

# Photocatalysis and vacuum ultraviolet light photolysis as ethylene removal techniques for potential application in fruit storage

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## Preface

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5. Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2019). Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions. Postharvest Biology and Technology, 147, 68-77.

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**Abstract**

Most fresh fruit and vegetables are highly perishable in nature and contribute to the highest percentage of food loss in the world annually (45%). Ethylene removal has been identified as an important postharvest strategy to reduce fruit and vegetable losses. The gaseous phytohormone ethylene, which is involved in the control of plant development, is produced in varying quantities by fruit and vegetables. In these produce, ethylene imparts many beneficial traits such as development of characteristic colour, taste, and flavour. However, ethylene exposure also accelerates ripening and senescence, which may result in pronounced quality losses. Removal of ethylene in and around these commodities can slow down metabolic processes, and thus can potentially extend their storage life. Conventional ethylene removal techniques (such as potassium permanganate, adsorbers, ozone, thermal catalytic units, etc.), may suffer from certain limitations including rapid saturation, need for frequent replacement, additional waste disposal requirement for end products, toxicity, or high costs. To address these limitations, the main aim of this study was to investigate two non-conventional techniques of ethylene removal, i.e. photocatalytic oxidation (PCO) and vacuum ultraviolet (VUV) radiation photolysis for application in fruit and vegetable storage. The study also aimed at understanding the effects of process parameters (such as flowrate, lamp power and in case of PCO catalyst area), and storage parameters, relevant in practical fruit and vegetable storage (such as temperature, humidity and oxygen concentration), on the ethylene removal efficiency of the two techniques.

To achieve the set goal, PCO and VUV reactors were developed, which were principally based on UV lamps with emission maxima at 254 nm and 254+185 nm, respectively. In case of PCO reactor, titanium dioxide ( $\text{TiO}_2$ ) coated onto glass slides was used as a catalyst. These reactors were designed as filtration devices to remove ethylene from the air present in fruit and vegetables storage areas. To carry out an in-depth study of the aforementioned techniques, several experiments were conducted in batch reactors as well as in continuous flow through the reactors. Experiments at varying ethylene concentrations were performed to elucidate the kinetics of ethylene oxidation reactions. Short-term fruit storage studies were conducted by connecting the reactors to fruit storage areas with the help of an air pump and the impact on fruit physiology and quality was assessed.

The results showed that the efficiency of the two considered techniques depended on the initial ethylene concentration, and at low ethylene concentration, the removal rates were slower. It was

observed that slower flow rates provided more time for reaction to occur, while higher lamp power resulted in the production of a higher number of oxidizing species thereby enhancing ethylene removal in both cases. Furthermore, oxygen was found to favour ethylene removal in both processes. In contrast, relative humidity adversely affected the ethylene removal efficiency of PCO but showed a beneficial impact in VUV photolysis. This suggests that hydroxyl radicals obtained by dissociation of water molecules were the dominant oxidizing species in VUV photolysis. Low temperature seemed to adversely affect the efficiency of VUV photolysis, which was not the case in PCO. Overall, the reaction rates were found to be much higher for VUV photolysis than for PCO. However, ozone was produced as a by-product in VUV photolysis, thus use of an effective ozone scrubber coupled with VUV photolysis-based filter is recommended. The storage studies showed that both techniques could effectively reduce ethylene concentration generated under fruit storage conditions. None of the two techniques exhibited detrimental effects on fruit physiology and visual quality during short-term storage (up to 10 d).

The potential of PCO and VUV photolysis for ethylene removal is reflected in the different parts of this thesis. The experimental data obtained from this work deepened the understanding of how process parameters and fruit storage conditions affected the ethylene removal capacity of the PCO and VUV photolysis techniques. The shortcomings of these processes and, thus, the points of improvement were also highlighted. These results provide substantial contributions to the scientific knowledge on ethylene management as well as to the horticultural industry by aiding in the development of efficient ultraviolet light-based ethylene removing systems. For future perspectives, in-depth study into the impact of both these techniques on fruit quality and safety (flavour, nutritive properties, microbiology) should be done, especially in long term storage.

## **Zusammenfassung**

Frisches Obst und Gemüse ist von Natur aus leichtverderblich und trägt jährlich zum höchsten prozentualen Anteil (45%) der Nahrungsmittelverluste in der Welt bei. Das Entfernen von Ethylen wurde als eine wichtige Nachernte-Strategie zur Verringerung von Obst- und Gemüseverlusten identifiziert. Das gasförmige Phytohormon Ethylen ist an der Kontrolle der Pflanzenentwicklung beteiligt und wird von den verschiedenen Obst- und Gemüsesorten in unterschiedlichen Mengen produziert. Bei vielen gartenbaulichen Erzeugnissen unterstützt es die Ausbildung positiver Produkteigenschaften, wie der charakteristischen Farbe, des Geruchs und des Geschmacks. In manchen Produkten kann die Ethylenexposition allerdings auch Reifung und Seneszenz beschleunigen und so zu deutlichen Qualitätsverlusten führen. Entfernt man das Ethylen in und um diese Güter, verlangsamt man deren Stoffwechselprozesse und erhöht damit deren Lagerfähigkeit. Hauptziel dieser Studie war es deshalb zwei nicht-konventionelle Methoden zur Entfernung von Ethylen in der Obst- und Gemüselagerung, i) photokatalytische Oxidation (PCO) und ii) Vakuum-Ultraviolett (VUV)-Strahlungs-Photolyse, zu untersuchen und zu optimieren. Die Studie vertieft auch das Verständnis der Auswirkungen von praxisrelevanten Prozess- (Durchflussrate, Lampenleistung und, nur bei PCO, Katalysatorfläche) und Lagerungsparametern (Temperatur, Feuchtigkeit und Sauerstoffkonzentration) auf die jeweilige Effizienz der Ethylenentfernung der zwei Techniken.

Um die gesetzten Ziele zu erreichen, wurden PCO- und VUV-Reaktoren entwickelt, die hauptsächlich auf UV-Lampen mit Emissionsmaxima von 254 nm bzw. 254 + 185 nm basieren. Im Falle des PCO-Reaktors wurde auf Glasobjektträger aufgetragenes Titandioxid ( $\text{TiO}_2$ ) als Katalysator verwendet. Die Reaktoren wurden als Filtereinheiten entwickelt, die das Ethylen aus der Luft in Obst- und Gemüselager entfernen. Um diese beiden Prozesse eingehend zu untersuchen, wurden Experimente sowohl in Batch-Reaktoren als auch in kontinuierlichem Durchfluss-Reaktoren durchgeführt. Dabei wurden unterschiedliche Ethylenkonzentrationen verwendet, um die Kinetik der Ethylenoxidation aufzuklären. Um die Auswirkungen der Methoden auf die Fruchtphysiologie und -qualität bewertet zu können, wurden weiterhin Kurzzeit-Lagerversuche durchgeführt, bei denen die Reaktoren mit Hilfe einer Umlaufpumpe an die Lagercontainer angeschlossen waren.

Die Ergebnisse zeigten, dass die Effektivität beider Methoden von der Ethylenausgangskonzentration abhingen. Bei niedrigen Ethylenanfangskonzentrationen waren die Entfernungsraten auch immer gering. Niedrige Durchflussraten verlängerte die Reaktionszeit, während hohe Lampenleistungen die Menge an oxidierenden Spezies erhöhte und so immer die Effizienz der Ethylenentfernung verstärkte. Darüber hinaus begünstigten hohe Sauerstoffkonzentrationen bei beiden Prozessen die Ethylenentfernung. Im Gegensatz dazu verringerte eine hohe relative Luftfeuchtigkeit die Effizienz der Ethylenentfernung bei der PCO, erhöhte sie jedoch bei der VUV-Photolyse. Dieses Phänomen legt nahe, dass Hydroxylradikale, die durch Dissoziation von Wassermolekülen entstehen, die dominierende reaktive oxidative Spezies in der VUV-Photolyse waren. Niedrige Temperaturen schienen die Effizienz der VUV-Photolyse, aber nicht der PCO, negativ zu beeinflussen. Insgesamt waren die Reaktionsraten bei der VUV-Photolyse viel höher als bei der PCO. Bei der VUV-Photolyse wurde jedoch Ozon als Nebenprodukt erzeugt, weshalb hier zusätzlich die Verwendung eines effektiven Ozonwäschers empfohlen wird. Die Lagerstudien zeigten, dass beide Techniken die Ethylenmengen, die unter den Lagerbedingungen von den Früchten erzeugt werden, effektiv reduzieren können. Bei einer Kurzzeitlagerung wirkte sich keine der beiden Techniken nachteilig auf Physiologie und visuelle Qualität der untersuchten Früchte aus.

Das entsprechende Potenzial von PCO und VUV zur Entfernung von Ethylen wird in den verschiedenen Teilen dieser Dissertation aufgezeigt, analysiert und umfassend bewertet. Die in dieser Arbeit gewonnen experimentellen Daten vertiefen somit das Verständnis der Einflüsse von Prozessparametern bzw. von Lagerbedingungen von Früchten auf die jeweilige Kapazität der Ethylenentfernung von PCO bzw. VUV-Photolyse. Die potentiellen Nachteile der jeweiligen Prozesse sowie die damit verbundene notwendigen Verbesserungen wurden ebenfalls evaluiert. Diese wissenschaftlichen Ergebnisse liefern somit einen wesentlichen Beitrag zu der Entwicklung effizienter, auf ultraviolettem Licht basierender Ethylenentfernungssysteme und helfen so entscheidend mit, das Ethylenmanagements in den Nachernteketten gartenbaulicher Produkte deutlich und praxisnah zur verbessern. Perspektivisch sollten aber mögliche Auswirkungen der beiden Techniken auf Fruchtqualität und -sicherheit (Geschmack, Nährstoffeigenschaften, Mikrobiologie), insbesondere bei Langzeitlagerung, intensiv untersucht werden.

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**List of abbreviations**

Abbreviation	Description
1-MCP	1-Methylcyclopropene
ACC	1-Aminocyclopropane-1-carboxylic acid
ADP	Adenosine diphosphate
ATP	Adenosine triphosphate
AVG	Aminoethoxyvinyl glycine
CA	Control atmosphere
CTR	Constitutive triple response
EIN	Ethylene-insensitive
Eqn.	Equation
ER	Endoplasmic reticulum
FAO	Food and Agriculture Organization
PCO	Photocatalytic oxidation
PER	Percentage ethylene removal
RH	Relative humidity
RNA	Ribonucleic acid
ROS	Reactive oxygen species
SAM	S-adenosylmethionine
UV	Ultraviolet light
VUV	Vacuum ultraviolet light
WRAP	Waste and Resource Action Programme

Symbol	Description	Unit
R	Reaction rate	$\mu\text{L L}^{-1} \text{ min}^{-1}$
C	Ethylene concentration	$\mu\text{L L}^{-1}$
t	Time	min
K	Adsorption coefficient	$\mu\text{L L}^{-1}$

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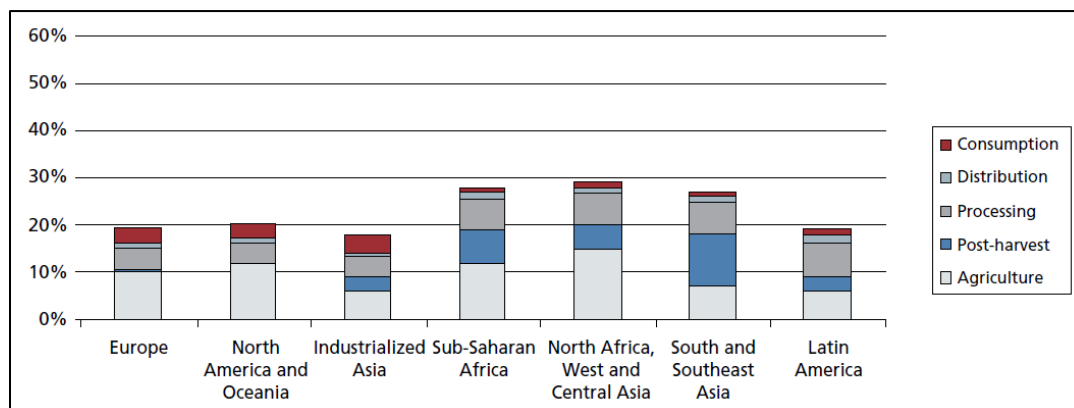


## 1. Introduction

*“Food security exists when all people, at all times, have physical and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life”* (FAO, 1996)

In the wake of the rising human population, there is a big challenge of fighting global hunger and ensuring food security. Currently, nearly one billion (about 815 million in 2016) people are undernourished and suffer from nutritional deficiencies (Porat et al., 2018). The world population is projected to increase to around 10 billion by 2050 and to feed this population, it is estimated that the food production would have to increase by 50%. Contrastingly, amidst this high demand of food, the amount of total food lost or wasted is one third of the total food produced which amounts to 1.3 billion tons per year (FAO, 2011). It was suggested that by 2050 if the food loss and waste is reduced by half, approximately 5498 trillion kilojoules less food per year would be needed to be produced (Porat et al., 2018). With the depleting agricultural land and resources, in order to cater to the food requirement of the ever-growing population utilizing the food production to the maximum and minimizing the waste seems a very logical resort. Out of the total food lost or wasted, fruit and vegetables constitute to 45% on mass basis of the total food losses (FAO, 2011). Fruit and vegetables are important source of nutrition with respect to vitamins, minerals, dietary fibre and, thus, can contribute to food and nutritional security. However, these are highly perishable products due to high water content and continued active metabolism after harvest (Mahajan et al., 2017). Distribution of fruit and vegetable losses or wastes at different stages of supply chains in different regions is shown in Figure 1-1.

Economically, the losses in postharvest are severe since all the investments in production, harvesting, processing and distribution is lost without commercial return. Reducing postharvest losses in fruit and vegetables can have numerous benefits, such as, higher food availability and nutrition to growing population, decrease in area needed for production and conservation of natural resources (Kader, 2003). After harvest, the quality of most fresh produce cannot be improved but only maintained. Strategies to maintain quality and, thereby, reducing postharvest losses include combination of temperature management, humidity control, suitable gas composition and ethylene management (Mahajan et al., 2017). Among these methods, reduction in ethylene concentrations has been suggested as one of the keys to reducing food waste (Blanke, 2014).



*Figure 1-1: Part of the initial production lost or wasted at different stages of the supply chain for fruit and vegetables in different regions (Source: FAO, 2011).*

### 1.1 Ethylene removal as a solution to reduction in fruit and vegetables loss

Ethylene is a gaseous plant hormone produced by higher plant tissues. In fresh fruit and vegetables, it is responsible for triggering rapid ripening and senescence. Ethylene accumulation is, thus, extremely detrimental in fruit and vegetable storage, especially in mixed loading where high ethylene producing commodities are stored close to highly ethylene sensitive commodities. Reducing ethylene concentrations from 100 ppb to < 5 ppb in many fresh produce handling areas increased shelf life by up to 60 % (Wills et al. 1999). According to one of the recommendations from the report by WRAP (Waste and Resource Action Programme) commissioned by UK government to identify ways of reducing wastage of fruit and vegetables, the fresh produce industry should consider installing ethylene removal/scrubbing equipment within storage facilities, particularly for the most susceptible product (Rees et al., 2011). Therefore, development and improvement of techniques/strategies to control and remove ethylene is quite important.

Conventional techniques for ethylene removal include air ventilation, use of different ab-/adsorbers and oxidisers (e.g. potassium permanganate), ozone, and catalytic oxidation (Martínez-Romero et al., 2007). Different techniques of ethylene removing/scrubbing are used according to the product, and type and volume of the storage space. In smaller storages or inside packages, use of sachets or sheets containing absorbing/adsorbing materials (such as activated carbons, clay, zeolite) and/or oxidisers (such as potassium permanganate) is suitable. However, these materials may get rapidly saturated, thereby, requiring frequent replacement, which may not



be ideal for long term storage or large storage volumes (Wills & Warton, 2004). After use, these materials may also pose additional problem of waste disposal. Air ventilation is an inexpensive and effective technique for ethylene removal in small to large storage spaces. However, air ventilation cannot be used in controlled atmosphere storage, as this would disturb the set conditions. Ethylene removing equipment based on ozone could be effective in treating large volumes in closed spaces as well as in controlled atmosphere storage. However, extreme caution is required in handling of ozone, as it is harmful to human health and high concentrations could be injurious to plant tissues (Smilanick, 2003). There are catalytic oxidation based units, which can oxidise ethylene in presence of a catalyst at high temperatures ( $>100\text{ }^{\circ}\text{C}$ ) (El Blidi et al., 1993). These units can operate in a continuous mode and treat large storage volumes. The requirement for high temperatures results in an energy intensive process, which may incur additional costs.

