/\text{ZrO}_2$ photocatalyst.¹⁶² The

authors have compared MWPCO and photocatalysis approaches in the removal of ethylene under different humidity conditions, and the reaction rate constants recorded for the removal of ethylene as a function of humidity are shown in Table 17. First, whatever the humidity content, coupling

Table 17. Impact of the Microwave Coupling on the Photocatalysis Efficiency^a

	apparent reaction rate k ($\times 10^5$ mol $^{1/2}$ L $^{1/2}$ g $^{-1}$ s $^{-1}$) at the following μ L of H ₂ O in the reactor		
	0 μ L	0.1 μ L	3 μ L
photocatalysis	19.9	27.6	5.16
microwave-coupled photocatalysis (MWPCO)	26.7	28.5	9.49
relative difference (%)	34.2	3.3	83.9

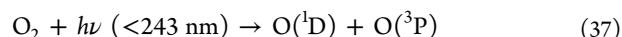
^aMicrowave-coupled photocatalysis (MWPCO) and photocatalysis efficiencies in terms of apparent reaction rate constants for ethylene removal under different humidity. Data taken from ref 162.

microwaves to photocatalysis allowed greater reaction rates to be obtained. For both systems, whereas a small amount of water provides OH radicals, beneficial for increasing the photocatalytic activity, the authors observed the negative influence of large amounts of water on the ethylene degradation rate constant. Basically, if excessive amounts of water exist on the catalyst surface, the reaction rates drastically decrease because the ethylene and oxygen reactant molecules cannot access active sites.^{153–155} Thus, the interest of coupling microwaves to photocatalysis was mainly seen as a result of the ability of microwave irradiation to facilitate the removal of excess water from the UV-irradiated catalyst surface.

However, it should be stressed that the final impact of the coupling is strongly depending on the humidity rate. Indeed, in dried conditions, the increase in the wettability by the microwave irradiation was assigned by the authors to facilitate the adsorption of the water reaction product, which produces OH radicals, and indirectly accelerated the rate of the photocatalytic oxidation. By contrast, at low relative humidity

(0.1 μ L of water), there is likely a sufficient amount of bound water molecules to create OH radicals on the surface of the catalyst, but not a sufficient amount to diminish the rate of photocatalysis oxidation in both MWPCO and photocatalytic oxidation. The benefit of applying microwaves remained thus limited, even if it increased the surface wettability and helped in removing water. The larger impact was obtained at high humidity content, at which the removal of excess water from the catalyst surface remained the key-step to control for hindering a too strongly marked drop in efficiency due to active site accessibility. Although the increase in reaction rates observed when associating microwaves to photocatalysis is non-negligible (*i.e.* +34.2% and +83.9% in dried and strongly humid conditions, respectively), the gain observed in reaction conditions for which photocatalysis alone is already very efficient (at 0.1 μ L water), remains, unfortunately, strongly limited, with a +3.3% reaction rate enhancement.

5.6.4. VUV/TiO₂ Photocatalytic Degradation of Ethylene. VUV/TiO₂ photocatalytic degradation can be considered as a possible method of ethylene elimination. During the past decade, few studies have been focused on the possibility of using vacuum ultraviolet (VUV) irradiation to increase the photocatalytic reaction rates in the presence of TiO₂ semiconductor materials. VUV with high-energy photons (185 nm wavelength corresponds to a photon energy of 6.7 eV) can dissociate oxygen and water to form O(¹D) and •OH:^{258,259}



The first works in the field concerned the VUV degradation of aqueous VOCs,^{260,261} but in recent years, the application of this technology has been extended to the treatment of gaseous