The limitations stated for all the above-mentioned techniques highlighted the need for a paradigm shift in ethylene management systems towards a more sustainable, safe and cost-effective approach. Thus, this thesis was focused on the investigation of two non-conventional ethylene removal techniques - photocatalysis (PCO) and vacuum ultraviolet radiation (VUV) photolysis - for application in postharvest storage of horticultural commodities. These techniques have certain advantages over the conventional methods. Neither technique generates solid waste; hence, no additional cost for waste disposal is involved. They also could operate continuously without frequent replacement of parts and they do not need elevated temperatures for operation. Both techniques are based on the use of ultraviolet irradiation, and mainly work on the principle of photogeneration of reactive oxygen species (ROS) that oxidize ethylene into carbon dioxide ( $\text{CO}_2$ ) and water. However, the mechanisms of ROS generation differ between the two techniques. Photocatalysis is a surface phenomenon (Ibhadon & Fitzpatrick, 2013). It is based on irradiation of the surface of a catalyst - normally a semiconductor such as titanium dioxide ( $\text{TiO}_2$ ) - with suitable wavelength, which results in an electron-hole pair separation. These surface-generated, electron-hole pairs react with surface adsorbed oxygen ( $\text{O}_2$ ) and water molecules to produce reactive species as shown in Figure 1-2a. On the other hand, in VUV photolysis, the radiation (100-200 nm) is able to dissociate  $\text{O}_2$  and water molecules in the gaseous state to produce ROS species (Figure 1-2b) (Huang et al., 2011). These ROS can break down various substances such as organic acids, microbes and some inorganic molecules (e.g. nitrous oxides ( $\text{N}_2\text{O}$ )) (Ibhadon & Fitzpatrick, 2013). Thus, PCO and VUV techniques have found good

applications in purification of water and air. There is a rapidly growing interest in photocatalysis and vacuum ultraviolet radiation photolysis for air and water purification as evident from the growing literature within the last three decades (Table 1-1).

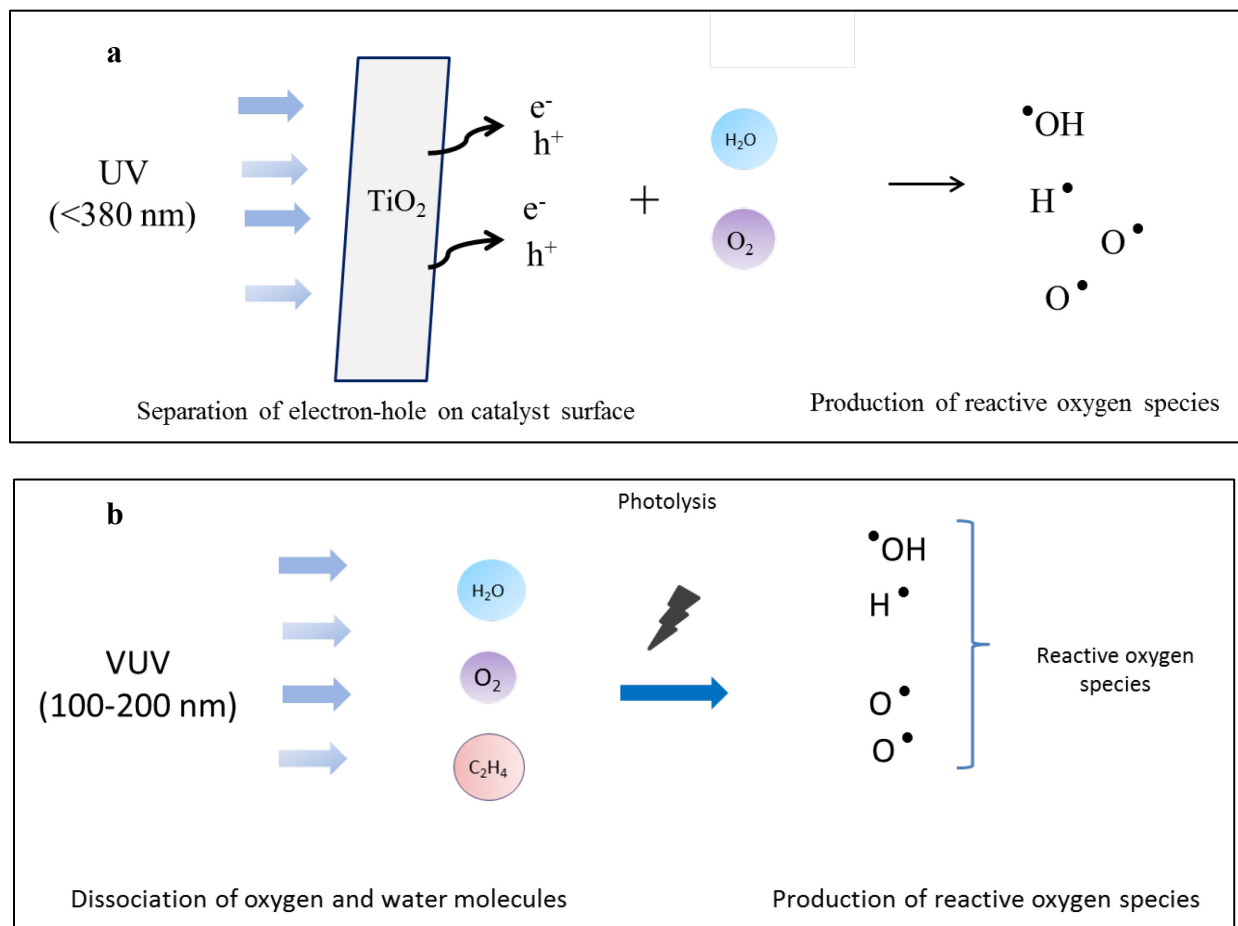


Figure 1-2: Generation of reactive oxygen species (ROS) in a) PCO b) VUV photolysis.

The oxidizing ability of PCO and VUV photolysis also makes these techniques applicable for removal of ethylene, which is of substantial interest along the postharvest value chain. However, there is limited scientific evidence to determine the effectiveness of these technologies to eliminate or reduce ethylene concentration along the postharvest supply chain of fresh produce. Information on the workability of these methods under conditions suitable for fruit and vegetable storage are lacking. Therefore, this study was undertaken to elucidate on the potential of using either PCO or VUV based techniques for ethylene removal, and to determine their efficacy under the realistic fruit storage conditions.

*Table 1-1: Number of articles found on web of science database on 23 May, 2018*

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Key words	Number of articles in 1990	Number of articles in 2017
Photocatalysis	10	4868
Photocatalysis and water	3	2243
Photocatalysis and air	1	261
Photocatalysis and ethylene	-	62
Vacuum ultraviolet radiation	3	140
Vacuum ultraviolet radiation and water	1	19
Vacuum ultraviolet radiation and air	1	18
Vacuum ultraviolet radiation and ethylene	-	5

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## **1.2 Research questions and hypotheses**

In order to achieve the focus of this study and establish that both PCO and VUV photolysis were reliable ethylene removing techniques for postharvest application, it was important to provide answer for the following research questions:

- How effective will PCO and VUV photolysis be in removal of ethylene compared to the use of scrubbers under mixed fruit load?
- How do the variable process parameters affect the efficiency of these methods, and which process parameter(s) as well as storage conditions play the most important role in terms of ethylene removal rate?
- Furthermore, since PCO and VUV photolysis application is aimed towards fruit and vegetable storage, it is important to inquire:
  - What are the impacts of extrinsic storage factors (such as temperature, relative humidity, O<sub>2</sub>/CO<sub>2</sub> gas composition and initial ethylene concentrations) on the efficiency of PCO and VUV photolysis?
  - Which of these techniques would perform best under realistic storage conditions for horticultural commodities?

Based on these research questions hypotheses were formulated for this PhD work:

- The novel ethylene removal techniques (PCO and VUV photolysis) can reduce ethylene from fruit storage under realistic storage conditions;
- Reaction process parameters significantly affect the efficiency of ethylene removal; and
- Cold storage, low O<sub>2</sub> concentration and high relative humidity would affect the efficiency of ethylene removal in PCO and VUV photolysis.

Based on the above stated hypotheses the aim and specific objectives of the study were identified.

### **1.3 Aim and objectives**

The aim of this study was to investigate PCO and VUV photolysis from the perspective of ethylene removal and their application in postharvest storage of fruit. The specific objectives of the study were:

- To investigate the efficiency of PCO and VUV photolysis in removing ethylene generated by stored fruit, and the subsequent impact on fruit physiology and quality;
- To determine the effects of different process parameters on the ethylene removal efficiency for PCO and VUV photolysis; and
- To investigate the effects of different fruit storage conditions on the performance of PCO and VUV photolysis based ethylene removal systems.

### **1.4 Thesis outline**

This thesis is structured into six chapters, and each of research chapters (3-5) stand as an independent component within the body of this thesis.

Chapter 1 is the introductory chapter that highlights the research hypothesis and objectives of this thesis.

Chapter 2 provides the theoretical background on ethylene and its role in the postharvest value chain. It provides a comprehensive assessment of current and emerging technologies for ethylene management. Furthermore, an extensive review is presented on the two ethylene removal techniques (photocatalysis and vacuum ultraviolet light photolysis), which are the focus of this study.

Chapter 3 discusses the role of ethylene in a mixed storage system with experimental data that emphasises on the impacts of mixed loading on fruit quality, and the benefits of ethylene removal.

Chapter 4 investigates the process parameters affecting the efficiency of VUV photolysis. This chapter also presents the results of an optimization study conducted to achieve maximum ethylene removal.

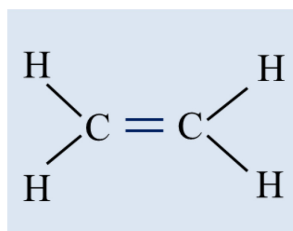
Chapter 5 is a comparative study on the impact of storage parameters on the efficacy of PCO and VUV photolysis. This chapter also reports on the kinetics of both the techniques along with the impact on apple storage.

Chapter 6 is the conclusive chapter that provides a summarized discussion of findings from this PhD work and the future perspectives based on the conclusions drawn from this study.

## 2. Theoretical background and literature review

### 2.1 Ethylene

Ethylene ( $C_2H_4$ ) is a colourless, flammable gas, which has a sweet or musky odour when pure. It is the simplest of alkenes as an ethylene molecule is constituted of four hydrogen atoms linked to two double-bonded carbon atoms as shown in Figure 2-1. Ethylene is a planar molecule and each H-C-H bond angle and H-C-C angle is  $117^\circ$  and  $121.5^\circ$ , respectively. The high electron density of the double bond makes the molecule susceptible to attacks by electrophiles. Some physical properties of ethylene are listed in Table 2-1.



*Figure 2-1: Structure of ethylene.*

*Table 2-1: Physical attributes of ethylene (Saltveit 1999, Abeles et al. 2012)*

Physical attributes of ethylene
<ul style="list-style-type: none"><li>• Colourless, flammable gas</li><li>• Molecular mass: <math>28.05 \text{ g mol}^{-1}</math></li><li>• Molecular diameter: <math>0.407 \text{ nm}</math></li><li>• Freezing point: <math>-181^\circ\text{C}</math></li><li>• Melting point: <math>-169.5^\circ\text{C}</math></li><li>• Specific volume: <math>861.5 \text{ mL g}^{-1}</math> at <math>21^\circ\text{C}</math></li><li>• Boiling point at <math>101.325 \text{ kPa}</math>: <math>-103.7^\circ\text{C}</math></li><li>• Triple point: <math>-162.2^\circ\text{C}</math></li><li>• Viscosity at <math>20^\circ\text{C}</math>: <math>10.08 \times 10^{-6} \text{ N s m}^{-2}</math></li></ul>

### 2.1.1 Ethylene as plant hormone

The physiological effects of ethylene on plants were earliest recognised in the nineteenth century by a Russian graduate student, Neljubow, who observed that pea seedlings had a horizontal growth under illumination from lamps. He later identified, as reported by Buchanan et al. (2000), ethylene, a component of the gas used for illumination, to be responsible for the abnormal growth. Later Gane (1934) proved that ethylene was produced by plants, and it could be quantified after gas chromatography was developed in 1959 (Martínez-Romero et al., 2007). Many decades of research studies have established ethylene as an endogenous plant growth regulator that affects various stages of development in plants including seed germination, adventitious root formation, stimulation of flowering, stimulation of fruit ripening, abscission and senescence (Goodlass & Smith, 1979; Pratt & Goeschl, 1969; Saltveit, 1999; Yang & Hoffman, 1984).

### 2.1.2 Sources of ethylene

Sources of ethylene can be biological as well as non-biological (Zagory, 1995). Some of these sources have been presented below:

**Burning of hydrocarbons and biomass:** Ethylene is a by-product of partial combustion of organic material. It could be added to the atmosphere through many anthropogenic activities such as exhaust from automobiles, forklifts, factories, boilers, etc. Burning of agricultural waste or wildfires are also common sources of ethylene.

**Microorganisms:** Various bacteria and fungi can also be sources of ethylene as ethylene is produced by them through bio-mass fermentation.

**Ripening rooms:** De-greening of bananas and citrus fruits is done commercially in ripening chambers. Usually commercial varieties of banana are ripened by exposure to 100-150  $\mu\text{L L}^{-1}$  ethylene for 24-48 h at 15-20 °C in ripening chambers (Kadar, 1996). By ventilation of these ripening chambers, the residual ethylene is released to the atmosphere.

**Plants:** Ethylene is biosynthesised by higher vascular plant tissues to control and regulate various growth and developmental activities. Ethylene biosynthesis in plant tissues is in low levels which may escalate during ripening of climacteric fruits, and also due to disease or injury. Ethylene can also be produced by rotting and decomposing plant material.

**Others:** Other sources of ethylene may include, volcanic eruptions, exposure of rubber materials to UV radiation or heat, etc.

### 2.1.3 Ethylene biosynthesis in plants

In higher plants, ethylene biosynthesis starts from the amino acid methionine, through a well-described mechanism commonly referred to as methionine cycle or Yang cycle (Abeles et al., 2012; Yang & Hoffman, 1984). The pathway for ethylene synthesis is represented in Figure 2-2. Methionine is converted to S-adenosylmethionine (SAM) catalysed by the enzyme SAM synthetase. In the next step, SAM is converted to 1-aminocyclopropane-1-carboxylic acid (ACC), catalyzed by the ACC synthase. In the final step, the ACC oxidase oxidises ACC to ethylene. Oxygen is required for the last step and low concentrations of CO<sub>2</sub> activate the ACC oxidase. Generally, the rate limiting step for ethylene biosynthesis is the production of ACC.

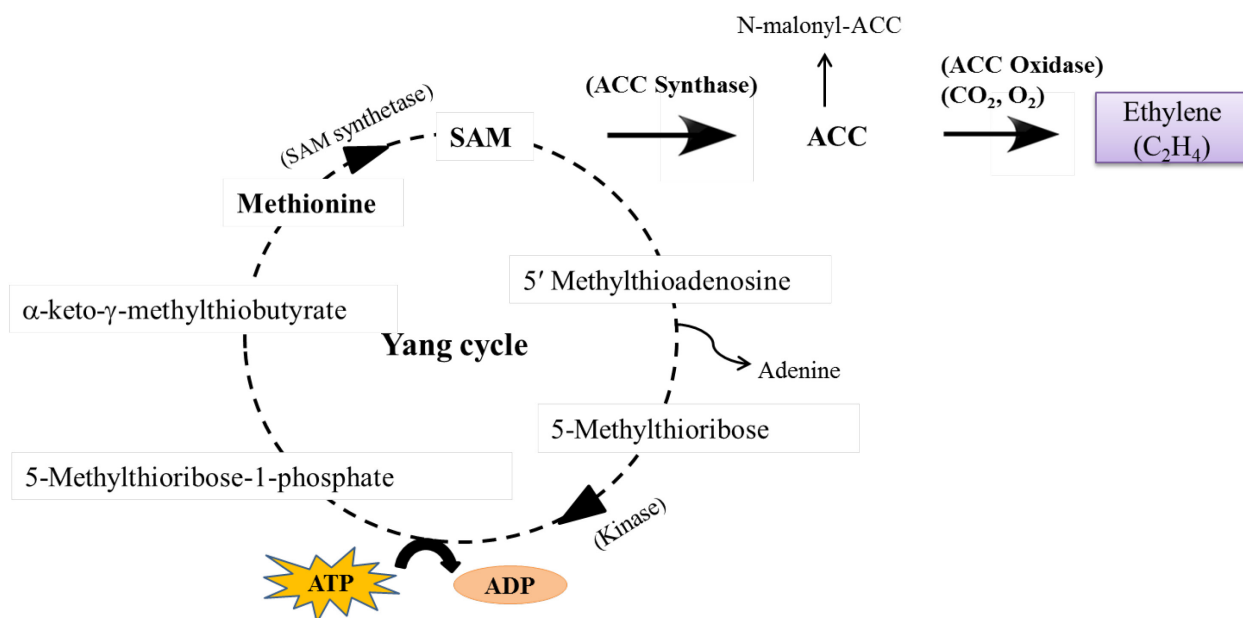


Figure 2-2: Metabolic pathway of ethylene synthesis. SAM: S-adenosylmethionine, ACC: 1-aminocyclopropane-1-carboxylic acid, ATP: adenosine triphosphate, ADP: adenosine diphosphate.