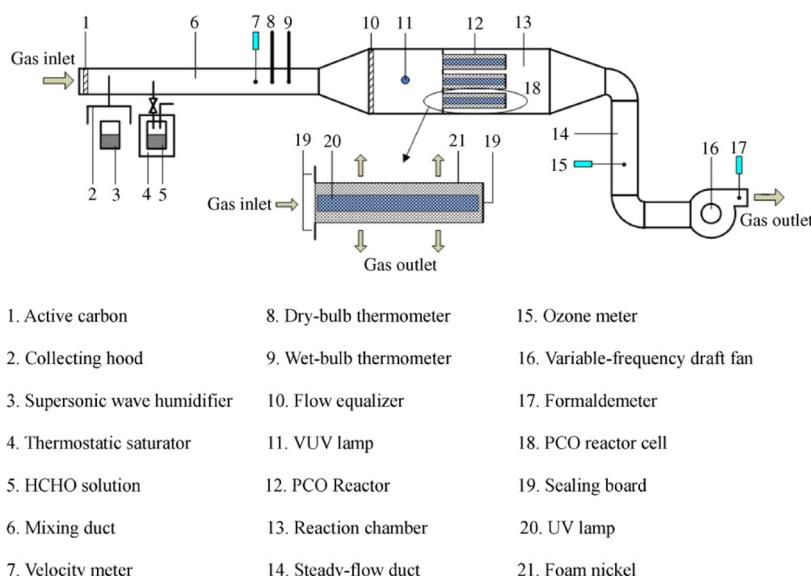


Figure 25. Schematic diagram of the experimental apparatus used in the study of Yang et al. for degrading gaseous formaldehyde. Reprinted with permission from ref 262. Copyright 2007 American Chemical Society.

VOCs.^{258–260} Although these works did not concern ethylene but rather compounds such as toluene, benzene, and formaldehyde, this hybrid method should also be effective for the elimination of ethylene, since interesting results were reported for gaseous formaldehyde. For example, in this case, Yang et al. investigated the influence of some reaction parameters, such as the concentration, the flow velocity, the relative humidity, and the light intensity, on the degradation performance shown by the hybrid TiO₂/VUV process.²⁶² The experimental apparatus used in the study of the hybrid TiO₂/VUV process is shown in Figure 25. The authors concluded that the conversion of formaldehyde could be remarkably improved by the combined use of TiO₂ and VUV compared to TiO₂/UV and VUV single processes, with this enhancement being especially emphasized at low formaldehyde concentrations (Figure 26). Moreover, they have shown the economic

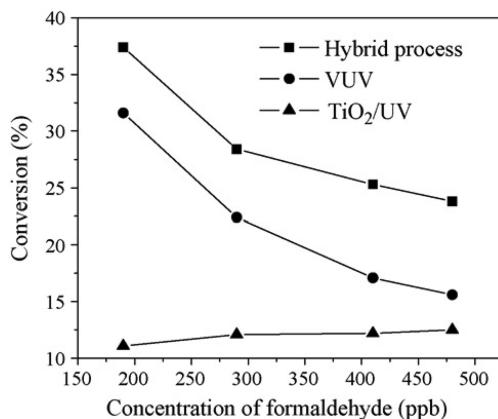


Figure 26. Influence of the formaldehyde inlet concentration in the 150–500 ppb range on the formaldehyde conversion in the TiO₂/VUV hybrid processes and in both VUV and TiO₂/UV single processes. Flow velocity: 0.6 m/s; relative humidity: 50–60%. Reprinted with permission from ref 262. Copyright 2007 American Chemical Society.

feasibility of the hybrid process, with a cost reduction of 60% per kg of removed formaldehyde when compared to the TiO₂/UV process. In addition, they evaluated that the operating cost remained rather low in comparison with those of heating, ventilation, and air-conditioning systems.

5.7. Targeting an Efficient Technology

Nowadays, UV-A—and, more globally, UV—photocatalysis is mainly limited by the recombination of photogenerated charges and by adsorption–desorption problems of reactants and products as well as of partially oxidized intermediates, that are taking place in the bulk and at the surface of the photocatalytic materials. In parallel to the search for and design of new, highly efficient photocatalytic materials for the removal of ethylene under the specific conditions of the storage or transfer of perishable fresh products (fruits and vegetables), the implementation of an ethylene removal technology should absolutely take into account the internal design of the photoreactor and the optimized management of the air-flow pattern and the temperature distribution inside the storage and transfer area.