Increased ethylene biosynthesis occurring during germination, stress, ripening etc. is generally accompanied by higher ACC production due to activation of ACC synthase. Another product of ACC synthase reaction is 5' methylthioadenosine, which is used for the re-synthesis of methionine through Yang cycle. Increased respiration enhances the production of ATP, which is



required in the methionine cycle; this, consequently, can enhance ethylene biosynthesis even without high intercellular methionine concentration (Barry & Giovannoni, 2007). Plants can also limit ethylene biosynthesis by converting SAM to N-malonyl-ACC instead of ACC. Apart from ethylene, rates of ethylene biosynthesis can be influenced by other hormones, such as auxins. Auxins enhance ACC synthase production thereby increasing ethylene synthesis.

#### **2.1.4 Role of ethylene in fruit ripening**

Based on ethylene response and production during ripening, fruits can be categorised into climacteric and non-climacteric. Fruits in which the onset of ripening is accompanied by a sudden burst of ethylene production and enhanced respiration are called climacteric such as apples, bananas, avocado, peach, tomatoes. In contrast, non-climacteric fruits (e.g. strawberry, cherry, grapes) lack this drastic increase in ethylene production during ripening (Saltveit, 1999). This categorisation, however, is not absolute. Many species of melons and capsicum show climacteric as well as non-climacteric behaviour (Barry & Giovannoni, 2007). Fruit ripening is often associated with changes in colour (breakdown of chlorophylls, and increase in carotenoids and/or anthocyanins), firmness (cell wall degradation), taste (conversion of starch to sugar) and flavour (production of volatile organic compounds) (Martínez-Romero et al., 2007). Ethylene can play an important role in bringing about these changes.

In past few decades, extensive physiological, biochemical, and molecular research on understanding the mechanism of ethylene perception and signal transduction (the means by which cells response to a signal), has been performed (Barry & Giovannoni, 2007; Burg & Burg, 1962; Yang & Oetiker, 1994). Based on these studies, some insight in the complex mechanism of signal perception and transduction has been attained. A schematic of this mechanism is shown in Figure 2-3. Ethylene is perceived by a receptor complex in the membranes of the endoplasmic reticulum (ER) of cells, which uses copper as a co-factor (Rodriguez et al., 1999). The signal is transduced through regulators [protein complex such as constitutive triple response (CTR), ethylene-insensitive [(EIN2), (EIN3)]. Ultimately, transcriptional factors [proteins that regulate by recruiting and activating RNA (ribonucleic acid) polymerase] regulate the target gene (Nath et al., 2007). The target gene or the set of target genes, which control fruit firmness, taste, colour and aroma etc. produce specific biological response (Bapat et al., 2010). During ripening of climacteric fruits, ethylene plays a major role in the signalling mechanism of the ethylene dependent gene expression, while other hormones are of secondary importance. This process is

accompanied by the autocatalytic ethylene biosynthesis (Pech et al., 2012). Contrastingly, in non-climacteric fruit, ethylene does not play a major role and the majority of gene expression is ethylene independent. Despite all recent efforts, the mechanisms of signalling are not yet fully understood and research is still going on in this area.

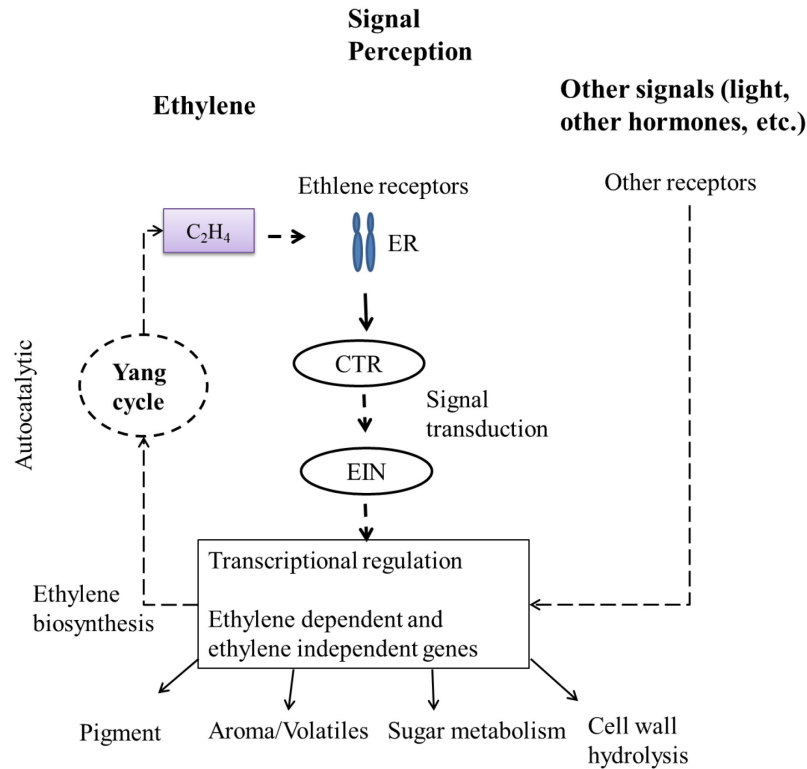


Figure 2-3: Schematic for pathway of ethylene dependent and independent ripening related events (ER: endoplasmic reticulum, CTR:constitutive triple response, EIN: ethylene-insensitive).

## 2.2 Effects of ethylene on fruit and vegetables

The effect of exogenous or externally present ethylene on fruit and vegetables varies depending on the type of commodity. In climacteric fruit types exogenous ethylene triggers ripening in the fruit, which results in an autocatalytic production of endogenous ethylene. Once ripening is triggered, ripening as well as ethylene biosynthesis continues, even if the external ethylene is removed, although at lower rates. In non-climacteric fruit and in non-fruit vegetables, development is accelerated with the increase in external ethylene concentration. This process, however, slows down if ethylene concentrations are reduced and even stops when ethylene is totally removed.

The impact of ethylene on fruit and vegetables may be considered beneficial or unwanted depending upon produce type, the degree of exposure and the desired outcome. Ethylene induced ripening in many fruits is certainly desired for the development of the characteristic colour, taste and flavour (Saltveit, 1999). For instance, ethylene is commercially used for de-greening of citrus fruit and ripening of green bananas (Rodrigo & Zacarias, 2007). However, over-exposure to ethylene may also lead to over-ripening and excessively soft fruit, which may be unwanted in handling, transport and storage, where the storage life of fruit and vegetables needs to be prolonged. Apart from ripening and senescence, ethylene may also increase pathogen susceptibility and other physiological disorders such as russet spotting in lettuce (Fan & Mattheis, 2000). Some beneficial and detrimental effects of ethylene are listed in Table 2-2. In view of these unwanted effects of ethylene on fruit and vegetables, there is a strong need to reduce or at least control ethylene concentration in fruit and vegetable handling areas.

*Table 2-2: Some beneficial and detrimental effects of ethylene in fruit and vegetables (modified from Saltveit 1999)*

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Beneficial effects	Detrimental effects
<ul style="list-style-type: none"><li>• Promotes colour development in fruit</li><li>• Stimulates ripening of climacteric fruit</li><li>• Promotes de-greening of citrus</li><li>• Promotes flowering in Bromeliaceae (e.g. pineapple)</li><li>• Reduces lodging of cereals by inhibiting stem elongation</li></ul>	<ul style="list-style-type: none"><li>• Accelerates senescence</li><li>• Stimulates chlorophyll degradation (e.g. yellowing)</li><li>• Enhances softening of fruit</li><li>• Stimulates phenylpropanoid metabolism</li><li>• Hastens toughening of vegetables</li><li>• Stimulates abscission of leaves (cabbage, cauliflower)</li></ul>

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### **2.2.1 Ethylene synthesis rates and sensitivity in fruit and vegetables**

Steady state rates of ethylene biosynthesis in plant tissues, e.g. in growing fruit tissues, are very small ( $0.1\text{-}0.2 \mu\text{L kg}^{-1} \text{ h}^{-1}$ ). However, upon ripening or also under biotic or abiotic stresses, ethylene biosynthesis may accelerate drastically. Threshold concentrations for ethylene activity

was previously considered to be  $0.1 \mu\text{L L}^{-1}$  (Knee et al., 1985). However, even at lower concentrations, ethylene is biologically active and could stimulate biological processes in many fruit and vegetables. In a study by Wills et al. (1999), 60% shelf life extension could be obtained in 23 produce by reducing ethylene concentrations to  $<0.005 \mu\text{L L}^{-1}$  compared to  $0.1 \mu\text{L L}^{-1}$ . Thus, the likely threshold for ethylene activity is much lower than  $<0.1 \mu\text{L L}^{-1}$ ; the actual threshold has, however, not yet been categorised due to difficulty in accurately measuring to such low concentrations (Wills, 2015). Different types of fruit and vegetables have different rates of ethylene synthesis and also their sensitivity to ethylene is different. Ethylene synthesis and sensitivity in few horticultural commodities is listed in Table 2-3.

*Table 2-3: Ethylene production and sensitivity in selected commodities (adapted from Blanke 2014)*

Type of produce	Commodity	Ethylene production	Ethylene sensitivity
Climacteric	Apple	++	+
	Avocado	+	+
	Banana	o	+
	Fig	o	–
	Kiwifruit	–	+++
	Passionfruit	+++	+
	Pear	+	+
	Tomato	o	+
Non-climacteric	Strawberry	–	o
	citrus	– – –	o

+++ very large  $>100$ ; + large  $10-100$ ; o intermediate level  $1-10$ ; – low  $0.1-1$ ; – – – very low  $<0.1 \mu\text{L kg}^{-1} \text{ h}^{-1}$  ethylene emission; +++ highly sensitive to ethylene; – very low sensitivity

Both these traits, namely, ethylene synthesis and sensitivity to ethylene, are not necessarily correlated (Martínez-Romero et al. 2007). Some fruit (e.g. kiwifruit, apples) are high producers of ethylene as well as highly sensitive to it, while some fruit and vegetables (such as strawberry, cucumber, lettuce, cauliflower) are low producers of ethylene but highly sensitive to it. In contrast, grapes, pineapple, peppers and others are neither high producers nor highly sensitive to ethylene.

### 2.3 Ethylene concentration in supply chain

Ethylene concentration in ambient air is generally low, in the range of 1-5 nL L<sup>-1</sup> (Abeles et al., 2012). However, as ethylene is a by-product of hydrocarbon combustion, in heavy traffic in urban areas ethylene concentrations may reach up to 1 µL L<sup>-1</sup> or more in the air. In handling areas of fruit and vegetables, especially in enclosed spaces such as storage rooms, shipping containers, and packages, ethylene concentration may increase many folds above that in ambient air. Rees et al. (2011) reported ethylene concentrations measured at various points in grocery supply chain of multiple retailers. These measurement points included: storage facilities, pack houses, depots, shop stores and in retail area. Highest ethylene concentration, up to 3.6 µL L<sup>-1</sup>, were found in the storage areas while lower concentrations were recorded in retail areas (0.002-0.035 µL L<sup>-1</sup>) and in shop store (0.018-0.048 µL L<sup>-1</sup>). Wills et al. (2000) also investigated ethylene concentration in fruit and vegetable handling areas in wholesale markets, distribution centres and retail stores through more than 700 measurements taken over a period of three years. Their recorded observations indicated higher ethylene concentrations up to 0.6 µL L<sup>-1</sup> in wholesale markets and distribution areas while lowest concentrations were found in supermarkets with a mean concentration of 0.017-0.035 µL L<sup>-1</sup>. This indicated supermarkets were well ventilated. In another study, on-site ethylene concentrations measured in apples supply chain were 4.5 µL L<sup>-1</sup> in cold storage, 0.5 µL L<sup>-1</sup> in sorting line and 0.11 µL L<sup>-1</sup> in CA store with ethylene scrubbing (Blanke, 2014). High ethylene concentrations in controlled atmosphere (CA) storage with apples (27-243 µL L<sup>-1</sup>), and pears (11-118 µL L<sup>-1</sup>) have also been reported in literature (Lawton, 1991).

In the preliminary work for this thesis, ethylene concentrations were measured at three different commercial packing/ripening facilities, which showed a wide variation in ethylene concentrations ranging from 180 µL L<sup>-1</sup> inside apple storage chamber without CA to 0.15 µL L<sup>-1</sup> inside short term fruit storage as shown in Table 2-4. An important observation in these stores was that mixed loading or different commodities were handled together there. Such mixed loading is common commercial practice due to space constraints. In a study by Lawton (1991), about 50 µL L<sup>-1</sup> ethylene (produced from apples) in a container ship with mixed fruit cargo was recorded, which was found to be contaminating nearby areas (0.5 µL L<sup>-1</sup> ethylene was detected in next hold carrying frozen cargo). Ethylene accumulation can be a serious problem in such loadings as ethylene producing commodities can be in close proximity of ethylene sensitive commodities. Proper segregation of commodities based on ethylene is beneficial; however, ethylene can easily

diffuse from one compartment to the other as ethylene has specific mass ( $1.178 \text{ kg m}^{-3}$  at  $15^\circ\text{C}$ ) similar to that of air ( $1.225 \text{ kg m}^{-3}$  at  $15^\circ\text{C}$ ) (Janssen et al., 2014). This highlights the necessity of an efficient ethylene scrubbing technology along the supply chain.

*Table 2-4: Ethylene concentration as measured in commercial fruit and vegetable stores*

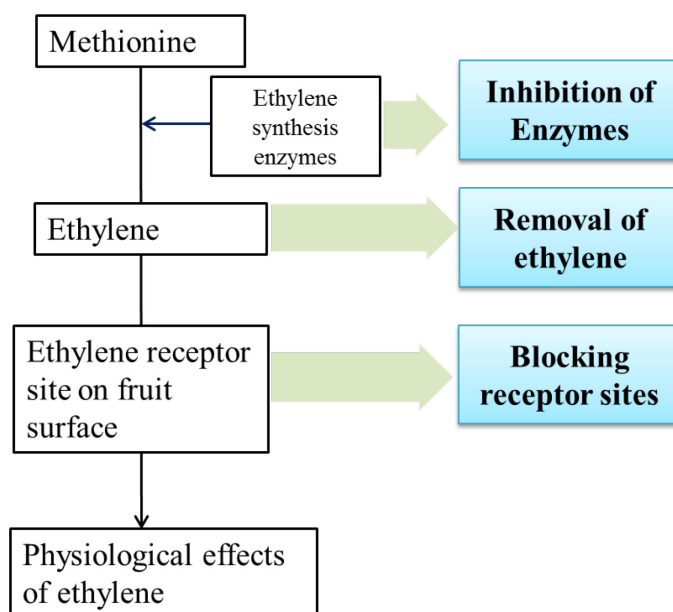
Store	Sampling area	Ethylene concentration ( $\mu\text{L L}^{-1}$ )
A	CA storage chamber of apples	$15.45 \pm 4.9$
	(T $2.7^\circ\text{C}$ , $\text{O}_2$ 13.4%, $\text{CO}_2$ 3.0%)	
	CA storage chamber of apples (T $2.4^\circ\text{C}$ , $\text{O}_2$ 3.2 %, $\text{CO}_2$ 1.4 %)	$11 \pm 2$
	Storage chamber of apple without CA	$180 \pm 2$
	Passage way	$9.25 \pm 0.5$
	Packaging Line	$5.99 \pm 0.1$
B	Outside ripening chamber	3.43
	Packaging line	0.7
	Loading area	1.29
	Cooling rooms	$2.16 \pm 0.14$
C	15 different points in the same mixed storage room	$0.15 \pm 0.1$

*Store A: Long term controlled atmosphere (CA) storage of apples, storage and packaging line for tomatoes, capsicum, apples, and other fruit and vegetables; Store B: Ripening chambers for ripening of bananas, storage and packaging lines of fruits; Store C: Short term storage of mixed load of fruits (apples, melons, oranges, pineapple, grapes) intended for daily supply of fresh-cut fruits.*

## 2.4 Ethylene management strategies

Strategies to prevent ethylene action in fruit and vegetables can broadly be classified into three categories (i) inhibition of ethylene biosynthesis, (ii) blocking the ethylene action at receptor level and (iii) removal of ethylene from the vicinity of fruit and fruit handling areas (Figure 2-4). Inhibition of ethylene synthesis may involve the use of chemicals that affect the biosynthetic pathway. Aminoethoxyvinyl glycine (AVG), for example, inhibits the activity of ACC synthase. Ethylene biosynthesis inhibition could also be obtained by genetic modification of the plant.

Certain storage conditions (hypobaric storage, i.e. storage at <50 kPa pressure, controlled and modified atmosphere storage, low temperatures etc.) are also known to reduce ethylene biosynthesis. For blocking ethylene receptor sites of fruit and vegetables, chemicals such as 1-methylcyclopropane (1-MCP) are used, which render ethylene ineffective. The last category involves physical removal of ethylene. For this purpose, many techniques are available. A review of these methods is provided in the next sections in which current methods of ethylene removal are discussed followed by an intensive review of the two emerging techniques, photocatalytic oxidation and vacuum ultraviolet radiation photolysis, which are the main focus of this PhD study.



*Figure 2-4: Some options to prevent ethylene action on the physiology of fruit and vegetables (modified from Abeles et al. 2012).*

#### **2.4.1 Ethylene removal from fresh produce storage: current methods and emerging technologies**

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# Ethylene Removal From Fresh Produce Storage: Current Methods and Emerging Technologies

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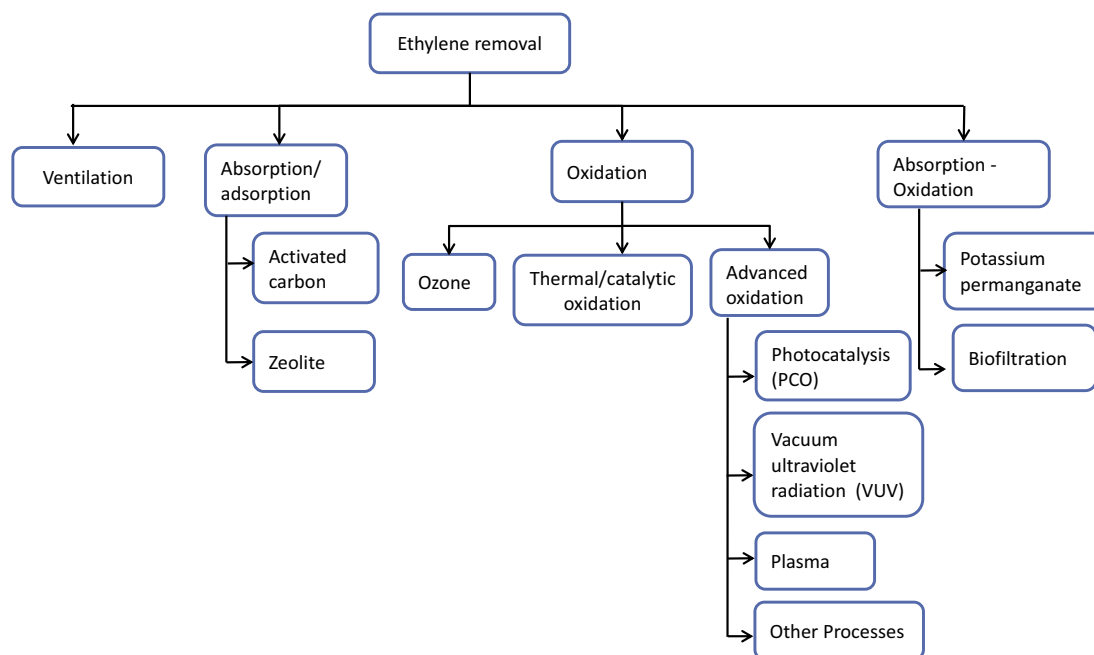
## Introduction

Ethylene is a colourless and odourless gas that acts as a plant ripening hormone. It is produced by plant tissues as a product of plant metabolism. Another source of ethylene is burning of hydrocarbons (Zagory, 1995). Among various effects of ethylene, it is responsible for rapid ripening and accelerated senescence in many climacteric and non-climacteric fresh produce (Ku et al., 1999; Saltveit, 1999). This effect of ethylene is often unwanted in postharvest storage and transport where the main focus is on extending shelf life of the produce. Thus, there are many existing and upcoming strategies of ethylene management and control. These strategies can be categorised into three groups; a) inhibition of endogenous ethylene production, b) inhibition of ethylene action and c) ethylene removal from the vicinity of the fresh produce. In the first category, products such as AVG (aminoethoxyvinylglycine) are used that affect the reaction pathway of ethylene biosynthesis and consequently the ethylene biosynthesis by the plant tissues is inhibited (Yuan and Carbaugh, 2007). Hypobaric storage (storage at low pressures <50 kPa), controlled and modified atmosphere storage (high CO<sub>2</sub> and low O<sub>2</sub>) can also reduce ethylene production (Burg, 2004; Wills et al., 1982). In these techniques although ethylene production is suppressed, if the produce is subjected to exogenous ethylene from other sources, the detrimental effect of ethylene cannot be prevented. In the second category, products such as 1-MCP (1- methyl cyclopropane) are used for inhibiting the ethylene action i.e. the 1-MCP blocks the ethylene receptors on the produce surface and with no access to the receptors, ethylene is unable to affect the produce (Sisler and Serek, 1997). 1-MCP is being widely used and has resulted in favourable results in terms of delaying ripening and senescence and in some cases, reducing the occurrence of disorders (Blankenship and Dole, 2003). However, the effect of 1-MCP is variable on different products and can result in uneven ripening of the produce after prolonged storage (Mahajan et al., 2014). Moreover, it leaves a residue on the fruit surface and thus, cannot be used for organic products. The third strategy is to remove ethylene present in the vicinity of the fresh produce which may include different techniques such as venting, absorption and oxidation which have been shown in Fig. 1. Commercially available products based on different methods have been listed in Table 1. The detailed discussions of the various conventional and emerging methods under ethylene removal have been done in the following sections.

## Current Methods

### Ventilation

This is one of the easiest techniques to remove ethylene from surrounding areas of fruits and vegetables. The storage area can be replenished with atmospheric air at regular intervals. Air ventilation in long distance transport for maintaining low ethylene levels in banana transport was reported by Wills et al. (2014). This technique is generally used in cooler areas for reducing temperature



**Figure 1** Different processes for ethylene removal.

**Table 1** Some commercially available products for ethylene removal

Method	Product name	Description	Company
Adsorption, Adsorption-oxidation	It's Fresh! PrimePro®	Palladium impregnated zeolite sheets	It's Fresh! Ltd, UK
	Extend-A-Life™ Produce Saver™	Filters, sachets	DeltaTRAK, Inc., USA
	KEEPPRESH®	Sheets, bags	AgraCo Technologies International LLC, USA
	Peakfresh Green Bags™	LDPE film impregnated with mineral Clay	Teck Blue Systems, SL Keepfresh, Spain
	EC-3+	Zeolite impregnated with potassium permanganate in sachets, filters, filtration system	Peakfresh, Australia
Oxidation with ozone High temperature catalytic oxidation	Bi-On®, ETHYL STOPPER Ryan®	Porous clay and potassium permanganate Natural clays and potassium permanganate (KMnO <sub>4</sub> ) in sachets and filters	Evert-Fresh Corp., USA
	ETI 25, 50 TMC Ethylene absorbers, TMC-5 Converter	ABSOTIL/purafil- Alumina pellets Sodium Permanganate pellets	Ethylene Control Inc., USA
	Bio-Turbo	Ozone	Bioconservación S.A, Spain
	SWINGTHERM-BS	Air filtration equipment	Sensitec Co., USA
	Catalytic converters	Air filtration equipment	Fruit Control Equipments srl, Italy
Photocatalytic oxidation	na	Air filtration equipment	The Magic Cube Company Ltd., Hong Kong
	na	Platinum aluminium granules used in air filtration equipment	Miatech, Inc., USA
	ECOscrub	Titanium dioxide + UV light based air filtration equipment	Fruit Control Equipments srl, Italy
	AiroCide® FRESH+™	Air filtration Catalyst + UV light	The Magic Cube Company Ltd, Hong Kong
			Besseling Group BV, The Netherlands
			Van Amerongen, The Netherlands
			Absorger, France
			KES Science & Technology, Inc.
			Fresh Plus International, USA

na: not available.

Adapted from Pathak et al. (2017a).

with the added benefit of ethylene removal. It is important to ensure that the replacement air must be ethylene free. As stated before ethylene is also produced from burning of hydrocarbons, thus, the exhaust from vehicles etc., may add to ethylene contamination in the air resulting in higher ethylene concentration in the air than normal (0.001–0.005 ppm) (Warton et al., 2000). Thus, conditioning of the outside replacement air may be required in non-optimal external atmosphere conditions. Excessive ventilation can also result in higher weight loss (Wills, 2015; Wills et al., 2012). Moreover, ventilation is not a suitable option in closed storages with controlled or modified atmospheres or refrigeration.

### Adsorption/Absorption

Highly porous substances such as activated carbon and zeolite (aluminosilicate minerals) are effective in adsorbing ethylene. These materials may be used in form of sheets, filters or pads for ethylene absorption. Palladium incorporated into activated carbon was reportedly found to be more effective in fruit storage with tomato as the test product compared to activated carbon alone (Bailén et al., 2006). A heat cartridge connected to activated carbon with 1% palladium was developed by Martínez-Romero et al. (2009) to prevent saturation of the absorber. Palladium impregnated, zeolite based sheets yielded good results in terms of effective ethylene removal in green bananas and avocado (Smith et al., 2009; Terry et al., 2007). These sheets have been commercialised and are available as packaging films, sheets, pads etc. (It's Fresh! Ltd., UK). Other products such as Peakfresh (Peakfresh, Australia) made of LDPE film impregnated with naturally occurring minerals and Green Bags™ (Evert-Fresh Corporation, USA) based on clay are available. However, the absorbers may get saturated after a period of use or when high ethylene concentrations are present and thus, would require replacement or regeneration.

### Oxidation

#### Using Ozone

Ozone is a strong oxidiser and its application in ethylene removal is well known (Smilanick, 2003; Suslow, 2004). It can oxidise impurities as well as disinfect microbes which makes it suitable for use in fruit and vegetables. An ozone concentration of 0.4 ppm effectively removed ethylene from apple and pear storage without affecting fruit quality. However, high ozone concentrations can be detrimental for stored fresh produce (Smilanick, 2003). Controlling ozone concentration especially with respect to the exposure to humans is a major challenge. The recommended safe limit of ethylene exposure in the USA is 0.1 ppm for an 8-h duration (US-OSHA (United States Occupational Safety and Health Administration)), and is even lower in other countries (e.g. New Zealand). Higher ozone concentrations are hazardous and can result in headaches, lung damage, chronic respiratory disorders and can even be fatal.

Filter systems based on ethylene removal using ozone are marketed by Bio-Turbo (Miatec, USA). Ethylene-laden air is drawn in from the fruit storage which is made to react with ozone inside the specialised chamber. After oxidation, clean CO<sub>2</sub> and H<sub>2</sub>O is returned back to the storage. Use of a catalyser to oxidise residual ozone ensures no ozone leakage into the environment as provided in the data by the company.

#### Catalytic Oxidation

At high temperatures, ethylene can be oxidised in the presence of catalysts into carbon dioxide and water. El Blidi et al. (1993) developed an industrial type prototype for oxidation of ethylene at temperatures 100–120 °C in presence of catalysts of manganese and copper. This prototype was tested in storage of golden delicious apples and was able to retain the quality close to the initial properties even at the end of storage. Commercial equipment based on these methods are available such as Swingtherm (Fruit Control Equipments srl, Italy). Companies such as Van Amerongen (The Netherlands), Absorger (France), Besseling Group (The Netherlands) also manufacture similar systems for ethylene removal in fresh produce storage.

#### Photocatalysis or Photocatalytic Oxidation (PCO)

Photocatalysis or photocatalytic oxidation (PCO) is a relatively new technique for application in the postharvest sector for ethylene removal. It involves irradiation of a semiconductor with a suitable wavelength radiation. Semiconductors have a small energy gap between their valence band and conduction band. Radiation with a suitable wavelength can excite electrons from the valence band to the conduction band, simultaneously generating holes in the valence band. These electron–hole pairs are highly reactive and combine with surface adsorbed water and oxygen molecules to produce reactive oxygen species such as hydroxyl radicals, superoxide ions etc. These species eventually oxidise ethylene into carbon dioxide and water. Titanium dioxide is the most commonly used catalyst owing to its easy availability, stability and low cost. Other photocatalysts are also available (Si, Au oxides etc). Extensive research into modifying the catalyst for better efficiency and light radiation utilisation is being carried out (Chen and Mao, 2007; Hussain et al., 2010). Several modifications for the activation of the catalysts in the visible light region are also being carried out for better application (Licciulli et al., 2017; Lin et al., 2014). Commercial equipment based on photocatalysis such as ECOscrub (Absorger, France) and AiroCide® (KES Science & Technology, Inc) are available. However, scientific reports on the efficiency and effectiveness of such equipment in maintaining fresh produce quality are few. Application of a photocatalytic reactor inside a refrigerator and in cold storage was reported by Kartheuser and Boonaert (2007) on the other hand, quality of papayas in storage with a photocatalytic reactor was reported by Lourenço et al. (2017).

### ***Oxidation Using Shortwave UV Light (Vacuum Ultraviolet Light VUV)***

Shortwave ultraviolet light (often referred to as vacuum ultraviolet radiation, VUV ( $\lambda < 200$  nm)) has high energy photons ( $\sim 6$  eV) that can dissociate water and oxygen molecules present in the atmosphere into reactive oxygen species. Commercially such lamps are available that produce major radiation at 254 nm (UV-C) and minor radiation at 185 nm (VUV). Use of such lamps in banana storage for ethylene removal was demonstrated in the early 1970s (Scott et al., 1971). The use of VUV radiation is extensively studied for purification of air and has demonstrated good results in ethylene removal as well as in removal of microorganisms which could be a major advantage for storage of fruits and vegetables storage. However, production of ozone as a by-product limits this process. Pathak et al. (2017b) studied various factors affecting this process and also found it effective in reducing ethylene produced by apples. However, research into the effect of this process on all fruit quality aspects is needed.

## **Adsorption-Oxidation**

### ***Using Potassium Permanganate***

Potassium permanganate ( $\text{KMnO}_4$ ) is one of the widely used products for ethylene management. In a complete reaction with  $\text{KMnO}_4$ , ethylene is oxidised to carbon dioxide and water in a complete reaction leaving behind residue  $\text{MnO}_2$  and  $\text{KOH}$ . Usually it is used with an additional adsorber/absorber material that absorbs the residue. These products are generally available as sachets (Purafil, USA) which can be placed close to the produce. In the first step, ethylene is absorbed by the absorbers and then oxidation takes place. In an incomplete oxidation, by-products such as potassium acetate may also be formed. Thus, by-products and end residue requires disposal. Moreover, in a study it was reported that  $\text{KMnO}_4$  had reduced efficiency at high humidity conditions (Wills and Warton, 2004). Thus, frequent replacement may be required in long storage durations or with high ethylene concentrations. Bi-On<sup>®</sup>, ETHYL STOPPER by Bioconservación S.A, Spain are filtration equipment and sachets, respectively based on porous clay and potassium permanganate. Recently, some products based on  $\text{NaMnO}_4$  have become available. According to the company (The Magic Cube Company Ltd.), it exhibits better efficiency than  $\text{KMnO}_4$  in ethylene removal.