Indeed, similarly to thermal catalysis, designing efficient processes requires taking into account photocatalytic reactor engineering as a key aspect. Recently, de Lasa, Serrano, and Salaices²⁶³ stated, “There is general agreement that an

important obstacle in the development of highly efficient photocatalytic reactors is the establishment of effective reactor designs for intermediate and large-scale use, as demanded by industrial and commercial applications.” The authors claimed that achieving a successful commercial implementation will require the optimization of several reactor design parameters, such as the photoreactor geometry, the type of photocatalyst, and the utilization of radiated energy. Novel designs of photocatalytic reactors are expected to be engineered for overcoming restrictive efficiency limitations and meeting the performance requirements for achieving a successful commercial implementation. Studying the interaction between the light, the catalyst, and the reactant gas flow, which needs a careful investigation of the UV source, of the reactor configuration and of the lamp location, as well as of the type, the distribution, and the impregnation modes of the catalyst, is required. This concerns the treatment of relatively large gas flows with low pressure drops and requires simultaneously good photocatalyst irradiation and efficient photocatalyst/reactant contact. This aspect remains highly challenging but is not specific to the photocatalytic oxidation of ethylene, so that the reader is likely referred to some well-documented reviews and books dealing with photocatalytic reactor engineering and design.^{263–272}

However, it is worth nothing that the present application of photocatalysis leads to operate the photocatalytic reactor in a somehow specific way, differing from the single-pass continuous flow mode and the batch reactor one. They are both basically used at the laboratory scale for studying reaction rates, determining kinetic rate laws, and establishing kinetic parameters used as experimental data for reactor scaling-up.^{273–277} Single-pass reactors are of concern when the pollutant target is continuously provided to the inlet of the reactor, while batch photoreactors are very often operating in a recirculating mode, with the volume to be treated—the reservoir—being largely greater than the real operating volume inside the photoreactor. This configuration is usually observed for devices designed for decontaminating or purifying atmospheres. However, one should not forget that air treatment devices are not usually operating in a real batch mode but in a semibatch mode.²⁶⁴ As an example, in the case of devices designed for removing ethylene from fresh product storage areas, the physiological production of ethylene by plants as well as the plant tissue respiration regularly provide to the overall volume, and therefore to the operating volume inside the reactor, a renewed input of ethylene and relative humidity, respectively.

6. CONCLUSIONS

It was first of interest to mention the origin of ethylene and its impact on the storage of fresh produce so that the interaction between the fresh product and its environment could be described in terms of storage environment characteristics such as temperature, relative humidity, ethylene content, and atmospheric composition. Many approaches have been developed for controlling ethylene production and for removing ethylene from the surrounding environment of fresh produce. By taking into account the very restrictive storage conditions for fresh products, photocatalytic technology appears to be a promising ecotechnology for removing ethylene from storage air.

Indeed, for more than three decades, photocatalysis, and especially that based on TiO₂, has attracted considerable scientific and practical interest. In parallel to the necessary understanding of mechanisms and reaction steps at the

molecular level, applied research in photocatalysis has to be focused on promising opportunities for which the advantages of the photocatalysis technology could meet the requirements of an important application field. The removal of ethylene for targeting better fresh produce storage and transfer is thus thought to be one of the promising activity fields for allowing photocatalysis to get out from the laboratory and semipilot scales and as a result to be very efficiently applied with benefits from the field and the producers through to consumers. Thus, through this multidisciplinary review, we hope to be successful in illustrating photocatalysis as a really promising technology, within a sustainable development approach, for replacing current ethylene removal technologies during the storage and the transfer of fresh fruits and vegetables. To fully achieve this goal, work remains to be performed on specifically adapting the TiO₂ photocatalyst to the ethylene molecule target and to the specific environment of fresh product storage. One should not forget also working at the photoreactor engineering level for providing ever more efficient processes (independently from the activity level of the photocatalyst), similarly as for all air treatment applications and indoor air applications, especially for which this aspect remains absolutely crucial due to the complexity of the targeted pollutant panel. If not absolutely necessary, such improvements would, however, lead to ever more efficient processes for a better implementation of the technology. By contrast, searching for better control and the optimization of the air-flow pattern and of the temperature distribution inside various kinds of containers loaded with the fresh products remains of high interest in order to suitably locate the (photocatalytic) ethylene removal device(s) and to adapt it/them to the size and the nature of the location as well as to the geometry of the loading (rows of vented pallets, porous boxes, etc.).

We claim that this review will encourage academics and industrials to conduct cooperative projects in the field of ethylene photocatalytic oxidation at the frontiers of chemistry, including chemists, biochemists, plant physiologists, and food scientists, from the laboratory scale to on-site measurement testing. It was highlighted that worldwide food technology could take advantage of photocatalysis technology for providing health and economical benefits and for globally contributing to both increased food quality and availability by reducing postharvest losses of fresh produce.

A concluding remark might be derived from the highly unexpected—although worthwhile—application field of Controlled Ecological Life Support Systems (CELSS) (or Bioregenerative Life Support Systems, BLSS), for which American, European, and Russian scientists have also developed a number of small complete plant growth systems for use in spaceflight research. Currently we are entering a new era of experimentation and hardware development as a result of long-term spaceflight opportunities available on the International Space Station for targeting the development of plant growth hardware as well as the design and building of innovative systems. Due to its advantages detailed in the above, UV photocatalysis technology is undoubtedly a promising technology to consider for long-term spaceflight applications. This unexpected field should remind us that targeting crossover research with border fields is fully one of the driving forces for developing promising technology from the laboratory scale and, thus, for helping it to democratize for domestic all-day life and industrial uses.

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Notes

The authors declare no competing financial interest.

[†]Conversion factor for ethylene in air: 1 ppm in air = 1.15 mg/m³ = 912 nL/L³⁹ (therefore, 1 ppb is close to nL/L).

Biographies



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Marie-Noëlle Ducamp graduated in 1979 from Nancy University in nutrition, food sciences, and biochemistry. She obtained her Ph.D. in biochemistry and chemistry technology of food in Montpellier. She

began her studies as a researcher at IRFA (Research Institute on Fruits and Agrumes) in 1981 in Avignon and later was a specialist in tropical crops and fruits in Montpellier. She worked in Ivory Coast and Trinidad and Tobago from 1991 to 1996 and then came back to CIRAD Montpellier (International Research Center for Agriculture and Development). Her research areas are the preservation of tropical fruits with physical and chemical techniques (plastic packaging, MAP, coating) and the limitation of chemicals in postharvest treatment, using molecules from natural origins. In 2005 she became Associate Professor at Montpellier SupAgro. She has authored 35 papers in peer-reviewed international journals.



Didier Robert is Assistant-Professor at the Chemistry Department at Saint-Avold Technological Institute from the University of Lorraine. Since 1996, his research has been focused on heterogeneous photocatalysis and its environmental applications in both wastewater and air treatments as well as in self-cleaning surfaces. In 2009, he additionally joined the research team headed by Valérie Keller at the Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC)—now Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES)—at Strasbourg University. He authored 70 international publications in the field of chemistry and photocatalysis. Editor-in-chief and cofounder of the Environmental Chemistry Letters periodical, published by Springer-Verlag in Berlin, he founded in 2000 the European meeting series SPEA “Solar Chemistry and Photocatalysis: Environmental Applications” and organized the first two editions held at Saint-Avold. Didier Robert has taught courses to undergraduates and doctoral students in the fields of organic chemistry and environmental chemistry. He has been invited as an external examiner and opponent of several adjunct professorships and doctoral degrees and participated in evaluation of research proposals in France and Europe. He has supervised several Ph.D. students and acted as a reviewer for several academic journals, many of which are top-ranked in the field.



Valérie Keller is CNRS research director at the Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé (ICPEES), in Strasbourg, a joined research unit newly created in 2013 between CNRS and Strasbourg University, and issued from the former Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC). She received her Ph.D. in chemistry and catalysis in 1993 from Louis Pasteur University in Strasbourg. After a postdoctoral period in Paris at the Laboratoire de Réactivité des Surfaces, headed by Prof. Michel Che, she returned to Strasbourg and was appointed in 1996 as CNRS research fellow at the LMSPC. She leads a research team developing mainly TiO₂-based materials for photocatalysis and solar photoconversion, as well as a strong interface between photocatalysis and life science. Applications in environmental reactions, energy, and health deal with air and water remediation, photocatalytic functionalized textiles, and photocatalytic and electro-photocatalytic water splitting for hydrogen production. She authored 80 papers and 12 patents. Her team was awarded the 2007 Alsace Regional award for innovation from the French national institute of industrial property. She acted as guest-editor for special issues of *Catalysis Today* and co-organized a European Material Research Society symposium.

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