### ***Bio-filtration***

Another technique for ethylene removal is bio-filtration which employs a microbial load for ethylene removal. Biofiltration can be carried out using bioscrubbers, biofilters and biotrickling filters (Delhoménie and Heitz, 2005). In bioscrubbers microbes are suspended in an aqueous medium whereas in biofilters and biotrickling filters, the microbial load is immobilised on a filter material. Biotrickling filters differ from biofilters in terms of the movement of nutrient solution. As the name suggests, biotrickling filters have a continuously trickling or circulating nutrient solution through the filter bed whereas in bio filters there may be occasional replenishment with a nutrient solution. The filtering material may consist of one or multiple layers of porous substances such as peat, compost or soil. Some examples of different filter materials reported in literature are peat soil (Elsgaard, 2000), granular activated carbon (inoculated with *Bacillus* or *Pseudomonas* strains) (Kim, 2003), active sludge, peat wood chips, humus with organic soil (Moghadam et al., 2015), perlite and glass beads (Lee et al., 2010). Ethylene is first absorbed by the porous media and then oxidation takes place at the biological film formed by the microbes. The end product of ethylene oxidation is water,  $\text{CO}_2$  and microbial cellular material. Kim (2003), by application of an activated granulated carbon biofilter, was able to achieve 100% ethylene removal in 14 min residence time for an inlet ethylene concentration of  $331 \text{ mg m}^{-3}$ . In another study (Moghadam et al., 2015), biofilter substrate was tested in a banana storage experiment by placing the substrate in cotton bags inside a fruit box containing bananas. At the end of 7 days storage at  $30^\circ\text{C}$ , bananas stored with substrate of biofilter had ripened to a lesser degree than the untreated control.

Biofiltration is advantageous in terms of being of low energy intensive, moderate cost and has a low maintenance cost. However, it is a slow process. Biofilters may be associated with problems of pressure drop and require a large surface area. Moreover, for application in horticulture storage often low temperatures  $< 15^\circ\text{C}$  are used, thus, it is important to ensure that the microbial strain being used has sufficient activity even at these temperatures.

## **Emerging Technologies**

### **Advanced Oxidising Species Based Techniques**

Several upcoming processes based on active oxygen species (similar to photocatalysis) have been shown to be effective in oxidation of ethylene and are being studied for potential application in ethylene removal in horticultural storage. In such processes advanced oxidation species such as hydroxyl radicals, superoxide ions are produced that convert ethylene into carbon dioxide and water in a complete reaction. Such processes may include various hybrid techniques, such as combination of PCO with ozone, PCO with VUV, combining VUV with ozone-assisted catalytic oxidation, and non-thermal plasma techniques. A hybrid process of VUV-PCO was reported to have higher ethylene removal efficiency compared to VUV, and PCO processes alone (Chang et al., 2013). Since ozone is produced in a VUV processes, coupling it with a secondary catalyst (Mn, Co, Fe, Ni supported on an aluminosilicate zeolite ZSM-5 (Zeolite Socony Mobil-5) or activated carbon with  $\text{TiO}_2$ ) has been demonstrated for better ozone removal and at the same time, better volatile organic compound oxidation can also be achieved (Huang et al., 2016). Ethylene degradation using non-thermal plasma discharge techniques such as dielectric barrier, and corona discharge for plasma generation have been reported (Ma and Lan, 2015). In the plasma reaction, highly reactive radicals such as charged hydrogen and charged

**Table 2** Advantages and limitations associated with various ethylene removal processes

Process	Principles/characteristics	Advantages	Limitations
Ventilation	Ventilation of storage units with fresh air from outside	<ul style="list-style-type: none"> <li>● Easy</li> <li>● Low cost</li> </ul>	<ul style="list-style-type: none"> <li>● Requires conditioning of fresh air</li> <li>● Excessive ventilation results in weight loss of product</li> </ul>
Absorption/adsorption	Use of porous materials such as activated carbon, zeolite	<ul style="list-style-type: none"> <li>● Can be used with small packages</li> </ul>	<ul style="list-style-type: none"> <li>● Need replacement when saturated</li> <li>● Regeneration is difficult</li> </ul>
Ozone based oxidation	Use of ozone gas to oxidise ethylene	<ul style="list-style-type: none"> <li>● Suitable for big storage spaces</li> <li>● Disinfectant properties</li> </ul>	<ul style="list-style-type: none"> <li>● High concentration of ozone-injurious to plant tissues</li> <li>● Hazardous to human health (&gt;1 ppm)</li> <li>● Handling difficulties</li> </ul>
Thermal catalytic oxidation	Use of high temperature in presence of catalyst	<ul style="list-style-type: none"> <li>● Continuous in operation</li> </ul>	<ul style="list-style-type: none"> <li>● Energy intensive</li> <li>● Need elevated temperatures</li> </ul>
Photocatalytic oxidation (PCO)	Use of ultraviolet light in presence of a catalyst for generation of electron hole pair and reactive oxidation species	<ul style="list-style-type: none"> <li>● Continuous in operation</li> <li>● Does not require elevated temperature or pressure</li> </ul>	<ul style="list-style-type: none"> <li>● Not efficient at low ethylene concentrations</li> <li>● Catalyst deactivation may occur with time</li> </ul>
Vacuum ultraviolet radiation photolysis (VUV)	Use of high energetic protons to generate reactive oxidation species	<ul style="list-style-type: none"> <li>● Continuous in operation</li> <li>● Does not require elevated temperature or pressure</li> </ul>	<ul style="list-style-type: none"> <li>● Production of ozone</li> <li>● Needs ozone filtration</li> </ul>
Plasma	Electric field and accelerated electrons required for production of reactive species such as charged hydrogen, charged oxygen	<ul style="list-style-type: none"> <li>● Continuous in operation</li> </ul>	<ul style="list-style-type: none"> <li>● Production of ozone</li> <li>● Needs ozone filtration</li> </ul>
Potassium permanganate	KMnO <sub>4</sub> oxidizes ethylene into carbon dioxide and water	<ul style="list-style-type: none"> <li>● Simple process</li> <li>● Can be used within small packages</li> </ul>	<ul style="list-style-type: none"> <li>● Cannot be regenerated</li> <li>● Needs frequent replacement</li> <li>● Toxic residue disposal problems</li> </ul>
Biofiltration	Oxidation by biofilm formed by microorganisms	<ul style="list-style-type: none"> <li>● Easy</li> <li>● Low cost</li> <li>● Low maintenance</li> </ul>	<ul style="list-style-type: none"> <li>● Slow process</li> <li>● Requires large surface area</li> <li>● Requires optimal environmental conditions for microbial growth and survival</li> </ul>

oxygen species are generated. [Graham et al. \(1998\)](#) developed a plasma reactor for potential use in the fruit and vegetable industry which was able to remove 78.2% of ethylene (initial 1 ppm concentration) in a single pass. Similarly, a reactor for application in cold humid fresh produce storage with a corona discharge plasma coupled with TiO<sub>2</sub> and activated carbon film was developed by [Ye et al. \(2013\)](#). However, these processes are in the fundamental stages of study. Although these techniques show good results in terms of ethylene degradation, complexities of these processes and ozone production are a challenge when it comes to actual application. Research on the impact of these processes on the quality of products, ease of application, and cost effectiveness is currently lacking.

## Conclusion

Various ethylene removal techniques have their own advantages and limitations as summarised in [Table 2](#). Currently, a variety of commercial products based on these techniques in the form of sheets, pads, and filtering equipment are available. Certain products give better results in terms of ethylene removal when placed inside fresh produce packages while others can be more suitable for large storage spaces. Thus, it is important to select the appropriate ethylene removal method depending on various factors such as ethylene sensitivity of the fruits, storage space, quantity of fruit etc. Comparable scientific data of the impact of different ethylene removal processes on fruit quality is missing which makes the comparison among these techniques difficult. Thus, for a comparative assessment of these products, scientific information regarding the efficiency of different commercially available products in actual storage conditions along with the cost analysis will be helpful. Overall, since ethylene plays an important role in ripening of many horticultural products, the advancement of ethylene removal technologies is much needed. Emerging technologies such as advanced oxidation-based processes still need further research in terms of practical applicability.

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## **2.5 Photocatalytic and photochemical oxidation of ethylene: potential for storage of fresh produce—a Review.**

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# Photocatalytic and Photochemical Oxidation of Ethylene: Potential for Storage of Fresh Produce – A review

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## Abstract

The phytohormone ethylene exerts numerous beneficial and detrimental effects on postharvest quality and storage life of fruit and vegetables. In view of the current global challenge of reducing postharvest losses and waste of fruit and vegetables, the importance of ethylene management in the supply chain is paramount. For this purpose, various methods have been applied along the supply chain over the years; however, effective management of ethylene under real time storage and transport conditions still remains a challenging task. This review explores the potential of photocatalytic and photochemical oxidation of ethylene for effective removal of this gas along the value chain of fruit and vegetables. These techniques involve the use of ultraviolet (UV) radiation with or without a catalyst. In photocatalytic oxidation, a semiconductor such as titanium dioxide is essential which acts as a photocatalyst on irradiation with UV light and thus, facilitates the oxidation of ethylene at its surface. Whereas in photochemical oxidation, extreme short wave (i.e. below 200 nm) vacuum ultraviolet radiation (VUV) consisting of high-energy photons eliminate ethylene in the gaseous state. This review gives a brief overview of current commercial techniques used in ethylene removal and then focuses on the photocatalytic and the photochemical oxidation of ethylene, and the combination of both methods. The various factors affecting these processes are also discussed including the advantages and the drawbacks associated with them and current applications of these methods in fruit and vegetable storage systems are highlighted. In addition, a future outlook on the application of these methods in postharvest storage of fresh produce is given.

**Keywords:** *Postharvest, titanium dioxide, UV light, reactive oxygen species, fruit and vegetables*



## Introduction

Ethylene is a gaseous plant hormone that exhibits both, beneficial and detrimental effects in postharvest storage of fresh produce. Beneficial effects include the development of characteristic colour, taste and flavour of fruit and vegetables (F&V). On the other hand, it may induce detrimental effects such as the promotion of senescence, leading to discoloration and softening, and increased susceptibility to decay, all of which shorten the storage life. F&V are highly perishable products and together with roots and tubers, form the highest share (40-50%) of total food wasted per year globally (FAO 2015). One inherent cause of fresh produce waste is the natural process of ripening and senescence. Hence, slowing down ripening is of utmost importance in postharvest management of F&V (Bapat et al. 2010). In this context, ethylene management plays a pivotal role in enhancing the postharvest storage life, in maintaining the quality of fresh produce for longer periods and also in reducing postharvest losses (Blanke 2014; Wills and Golding 2015).

During storage, F&V are exposed to endogenous ethylene, i.e. synthesized by the produce through metabolic processes, as well as to exogenous ethylene present in the atmosphere (Salveit 1999). Effects of ethylene on growth and the development of F&V can be beneficial or detrimental depending on its functional role and extent of exposure. For example, ethylene accelerates chlorophyll degradation. This reaction is desirable in degreening of citrus fruits (Rodrigo and Zacarias 2007), but it is detrimental in the case of broccoli or green leafy vegetables (Fan and Mattheis 2000a). Wills (2015) suggested that in general, ethylene could induce physiological responses in fresh produce even at concentrations below  $0.001 \mu\text{L L}^{-1}$ . The threshold for its physiological effects on F&V, however, may vary widely. A summary of detrimental effects of ethylene on F&V is provided in Table 1.

In the holding areas of F&V, higher than normal concentration of ethylene in air may occur due to ethylene emission from climacteric fruits as well as from movements of trucks, tractors or gas powered forklifts, as ethylene is also a by-product of combustion of hydrocarbons (Zagory 1995; Wills et al. 2000). Along the F&V supply chain, however, high ethylene accumulation occurs during transportation and storage. In mixed loading where both ethylene sensitive and ethylene producing commodities are often stored together, this can be highly detrimental (Wills 2015), as ethylene can easily diffuse from

one shelf to the other because it has nearly the same specific mass (0.97-0.99 kg m<sup>-3</sup>) as air (1.27 kg m<sup>-3</sup>) (Blanke 2014). Rees et al. (2011) investigated the ethylene concentrations at various points in the F&V supply chain including retail areas, depots, shop stores, pack-houses and storage facilities. The authors found lowest ethylene concentrations (< 0.05 µL L<sup>-1</sup>) in retail areas and shop store rooms, indicating that good ventilation prevented accumulation of ethylene. Highest ethylene concentrations (up to 3.6 µL L<sup>-1</sup>) were found in storage facilities. In both, climacteric and non-climacteric fruit, postharvest life linearly increased when ethylene concentrations were logarithmically decreased from 10 to 0.001 µL L<sup>-1</sup> (Wills et al. 2001, Pranamornkith et al. 2012). Even at low concentrations ethylene could have detrimental impact depending on the storage temperature and exposure time. Thus, implementation of suitable ethylene control technologies at the critical points of the entire F&V supply chain can effectively minimise ecological and economical losses due to unnecessary waste of fresh produce.

Several physiologically active compounds have been shown to be useful in preventing the effects of ethylene. Beneficial effects of ethylene biosynthesis inhibitors, such as aminoethoxyvinylglycine, on postharvest quality have been demonstrated in apples and stone fruits (Silverman et al. 2004); both alone and in combination with controlled atmosphere (CA) storage (Garner et al. 2001). Inhibitors of ethylene action such as 1-methylcyclopropene (1-MCP) effectively impede ethylene action and, consequently, help to extend storage life and maintain quality of F&V (Blankenship and Dole 2003; Watkins 2006). On the other hand, ethylene absorbers such as zeolite, palladium, activated charcoal, and the oxidizers potassium permanganate (KMnO<sub>4</sub>) and ozone have also been regularly applied to prevent the accumulation of ethylene (Bailén et al. 2006; Smith et al. 2009). Other ethylene management methods include venting by air, high temperature catalytic oxidation, hypobaric storage, and application of bio-filtration (El Blidi et al. 1993; Li et al. 2006; Elsgaard 2000). The drawbacks of these techniques include their limited effectiveness in ethylene removal, the need for long exposure time and the challenges of waste disposal or high cost (Keller et al. 2013, de Chiara et al. 2015; Maneerat et al. 2003). These methods remain relevant and are used in daily practices. However, emerging techniques based on photocatalytic and photochemical oxidation of ethylene offers an alternative approach that could help reduce some of these historical drawbacks.

Photocatalytic oxidation of ethylene involves the use of a catalyst such as titanium dioxide (TiO<sub>2</sub>). At the catalyst surface, illumination with UV radiation produces reactive oxygen species (ROS), which oxidize ethylene into carbon dioxide (CO<sub>2</sub>) and water. On the other hand, irradiation with extreme shortwave vacuum UV radiation (VUV) induces photochemical oxidation processes, leading to production of ROS in the gaseous phase by decomposing O<sub>2</sub> and water molecules, and these reactive species oxidize ethylene. These techniques have been extensively studied and have been regularly implemented for air and water purification (Farhanian and Haghghat 2014; Jiang et al. 2015). However, limited attention has been given to the application of these techniques in postharvest storage of F&V, although they hold great potential for effective removal of ethylene in postharvest storage systems (Maneerat and Hayata 2008; de Chiara et al. 2015).

Furthermore, only few review articles have been published on methods of ethylene inhibition and control (Sisler and Serek 1997; Martínez-Romero et al. 2007; Keller et al. 2013; Scariot et al. 2014). All of these publications lack a concise review on the use of photocatalytic and photochemical oxidation of ethylene in fresh produce storage. Hence, this review presents recent advances on ethylene management via photocatalytic and photochemical oxidation in postharvest storage. Also, advantages and drawbacks of the photocatalytic and photochemical ethylene oxidation as well as its implications on storage of fresh produce are presented.

## **Commercially available technologies for ethylene management**

Inhibition, control and removal of ethylene in fresh produce supply chains have received widespread attention over the years leading to the development of various ethylene management technologies (Table 2). The currently available commercial ethylene control systems and techniques can be grouped according to their mode of action. This includes the inhibition of ethylene biosynthesis and of its action, and the absorption, adsorption, oxidation, catalytic oxidation and photocatalytic oxidation of ethylene, as listed in Table 2.

In plants, ethylene production can be prevented by the application of chemical biosynthesis inhibitors such as aminoethoxyvinylglycine (AVG). AVG inhibits the activity of the enzyme of ethylene biosynthesis, the ACC synthase (EC 4.4.1.14) that converts S-adenosyl methionine into 1-amino-cyclopropane carboxylic acid (ACC) (Scariot et al.

2014). The latter is the direct precursor of ethylene (Watkins 2002). The commercially available product ReTain® (Valent BioSciences Corporation, USA) is based on the application of AVG.

The inhibition of endogenous production may; however, become ineffective if the produce is – additionally - exposed to exogenous ethylene because the action of ethylene is independent of its source (Wills 2015). Hence, preventing the action of ethylene by inhibiting the binding to its specific receptor molecule, finally triggering the complex cascade of physiological reactions showed to be an effective alternative (Sisler and Serek 2003; Blankenship and Dole 2003). Blankenship and Dole (2003) showed that the gaseous, low mass 1-methylcyclopropene (1-MCP) indeed competitively and reversibly binds to the ethylene receptor site, thus, preventing ethylene action. 1-MCP, active even at low concentrations ( $< 1 \mu\text{l L}^{-1}$ ), is assumed to be non-hazardous and leaves no residues. It is relatively easy to use but it is unstable in solution (Watkins 2006). However, 1-MCP can be incorporated with  $\alpha$ -cyclodextrin to maintain its stability. This development represented a major step towards its commercialization, as it was then possible to release 1-MCP from the complex to expose to the horticultural products (Mahajan et al. 2014). Various 1-MCP products are commercially available such as SmartFresh<sup>SM</sup> (AgroFresh, Inc. USA).

Research has been conducted on the application of 1-MCP on F&V for extending the shelf life of the produce (Li et al. 2016; Valero et al. 2016; Rupavatharam et al. 2015; Watkins 2006; Blankenship and Dole 2003). Though 1-MCP is an effective, low cost option, it can cause various disorders. These include wooliness, internal breakdown and reddening in peach and nectarines, chilling injury in citrus fruits, CO<sub>2</sub> injury in CA storage in apples and also increased susceptibility towards diseases in avocado, mango and papaya (Watkins 2006). Application of 1-MCP may cause uneven ripening or the treated fruit may not be easily ripened later (Wills 2015). Hence, in many cases a technical solution that simply removes ethylene from the produces' environment may be more advantageous in reducing exogenous ethylene induced losses.

Current methods applied for this purpose include the use of adsorbers such as activated carbon and zeolite. Activated carbon is produced from wood, peat, char, fossil oil, and coconut and nut shells. This type of carbon has a good ethylene adsorption capacity owing to its high specific surface area, which may range between 500 and 1500 m<sup>2</sup> g<sup>-1</sup> (Wang et al. 2009). Bailén et al. (2006) reported that the use of activated carbon with

1% palladium (Pd) was more effective than activated carbon alone in maintaining the quality of tomatoes in MAP system. Martínez-Romero et al. (2009) developed a hybrid system of activated carbon plus 1% Pd and a heat cartridge that could generate heat pulses to prevent the saturation of carbon by deposited gases.

The highly microporous aluminosilicate minerals (molecular sieves) zeolites are other effective physical ethylene adsorbents (Limtrakul et al. 2001). Zeolites can be used in filters, in form of sachets or incorporated into films (Li et al. 2012) and in storage of fresh produce (García et al. 2014). Palladium impregnated zeolite was found effective in ethylene removal from green banana and avocado, and maintained the green colour of banana and avocado for a longer time than fruits without such treatment (Terry et al. 2007; Smith et al. 2009). These compounds are commercially available as sachets or sheets (It's Fresh! Ltd, UK). Other packaging films incorporating clay/zeolites are available, like PEAKfresh® (Peakfresh, Australia) and Green Bags™ (Evert-Fresh Corporation, USA). However, the use of adsorbers may have a constraint in terms of their ethylene adsorption capacity. They may not be adequate for large volume storage and it may need replacement often. This practice is not feasible in a CA storage facility.

Potassium permanganate ( $\text{KMnO}_4$ ) is one of the most commonly used oxidizers for ethylene. In order to increase the surface area of absorption,  $\text{KMnO}_4$  is often supported on zeolite and alumina. Sachets and filters for warehouses based on  $\text{KMnO}_4$  are manufactured by companies such as ProdeW Water & Air Innovations (USA), CargoDepot (Mexico) or DeltaTRAK, Inc. (USA). Products with  $\text{KMnO}_4$  embedded in inert media such as natural zeolite are commercially available, for example from Ethylene Control Inc. (USA) or porous clay in Bi-On® from Bioconservación (Spain). These products adsorb ethylene while  $\text{KMnO}_4$  oxidizes it. Alumina impregnated with  $\text{KMnO}_4$  is marketed by Ozeano (Spain). A major drawback of  $\text{KMnO}_4$  is that it gets saturated overtime resulting in reduced efficiency. For short storage durations,  $\text{KMnO}_4$  is well suited for ethylene removal; however, for longer storage durations with high ethylene producing commodities  $\text{KMnO}_4$  may get rapidly saturated, thereby requiring frequent replacement (Wills 2015). Additionally, the oxidation reaction leads to the formation of by-products that need further disposal. In a complete reaction  $\text{KMnO}_4$  oxidizes ethylene into  $\text{CO}_2$  and water, while  $\text{KMnO}_4$  itself is converted into  $\text{MnO}_2$  and  $\text{KOH}$ . An incomplete oxidation reaction produces intermediates, such as, potassium acetate which may

remain bound to the residue (Keller et al. 2013). Thus, these by-products along with the support residue raise further disposal issues.

Another successful ethylene oxidizer in industrial application is ozone. It is enlisted as GRAS and it is permitted to be used as a secondary direct additive to food (Yaseen et al. 2015), but it has restricted use as the safety level of exposure to human health is 0.1  $\mu\text{L L}^{-1}$  (Smilanick 2003). Large amounts may also cause damages in plant species leading to more ethylene production. For example, a daily exposure of 3.25  $\mu\text{L L}^{-1}$  of ozone injured apples (Smilanick 2003). Control and regulation of ozone concentrations is the main challenge in this method. Bio-Turbo by Miatech, Inc. (USA) uses ozone for oxidation of ethylene. Ozone generators for installation in cold storage of F&V are commercially available from Eco sensors (USA) and Ozone solution Inc. (USA).

Catalytic oxidation of ethylene at high temperatures in the presence of catalysts such as oxides of copper, manganese, and oxidation promoters- calcium, potassium, and sulphur has been studied by Conte et al. (1992) and El Blidi et al. (1993). These authors achieved almost 100% ethylene removal at temperatures between 100-130 °C. El Blidi et al. (1993) applied this technique on storage of golden delicious apples and they observed that even after 134 days of storage the fruit retained most of their properties. Swingtherm by Fruit Control Equipments srl (Italy) is an example of equipment based on high temperature catalytic oxidation of ethylene. Platinum aluminium granules were used as catalysts in the ethylene converter by Van Amerongen (The Netherlands). Other ethylene converters based on catalytic combustion are marketed by Absorger (France), and Besseling Group (The Netherlands). High temperature catalytic oxidizers may involve high energy requirements, as the air needs to be heated and cooled subsequently.

Bio filtration is another technique of ethylene removal. It utilizes a biologically active filter material such as layers of compost, peat or soil that contains ethylene-degrading microorganisms (Kim 2003). However, this is a slow process (Lin et al. 2013) and may have problems of pressure drop and may also require larger area (Delhoménie and Heitz 2005), which may limit its commercialization. Hypobaric or low pressure storage may also aid in decreasing ethylene production and thereby reducing postharvest senescence in fresh produce (Li et al. 2006), but it is expensive and this impedes its industrial application for removal of ethylene (Maneerat et al. 2003).

Photocatalytic oxidation (PCO) is an emerging technique for ethylene removal. It involves a photoreaction, which occurs in the presence of light and a catalyst such as  $\text{TiO}_2$  (Ibhadon and Fitzpatrick 2013). PCO is cost effective, can be operated at room temperature and atmospheric pressure, and can oxidise a wide range of both organic and inorganic pollutants (Lin et al. 2013; Mo et al. 2009). Commercial devices based on photocatalysis using  $\text{TiO}_2$  for postharvest application are AiroCide® by Kes Science and Technology (USA), FRESH+™ marketed by Catalyx Technologies (USA) and ECOscrub by Absorger (France). PCO may provide an alternative to high temperature catalytic oxidisers in terms of reduced energy requirements. However, further real-time applied research for fresh produce in storage facilities or shipping containers is required to provide much needed scientific evidence of PCO technique. This will also help in its optimization for practical storage conditions.

#### **Photocatalytic oxidation of ethylene**

Photocatalysis is a low cost, environmental-friendly technology that can be used to degrade a variety of pollutants in aqueous and gaseous phase (Ibhadon and Fitzpatrick 2013). It can be described as a chemical reaction that occurs in presence of a photon activated catalyst (Hay et al. 2015). This photocatalyst is usually a semiconductor, which is activated by absorbing photons of suitable wavelengths and remains unconsumed at the end of the reaction. Among semiconductors, employed for photocatalysis,  $\text{TiO}_2$  is the most popular (Farhanian and Haghighat 2014). This is attributed to its unique properties such as biological and chemical inertness, high ultraviolet absorption, high stability and low costs (Nakata et al. 2012).

In nature,  $\text{TiO}_2$  mostly exists in three mineral forms – anatase, rutile and brookite (Macwan et al. 2011). Due to its specific photochemical properties such as brightness, high refractive index and resistance to discoloration, it finds application as white pigment in paints, sunscreens, ointments and toothpaste (Weir et al. 2012). The American Food and Drug Administration (FDA) have also approved it for use in food and drugs (Othman et al. 2014; Bodaghi et al. 2013). The discovery of the photocatalytic effect of  $\text{TiO}_2$  electrode in water splitting (Fujishima and Honda 1972), led to an increased interest in  $\text{TiO}_2$  among researchers. Today,  $\text{TiO}_2$  finds promising application in the field of photovoltaics, photocatalysis, photo/electrochromics and sensors (Chen and Mao 2007). Due to its capability to mineralize a variety of organic and inorganic

compounds, it is extensively investigated for applications in water and indoor air-purification (Lazar et al. 2012; Lin et al. 2013; Mo et al. 2009). In indoor air purification, PCO has been found to be effective against many volatile organic compounds such as trichloroethene, acetone, toluene, benzene, formaldehyde or acetaldehyde (Lin et al. 2013). PCO of ethylene has also been widely studied as ethylene, being a precursor of hazardous tetrachloroethene (Westrich et al. 2011), also adds to indoor air pollution.

## Reaction mechanism

In semiconductors, a small energy difference exists between their valence band and the conduction band, which is known as band-gap (López and Gómez 2012). When a semiconductor is irradiated with radiation of energy greater than its band-gap, electrons in the valence band are excited to the conduction band, leaving behind holes in the valence band. These electron-hole pairs are highly charged and can initiate reduction and oxidation reactions. The band-gap of TiO<sub>2</sub> is about 3-3.4 eV. This band-gap excitation is achieved in TiO<sub>2</sub> using photons with wavelengths near 380 nm UV band (Lin et al. 2014a, b).

The general equation involved in photocatalytic oxidation is:



In presence of air and water, the energy rich electron-hole pairs produce hydroxyl ions (OH•) by oxidation of water molecules and superoxide ion (•O<sub>2</sub><sup>-</sup>) by reduction of oxygen.



Apart from these reactions there can be other possible reaction pathways (summarized in Table 3). These active radicals decompose a variety of organic compounds including ethylene (C<sub>2</sub>H<sub>4</sub>) into CO<sub>2</sub> and water.



The overall reaction can be summed up as (Hussain et al. 2011):



A detailed mechanism of photocatalytic oxidation of organic compounds by TiO<sub>2</sub> has been presented in a review by Augugliaro et al. (2012). However, the exact reaction



mechanism is uncertain as various types of reaction intermediates are reported in the literature. Yamazaki et al. (1999) proposed that ethylene degradation involves formation of  $\text{C}_2\text{H}_5\text{OH}$  radicals and this was the rate determining step. According to Park et al. (2001), PCO of ethylene proceeds by formation of carbon monoxide (CO), which is oxidized to  $\text{CO}_2$ . Tanaka et al. (2006) reported formic acid ( $\text{HCOOH}$ ), formaldehyde ( $\text{HCOOH}$ ) and carbonate ions as intermediate products of photocatalytic degradation of ethylene over  $\text{TiO}_2$  films incorporated with silica and zeolite. Hauchecorne et al. (2011), through their Fourier transform infrared spectroscopy (FTIR) study on photocatalytic degradation of ethylene, observed a change in the dipole moment of the ethylene molecule when brought near the catalyst. They presented a new hypothesis on the cleavage of CC-double bond and suggested that decomposition of ethylene occurs through the formation of  $\text{HCOOH}$  and  $\text{HCHO}$ .

### Catalyst modification

Photocatalytic systems suffer from drawbacks such as catalyst deactivation and low efficiency. For instance, the white catalyst  $\text{TiO}_2$  used in a photocatalytic system was observed to show yellowing and also impaired photocatalytic activity (Jeong et al. 2013). Additionally, it was suggested that the accumulation of reaction intermediates in PCO may be one of the causes of  $\text{TiO}_2$  deactivation (Cao et al. 2000). However, heating the catalyst to high temperatures or exposure to UV at high humidity could help to recover the catalyst (Jeong et al. 2013). The major factors involved in improvement of photocatalytic efficiency include effective utilization of photons and prevention of electron-hole recombination (Tytgat et al. 2012). Thus, in order to achieve improved photocatalytic capability both chemical (catalyst modification) and engineering (optimization of reactor and process parameters) approaches are required.

Catalyst modification may involve synthesis of nano  $\text{TiO}_2$  (Chen and Mao 2007), doping of catalyst, synthesis of a visible-light photocatalyst (Kumar et al. 2005; Lin et al. 2014a, b) and noble metal deposition (Anpo and Takeuchi 2003). Research focusing on the synthesis of new photocatalytic materials has been extensively reported in literature (Chen and Mao 2007; Macwan et al. 2011; Nakata et al. 2012). Reducing the size of catalyst material enhances its photocatalytic activity due to increased surface area (Park et al. 2001). Thus, nanoparticles may show different chemical and physical properties because surface area and surface area to volume ratio increases tremendously (Chen

and Mao 2007). Pure nanoparticles are the first generation nanomaterials and doping them with metals forms the second generation nanomaterials. It has been observed that metal ion implantation in  $\text{TiO}_2$  can shift the absorption band of  $\text{TiO}_2$  towards visible light spectrum. The effectiveness of the shift was reported to be in the order Vanadium>Chromium>Manganese>Iron>Nickel (Anpo and Takeuchi 2003).

Nanomaterials doped with non-metals are referred to as the third generation nanomaterials.  $\text{TiO}_2$  doped with non-metals such as carbon and nitrogen has been reported to display an increased visible light activity in PCO of ethylene (Kumar et al. 2005; Lin et al. 2014a, b).

Furthermore, addition of small amounts of noble metals such as Platinum or Rhodium to the  $\text{TiO}_2$  can also increase the efficacy of photocatalytic degradation of volatile organic compounds by reducing the electron-hole recombination (Young et al. 2008; Kudo 2011). These noble metals act as electron sink, and the photoformed electrons pass to the surface of the noble metals, while the holes remain on the catalyst surface (Tytgat et al. 2012). Thus, electron-hole recombination is prevented, which makes electrons and holes available for oxidation reactions (Anpo and Takeuchi 2003). However, negative effects of noble metal (gold or platinum) addition on ethylene photo-oxidation have been reported (Belapurkar et al. 2010; Fu et al. 1996). Highly dispersed  $\text{TiO}_2$  species can be obtained by anchoring the catalyst on various supports such as porous glass, silica or zeolite. These species show higher catalytic activity than catalyst without support (Anpo and Takeuchi 2003). The use of  $\text{TiO}_2$ -based binary oxides such as  $\text{TiO}_2/\text{SiO}_2$  (de Chiara et al. 2015) and  $\text{TiO}_2/\text{ZrO}_2$  (Tibbitts et al. 1998) have displayed better efficiency in ethylene removal than  $\text{TiO}_2$  alone.

#### Reaction kinetics and process parameters

The Langmuir Hinshelwood equation is the most commonly used equation in kinetic studies of photocatalytic ethylene oxidation (Ibhadon et al. 2007; Lin et al. 2014a, b). According to the Langmuir Hinshelwood kinetics, the photocatalytic oxidation rate (R) is proportional to the surface coverage,  $\theta$  (Ibhadon et al. 2007). R is a function of the initial concentration of ethylene ( $C_E$ ) (Eq. 6). Obee and Hay (1997) used the bimolecular form of Eq. (7) under the assumption that reaction products do not have an influence on the oxidation rate and the reaction kinetics is mostly dominated by competitive interaction between water ( $C_W$ ) and initial concentration of ethylene ( $C_E$ ). Further on, these authors

modified the equation to include explicit temperature dependence (Eq. 8). They assumed that the temperature-dependent form of the Langmuir adsorption constants for monolayer adsorption on a homogeneous surface can be applied to both ethylene and water, and the rate constant (k) followed Arrhenius temperature dependence. Recently, models based on triple-molecular Langmuir Hinshelwood equation were developed by Lin et al. (2014a) based on the light intensity (I) and O<sub>2</sub> concentration (C<sub>O2</sub>) (Eq. 9).

$$R = -\frac{dC_E}{dt} = k\theta = \frac{k K C_E}{1 + K C_E} \quad (\text{Eq. 6})$$

$$R = k \frac{K_E C_E}{1 + K_E C_E + K_W C_W} \quad (\text{Eq. 7})$$

$$R = k' \exp\left(\frac{E}{R_g T}\right) \frac{K'_E \frac{\exp(-\Delta H_E / R_g T)}{\sqrt{T}} C_E}{1 + K'_E \frac{\exp(-\Delta H_E / R_g T)}{\sqrt{T}} C_E + K'_W \frac{\exp(-\Delta H_W / R_g T)}{\sqrt{T}} C_W} \quad (\text{Eq. 8})$$

$$R = I^\alpha k' \exp\left(\frac{E}{R_g T}\right) \frac{K'_E \exp\left(\frac{-\Delta H_E / R_g T}{\sqrt{T}}\right) C_E}{1 + K'_E \exp\left(\frac{-\Delta H_E / R_g T}{\sqrt{T}}\right) C_E + K'_W \exp\left(\frac{-\Delta H_W / R_g T}{\sqrt{T}}\right) C_W} \left( \frac{K'_{O_2} \exp\left(\frac{-\Delta H_{O_2} / R_g T}{\sqrt{T}}\right) C_{O_2}}{1 + K'_{O_2} \exp\left(\frac{-\Delta H_{O_2} / R_g T}{\sqrt{T}}\right) C_{O_2}} \right) \quad (\text{Eq. 9})$$

where k is the reaction rate constant (μmol cm<sup>-2</sup> h<sup>-1</sup>), K the adsorption coefficient of the reactant (ppmv<sup>-1</sup>), C<sub>E</sub> (ppmv) the concentration of the reactant A; Subscripts E, W and O<sub>2</sub> are for ethylene, water and oxygen, respectively; k' ((μmol cm<sup>-2</sup> h<sup>-1</sup> (mW cm<sup>-2</sup>)<sup>-1</sup>)<sup>α</sup>) is the intrinsic rate constant for a given UV intensity; α is order constant; K' (K<sup>1/2</sup> ppmv<sup>-1</sup>) is the temperature dependent adsorption equilibrium constants; E (kcal mol<sup>-1</sup>) is the apparent activation energy; ΔH<sub>E</sub> and ΔH<sub>W</sub> (kcal mol<sup>-1</sup>) are the changes in enthalpy accompanying adsorption of ethylene and water respectively; T(K) is the temperature and R<sub>g</sub> is the gas constant (1.99 × 10<sup>-3</sup> kcal mol<sup>-1</sup> K<sup>-1</sup>); I is the light intensity (mW cm<sup>-2</sup>); α is the order constant.

#### Ethylene concentration

A strong dependence of PCO rate on initial ethylene concentrations has been reported (Lin et al. 2014a, b). In general, at low ethylene concentrations, the oxidation rate increases linearly with the ethylene concentration. At higher concentrations of ethylene, the rate appears to stabilize. If ethylene concentration is increased further, the oxidation rate may even decrease again. For instance, Lin et al. (2014b) reported that on varying

the initial ethylene concentration from 100 to 900  $\mu\text{L L}^{-1}$ , the oxidation rate initially increased and then levelled off. In a similar study, Lin et al. (2014a) observed an increase in the oxidation rate up to an initial ethylene concentration of 459  $\mu\text{L L}^{-1}$  and beyond that concentration, the rate decreased again. In these two studies, different photocatalysts were used, namely N-doped and C-doped  $\text{TiO}_2$ , respectively.

The effect of the ethylene concentration can be explained on the basis of the number of active sites available on the catalyst surface. According to Langmuir Hinshelwood kinetics, the reaction rate is proportional to the fraction of available active sites (Lin et al. 2014a). Initially, the reaction rate increases linearly with increase in initial ethylene concentration as the number of active sites is higher than that of adsorbed ethylene molecules. However, after a certain threshold, all active sites are possibly occupied by ethylene molecules. Consequently, a further increase in ethylene concentrations no longer affects the reaction rate. It was suggested that this ethylene concentration threshold depends on both light intensity and the nature of the catalyst (Hay et al. 2015). Sometimes the initial concentration of ethylene may be high enough to be beyond this threshold. In such a case, ethylene will immediately saturate the active catalytic sites; hence, any further increase in ethylene concentrations does not affect the reaction rate. Thus, PCO is suggested to be a first order reaction at low ethylene concentration but at higher concentration it becomes of zero order (Lee et al. 2015).

#### *Water vapour*

In literature, the effect of water vapour on photocatalytic ethylene removal is much debated due to the contradicting or diverging results obtained. In some studies, it was observed that the presence of water decreased the photocatalytic activity (Tytgat et al. 2012), while in others; low concentrations of water seemed to have a beneficial effect (Lin et al. 2014b). Tytgat et al. (2012) observed that an increase in RH from 0 to 25% decreased the ethylene degradation efficiency by 17%. Yamazaki et al. (1999) reported a gradual decrease in the PCO reaction rate on increasing water vapour. On the contrary, in their study on C-doped  $\text{TiO}_2$ , Lin et al. (2014b) reported an initial rapid decrease in reaction rate followed by a gradual and continuous decrease on increasing water vapour concentration. In contrast, Park et al. (2001) reported that an increase in water vapour pressure up to 0.667 kPa showed a favourable effect on PCO rates but beyond that, the reaction rate decreased. Based on a study on N-doped  $\text{TiO}_2$ , a similar effect was observed

by Lin et al. (2014b). The authors reported that water concentrations up to 1561  $\mu\text{L L}^{-1}$  enhanced the PCO rate; but above this concentration, PCO of ethylene decreased. Hussain et al. (2011) also observed that complete removal of water by drying the catalyst significantly reduced ethylene degradation. Thus, presence of water seems to favour PCO, possibly because of the generation of hydroxyl ions, which are believed to be the primary oxidant in photocatalysis (Westrich et al. 2011).

Additionally, water molecules behave as hole-traps, i.e. they combine with the holes thus preventing electrons from recombining with the holes; consequently, overall PCO efficiency increases (Lin et al. 2014b). However, at high RH the decrease in reaction rate could be explained by the competition for active sites between water and ethylene molecules. This may be because polar water molecules are more strongly adsorbed on the polar N or C-doped  $\text{TiO}_2$  surface than the non-polar ethylene (Lin et al. 2014a, b). Thus, water molecules accumulated on the surface of  $\text{TiO}_2$  may effectively block the active sites (Jeong et al. 2013). Owing to less number of active sites available for ethylene absorption, ethylene degradation effectively decreases (Yamazaki et al. 1999).

#### *Temperature*

Temperature has a favourable effect on PCO of ethylene, which may be linked to adsorption affinity of water and ethylene (Westrich et al. 2011; Obee and Hay 1997). Water molecules, being polar in nature are adsorbed on the catalyst surface through strong hydrogen bond, while ethylene, being non polar, is bound by weak dipole-induced dipole interactions. Thus, in case of water the adsorption energy is higher than ethylene. Generally, adsorption affinity of any molecule decreases with increase in temperature (Obee and Hay 1997). At high temperatures, adsorption affinity of water, which has higher adsorption energy decreases to a greater extent than ethylene. Consequently, water is desorbed from catalyst surface, making active sites on the catalyst surface available for ethylene and thus, increasing the PCO rate (Obee and Hay 1997). Fu et al. (1996) studied the effect of temperature in the range of 30-110  $^{\circ}\text{C}$  on the amount of ethylene converted and observed a continuous increase in the specified temperature range. Whereas, Hussain et al. (2011) reported a small increase in ethylene conversion percentage when temperature was increased from room temperature to 35  $^{\circ}\text{C}$ , but further increase in temperature (tested up to 80  $^{\circ}\text{C}$ ), keeping other factors constant, showed a decrease in the percentage of ethylene converted. Regarding

refrigerated conditions, Hussain et al. (2010) successfully demonstrated ethylene removal at 3 °C using novel TiO<sub>2</sub> nanoparticles for potential application in cold storage in fruits and vegetables.

On the other hand, impact of high temperature (60-520 °C) on PCO of ethylene was investigated by Westrich et al. (2011). These authors found that the maximum ethylene oxidation rates were obtained between 100-200 °C. Any further increase in temperature decreased the photocatalytic activity with a value near zero at 500 °C. The increase in oxidation rate with rise in temperature was attributed to changes in adsorption energies of water and ethylene, while the decrease at higher temperatures was attributed to the loss of surface hydroxyl ions and/or recombination of electron-hole pairs. Maneerat et al. (2003) observed a small difference (< 10%) in the decomposition of ethylene between 5 and 25 °C. Yamazaki et al. (1999) reported that the reaction rate was 1.7 times faster at 65.7 °C than at 30 °C, which was again attributed to a decrease in absorption of water molecules that compete with ethylene molecules. However, no significant differences were observed in their activity between 65.7 and 81.3 °C.

#### *UV radiation wavelength and intensity*

Band gap of TiO<sub>2</sub> is 3-3.4 eV and corresponding to this band gap energy, radiation wavelengths below 380 nm should be effective in electron-hole generation (Lin et al. 2013). In N- and C-doped TiO<sub>2</sub> (band gap 2.8 eV), wavelengths greater than 400 nm were found to be effective for PCO of ethylene (Lin et al. 2014a, b). Chang et al. (2013) conducted a comparative study on the influence of radiation of different wavelengths on ethylene PCO. Their results indicated that UV<sub>254 nm</sub> was more effective in ethylene removal than UV<sub>365 nm</sub>. Other studies have shown that ethylene is sensitive to UV and on direct exposure of ethylene (~ 7%) to UV<sub>254 nm</sub> photolysis occurred (Tytgat et al. 2012; Chang et al. 2013). Tytgat et al. (2012) reported that photolysis increased up to 14% when the fixed bed reactor was filled with glass beads. These authors suggested that it could be due to an increase in path length of ethylene and subsequent increase in reaction time between photons and ethylene. Also, less photon escaped the reactor owing to more light scattering.

Radiation intensity also plays a key role in photo-degradation. Higher intensities increased the ethylene conversion (Hussain et al. 2011; Chang et al. 2013). Hussain et al. (2011) reported that the use of converging pipes and lens prevented UV scattering,

which subsequently increased its intensity and enhanced the ethylene degradation. In literature, an energy flux rate of  $1 \text{ mW cm}^{-2}$  is reported to be sufficient for photocatalytic reaction catalysed by  $\text{TiO}_2$  (Maneerat et al. 2003). Yamazaki et al. (1999) reported that it is a first order reaction with respect to radiation intensity. At higher intensities, the higher amounts of photons lead to a higher probability of ethylene oxidation. According to the reported reaction rate equation (Eq. 9), the reaction rate is a function of radiation intensity.

#### *Oxygen concentration*

Presence of oxygen has been observed to exert a positive effect on photocatalytic removal of ethylene (Lin et al. 2014a, b; Park et al. 2001). Park et al. (2001) observed that the addition of oxygen influenced the distribution of  $\text{CO}_2$  and CO as the PCO end products. Higher  $\text{O}_2$  concentration resulted in increased  $\text{CO}_2$  production, and consequently CO concentration was reduced. Additionally, the authors proposed that in ethylene oxidation, first CO is produced and then this is oxidized into  $\text{CO}_2$  in the presence of excess oxygen. Thus, maintaining an appropriate  $\text{O}_2$  concentration could be important in complete oxidation of ethylene.

An enhanced reaction rate was also obtained in some studies on PCO of ethylene by increasing  $\text{O}_2$  concentration. For instance, Lin et al. (2014a, b) observed that the ethylene removal rate was sensitive to  $\text{O}_2$  mole fractions of up to 0.05. After that, the reaction rate stabilized and any further increase in  $\text{O}_2$  had no influence on it. Similar observations were made by Yamazaki et al. (1999). These authors also found that the reaction rate increased with increasing  $\text{O}_2$  concentration but became steady beyond a threshold oxygen mole fraction of 0.2. In contrast, the data obtained from the study done by Maneerat et al. (2003) indicated that PCO reaction rates for ethylene were independent of  $\text{O}_2$  concentration. In this study, however, the authors also mentioned that above 1%  $\text{O}_2$  ethylene oxidation might be independent of  $\text{O}_2$ .

Lee et al. (2015) studied the PCO of ethylene using a microwave discharge electrodeless lamp. These authors found that ethylene removal efficiency was 1-5% higher in  $\text{O}_2$  than in air. Based on the summary from literature, no specific limit of  $\text{O}_2$  concentration essential for ethylene oxidation has been determined. This is possibly due to the variation in the nature of catalysts and other parameters used. However, the positive effect of  $\text{O}_2$  on PCO rates can be attributed to the formation of superoxide ions (Eq. 3).

Superoxide ions play an important role in PCO as shown in Table 3. Moreover, O<sub>2</sub> molecules absorb electrons to form superoxide ions and this prevents the electron-hole recombination, consequently increasing overall reaction rate.

#### *Gas flow rate and residence time*

Gas flow rate and residence time are other relevant factors in PCO. The residence time is the duration for which the reactant gas (ethylene) remains inside the reactor from entry to exit and is determined by the flow rate (Lee et al. 2015). Generally, at higher flow rates (low residence time), less amount of ethylene is removed due to reduced contact time between the pollutant and reactive species (Tibbitts et al. 1998; Hussain et al. 2011).

Lin et al. (2014a, b) conducted detailed studies on the effect of flow rate on ethylene PCO. In those studies, they observed that ethylene degradation increased up to a threshold of 1 L min<sup>-1</sup> and became constant thereafter. These authors suggested that at low flow rate (< 1 L min<sup>-1</sup>), mass transfer of the reactant from the bulk phase to the surface of catalyst occurs, while at higher flow rates mass transfer is negligible so the reaction rate remains unaffected. The increase in the residence time may increase the percentage of ethylene removed, but as the amount of ethylene treated per unit time decreases this may lead to inefficient energy utilization (Lee et al. 2015). Therefore, an optimized flow rate is required for an efficient PCO process.

#### *Reactor design and catalyst loading*

In the study of PCO, apart from other factors, the engineering aspect related to process optimization is also important as an efficient reactor can optimize photon efficiency and thus affect the overall photocatalytic performance (Tytgat et al. 2012). Several designs of the reactors have been discussed in literature such as flat plate, tubular, annular and monolith honeycomb reactors (Zhao and Yang 2003; Mo et al. 2009; Paz 2009; Ibhadon and Fitzpatrick 2013). An efficient reactor design should ensure uniform radiation distribution at the surface of catalyst leading to a better utilization of photons. In reactor design, UV source and radiation intensity (discussed before), catalyst amount and loading or distribution of the catalyst are also important factors to consider.

On the basis of the catalyst loading in the reactor, there can be several types of reactors such as a fixed bed reactor in which a fixed layer of catalyst powder or pellets (or glass



beads coated with catalyst) is present (Maneerat et al. 2003; Ibhadon et al. 2007; Tytgat et al. 2012); slurry type reactors in which the catalyst is in aqueous state (Maneerat et al. 2003; Maneerat and Hayata 2006a); and fluidized bed reactor in which the catalyst is in fluidized state (de Chiara et al. 2014). Fluidized bed reactors can provide a better contact between the pollutant and the catalyst (Baek et al. 2013; de Chiara et al. 2014), but the flow rate need to be monitored in order to achieve optimal fluidized state of the catalyst. High flow rate can easily lead to expulsion of catalyst out of the reactor. Moreover, owing to the poor fluidization behaviour of  $\text{TiO}_2$ , a support material is usually needed. In another study, de Chiara et al. (2014) used glass beads and aluminium microspheres to coat  $\text{TiO}_2$  onto them in a fluidized bed type reactor for PCO of ethylene. They reported that collision among the support material in the fluidized state lead to separation of coated material from the support which in turn clogged the filters of the reactor. Thus they emphasised the need of a stable coating. Apart from these, reactors with a thin layer of the catalyst coated onto their reactor walls or on glass plates are also commonly used (Lin et al. 2014a, b).

Increasing the amount of catalyst may have a favourable effect on ethylene conversion as observed by Yamazaki et al. (1999). These authors reported an increase in ethylene conversion with increase in the ratio of  $\text{TiO}_2$  to the inlet molar flow rate of ethylene. Maneerat et al. (2003) observed that increasing the amount of  $\text{TiO}_2$  from 0.01 to 2 g changed the total ethylene removed from nearly 20 to 100% under the same conditions and time interval. In a similar study, Maneerat and Hayata (2006a) used different concentrations of  $\text{TiO}_2$  in aqueous solution and reported that  $10 \text{ g L}^{-1}$  concentration of  $\text{TiO}_2$  was more effective in ethylene removal, compared to  $0.1 \text{ g L}^{-1}$ . Increase in ethylene removal efficiency on increasing catalyst concentration could be attributed to the total surface area of the catalyst that becomes available for photocatalysis (Tytgat et al. 2012). According to Chang et al. (2013), it is the  $\text{TiO}_2$  contact area that affects ethylene decomposition. Hence, a linear increase in the amount of catalyst may not result in a linear increase in the ethylene removal. This is because only the effective surface area of catalyst coming in contact with UV radiation is responsible for ethylene degradation (Tytgat et al. 2012). The UV radiation is almost totally absorbed by the first 10-15  $\mu\text{m}$  of catalyst layer (Yamazaki et al. 1999). This implies that increasing the amount of catalyst after a certain point may impede photon penetration in lower catalyst layers, thus, decreasing ethylene removal. For example, increasing the amount of catalyst from 1 to 2

g for PCO of ethylene showed a gradual increase in conversion rate, but, further increase of catalyst to 3 g led to a decrease in conversion (Hussain et al. 2011). Thus, proper distribution of the catalyst is crucial in order to achieve total absorption of photons and prevent unnecessary utilization of catalyst (Lin et al. 2013; Tytgat et al. 2012).

### Photochemical oxidation

Ethylene can be photochemically oxidized in the gaseous state by vacuum ultraviolet (VUV) radiation (wavelength <200nm). The high energy photons of VUV produce highly reactive oxygen species (ROS) such as O (<sup>1</sup>D), O (<sup>3</sup>P) or O<sub>3</sub>, and hydroxyl radicals (•OH) by the dissociation of O<sub>2</sub> and water molecules in the gas phase (Zhang et al. 2004; Jeong et al. 2004; Fu et al. 2011). VUV photons react with oxygen forming atomic oxygen and ozone (Eq. 10, 11, 12). Water molecules have a continuous absorption spectrum between wavelengths of 175 nm and 195 nm (Chang et al. 2013). These molecules in the gaseous state absorb the photons and as a result hydroxyl ions (•OH) are produced (Eq. 13). ROS and abundant hydroxyl species play a major role in oxidation of ethylene (Eq. 14, 15, 16). Photolysis or direct decomposition of ethylene on exposure to UV radiation (UV<sub>254+185</sub>, UV<sub>254</sub>) also occurs, which is reported to be ~ 7% as shown in Eq. 16 (Tytgat et al. 2012; Chang et al. 2013).



Commercial ozone-producing UV lamps (UV<sub>254+185</sub>) with major emission at 254 nm and minor emission (~ 5%) at 185 nm are available. The emission at 185 nm (VUV) corresponds to a photon energy of 6.7 eV (Jiang et al. 2015), and produces ROS as mentioned before. The ozone produced in the process is a by- product of the process and is not responsible for major ethylene removal (Kim et al. 2014). Earlier atomic oxygen was considered to be the main oxidising species in ethylene decomposition (Jozwiak et

al. 2001; Shorter and Scott 1986). However, in recent studies it has been suggested that in the VUV photochemical process the oxidation is mainly due to the 185 nm radiation itself and hydroxyl radicals (Kim et al. 2014).

The ozone produced can be utilised in further oxidation of the pollutant (ethylene) with the help of a catalyst. Ozone is a strong oxidant but direct oxidation of VOCs is not very effective, however ozone becomes highly active for VOC oxidation with the assistance of catalyst. Metals (such as silver, palladium) and transition metal oxides are effective in decomposition of ozone (Huang et al. 2016b). Studies based on such a method in which a combined action of VUV and ozone assisted catalysis are being done (Huang et al. 2016a, b).

#### **Combined photochemical and photocatalytic oxidation (Hybrid VUV-PCO)**

Photocatalytic and photochemical oxidation present good potential for ethylene removal however, individually both processes have certain drawbacks. PCO suffers from catalyst deactivation and lower efficiency especially under high humidity conditions. High humidity is essential in the storage of fresh produce in order to minimize mass loss. Although VUV photochemical oxidation is more effective at high RH, O<sub>3</sub> is produced in the process, which could be toxic to plant tissues. Moreover, in VUV process only a small part (5-8%) of the irradiation corresponding to 185 nm is utilised and the rest is wasted (Huang et al. 2016a). The hybrid technique via coupling of VUV with UV/TiO<sub>2</sub> presents can help address these shortcomings. In VUV-PCO the entire radiation is used, 254 nm in photocatalysis while 185 nm in photochemical process. The hybrid also shows a better activity at high RH condition because VUV is effective at high humidity conditions. The VUV irradiation can minimise the formation of partially oxidised volatile species and effectively eliminate non-volatile by-products from the photocatalyst surface; thereby preventing photocatalyst deactivation (Quici et al. 2010). Additionally, O<sub>3</sub> generated by VUV could be directly decomposed by UV (254 nm).

The hybrid VUV-PCO process can be obtained by coupling of VUV (185 nm) and PCO (UV/TiO<sub>2</sub>) simply by replacing the UV lamp in the PCO process with a UV<sub>254+185</sub> lamp. This VUV-PCO hybrid technique has been reported to be more efficient in volatile organic compound (VOC) removal than VUV or PCO alone (Huang et al. 2011; Chang et al. 2013). Comparative efficiency of the three processes, PCO, VUV and hybrid VUV-PCO in removal of toluene for the same reactor configuration was reported by Yang et al.

(2007). These authors found that the higher efficiency of the hybrid process was due to the combined effect of photochemical oxidation in gas phase (VUV light - 185 nm) and PCO on the surface of  $\text{TiO}_2$  (UV at 254 nm / $\text{TiO}_2$ ). In another comparative study on ethylene, a similar hybrid system was reported to have a conversion efficiency of 45.1%, while that of PCO with  $\text{UV}_{254\text{ nm}}$  and  $\text{UV}_{365\text{ nm}}$  was 12.1% and 5.14%, respectively (Chang et al. 2013). The variation in the results obtained from these studies could be attributed to the differences in reactor configurations and other factors such as temperature, gaseous concentrations, and humidity. Benzene removal efficiency of VUV-PCO was also reported to be 20 times higher than that of PCO (Huang et al. 2013). The efficiency is higher in the hybrid system as there are possibilities of many reaction pathways for generation of ROS like  $\text{UV}_{254\text{ nm}}/\text{TiO}_2$ , VUV,  $\text{O}_3/\text{TiO}_2$ ,  $\text{VUV}/\text{UV}_{254\text{ nm}}/\text{O}_3$ , and  $\text{O}_3/\text{electron-hole}$  as illustrated in Table 3. Production of ROS in the hybrid system is shown in figure 1. In a study on cost analysis, the hybrid system was found to be more cost effective because 60% cost reduction was obtained in removal of formaldehyde (per kg) compared to  $\text{UV}/\text{TiO}_2$  alone (Yang et al. 2007).

However, the general focus of VUV-PCO studies has been on removal of air pollutants such as toluene (Huang et al. 2011; Kim et al. 2014), formaldehyde (Yang et al. 2007; Fu et al. 2012), and benzene (Jeong et al. 2005). Studies on ethylene removal by VUV-PCO are very limited (Chang et al. 2013). Practical application of this hybrid process for ethylene removal in storage of F&V has not been reported. Hence, its possible impact on quality remains unknown. However, the positive results on VOC removal obtained with hybrid VUV-PCO over normal PCO could have a high potential for application in ethylene removal from F&V storage.

#### Factors affecting hybrid VUV-PCO

Similar to PCO, hybrid VUV-PCO is also affected by the same factors but to a different extent. Increase in both, the flow rate and the initial ethylene concentration decreased the conversion efficiency (Chang et al. 2013). Irradiation with  $\text{UV}_{254\text{ nm}}$  and  $\text{UV}_{365\text{ nm}}$  alone often decreased the catalytic activity and the colour of the white catalyst ( $\text{TiO}_2$ ) is turned yellow. In contrast, with  $\text{UV}_{254+185\text{ nm}}$  no drop in efficiency or colour change of catalyst occurred (Jeong et al. 2004).

This could be attributed to the oxidation of reaction intermediates, which normally get absorbed on the catalyst surface rendering it inactive by reactive oxygen species and by

direct photolysis (Kim et al. 2014). Other factors affecting the efficiency of hybrid VUV-PCO such as the quantity of catalyst, oxygen and water vapour inside the reactor and the role of TiO<sub>2</sub> are discussed further.

#### *Effect of the amount of catalyst*

The amount of TiO<sub>2</sub> or the thickness of TiO<sub>2</sub> films used can be optimised for maximum pollutant removal efficiency in VUV-PCO. Pollutant conversion efficiency was reported to increase with increasing TiO<sub>2</sub> film thickness (mass) initially but was reported to decrease for thick films due to limitations in reactant diffusion and radiation transport through thick films (Quici et al. 2010). In other reports (Kim et al. 2014; Fu et al. 2012), only a slight difference was observed in organic pollutant conversion efficiency between VUV-TiO<sub>2</sub> and VUV without TiO<sub>2</sub>. This is because the photochemical oxidation was possibly more dominant than the catalytic removal. The small increase in ethylene conversion in the presence of TiO<sub>2</sub>, however, confirms its catalytic role. Chang et al. (2013) observed an increase in ethylene removal efficiency with increase in TiO<sub>2</sub> contact. For a retention time of 33 s and initial ethylene concentration of 100 µL L<sup>-1</sup>, the conversion of ethylene was 25.7% for a TiO<sub>2</sub> contact area of 173 cm<sup>2</sup>, but the conversion rose to 39% when the contact area was 259 cm<sup>2</sup>. Moreover, in presence of TiO<sub>2</sub>, conversion of CO to CO<sub>2</sub> was higher, which may be enhanced by increased contact time of the reactants on the TiO<sub>2</sub> surface. These authors also observed that TiO<sub>2</sub> decreased the production of secondary organic aerosols (SOA) produced in VUV-PCO. Presence of TiO<sub>2</sub> also reduced the total ozone production in the process as the active sites on the surface of TiO<sub>2</sub> can also cause the photodecomposition of O<sub>3</sub>:



Moreover, the electron affinity of ozone is 2.1 eV and that of O<sub>2</sub> is 0.44 eV. Hence, ozone can more easily capture the photo-generated electrons on TiO<sub>2</sub> (Eq. 17). Use of TiO<sub>2</sub> was justified as it increases the reaction rate in all conditions and has other advantages too, like increased water solubility of organic intermediates as well as inhibition of undesirable intermediates (Jeong et al. 2013).

#### *Oxygen and water vapour*

In VUV-PCO reactor systems, oxygen plays an important role in the removal of VOCs through the production of reactive O<sub>2</sub> species by UV radiation at the catalyst surface and

by the direct decomposition of VOCs in VUV. During the removal of VOCs by VUV, ROS are produced by direct decomposition of  $O_2$  by VUV photons (Eq. 10), which assists in VOC removal. Jeong et al. (2004) reported that under the irradiation of VUV alone, a higher conversion (46%) of toluene was observed in dry air than in dry nitrogen stream (10%). Moreover, in the absence of  $O_2$ , complete oxidation of CO to  $CO_2$  did not occur.

Regarding the role of water molecules in oxidation of pollutants in VUV-PCO system different effects have been reported. In order to observe the effect of water molecules on VUV-PCO, Jeong et al. (2004) carried out oxidation of toluene in pure nitrogen (without  $O_2$  interference). The authors reported a drastic increase in the conversion percentage of toluene from 10% at dry nitrogen stream to 91% in humidified nitrogen. This was attributed to the abundant  $OH^\bullet$  produced by direct decomposition as shown in Eq. 10, which is generally considered to be the primary species responsible for oxidation (Westrich et al. 2011). Similarly, in another study, the conversion of ethylene was reported to increase from 39.1 to 45.1% on increasing the RH from 1 to >86% (Chang et al. 2013). However, Quici et al. (2010) reported maximum pollutant (toluene) removal efficiency at moderately low humidity conditions (10% RH) compared to completely dry air or higher humidity.

At higher humidity, lower concentrations of ozone are generated and more pollutants are degraded (Zhang et al. 2004; Kim et al. 2014). The suppression of ozone formation in humidified air may be due to the competitive absorption of VUV radiation by  $O_2$  and water. Although, at high humidity there could be generation of secondary organic aerosols (SOA), as a result of gas to particle conversion of organic compounds in presence of UV  $254+185\text{ nm}$ . This is dependent on humidity, flow rate and initial concentration of ethylene. Hence, the removal of SOA through wet scrubbers was proposed by Jeong et al. (2004).

### **Applications of VUV/PCO/hybrid process in ethylene removal**

A comprehensive list of selected studies on the application of photocatalytic and photochemical oxidation of ethylene is presented in Table 4. However, it is noteworthy to state that reports on application of these techniques for ethylene removal in F&V storage are limited. Furthermore, studies focusing on implementing these techniques in F&V storage for antimicrobial effect has been extensively reviewed (Maneerat and

731 Hayata, 2006b; Hur et al. 2005). However, this has not been included within the scope of  
732 this current review.

733 In one of the early works, Scott et al. (1971) tested UV lamps (UV<sub>254+185 nm</sub>) for removal  
734 of ethylene produced by banana fruit. A 200 L cabinet with a 4 watt UV<sub>254+185 nm</sub> was  
735 used for storing bananas (27.2 kg) at 15 °C. In order to shield the fruits from the UV  
736 radiation, sheets of paper were placed between the lamp and the fruits. Carbon dioxide  
737 and O<sub>2</sub> levels were controlled by using calcium hydroxide and varying the entry of air  
738 into the cabinet, respectively. After 10 days of storage, with lamps switched off, a  
739 modified atmosphere of 0.5% CO<sub>2</sub> and 1% O<sub>2</sub> was developed in the cabinet. Then the UV  
740 lamp was switched on for 2 h and a decrease in ethylene from 0.25 µL L<sup>-1</sup> to < 0.0025 µL  
741 L<sup>-1</sup> was observed. Other volatile compounds emitted from bananas also showed a  
742 decrease, and no injury to the fruit was recorded. The actual mechanism of ethylene  
743 removal was not determined by the authors; however, atomic O<sub>2</sub> and not ozone was  
744 speculated to be responsible for removal of ethylene and other volatile compounds. In a  
745 subsequent study by Scott and Wills (1973), the air from a gas tight controlled room was  
746 circulated through an external scrubber consisting of different combinations of ozone  
747 producing (UV<sub>254+185 nm</sub>) and non-ozone (UV<sub>254 nm</sub>) producing UV lamps. Ethylene  
748 concentration was reduced in the controlled room from 10 ppm to < 0.01 µL L<sup>-1</sup> in 27 h.  
749 The system was effective in keeping the ozone below hazardous level. In order to  
750 remove the in-process generated CO<sub>2</sub>, use of slaked lime was suggested in the study.

751 In general, low temperatures and low O<sub>2</sub> atmospheres are used in fruit and vegetables  
752 storage. Shorter and Scott (1986) showed that ethylene can be removed from cooling  
753 rooms and low O<sub>2</sub> storage spaces using ultraviolet radiations. A cooling room (at 0 °C)  
754 was connected to an external ethylene scrubber consisting of a 50 W UV<sub>254+185 nm</sub> lamp.  
755 An air flow of 60 L min<sup>-1</sup> was maintained and rusted steel was used for removal of ozone.  
756 0.5, 5.0 and 10 mL of ethylene was injected into the cooling room at 2 h interval in each  
757 test. At the end of 50 h, the concentration detected in the cooling room 0.6, 0.8 and 1.8  
758 µL L<sup>-1</sup>, respectively after an injection. The lamps were operated for 200 hrs and the  
759 values showed little change during this time. In another experiment in the study, gas  
760 tight cabinet (700 L) with a 11 watt UV<sub>254+185 nm</sub> lamp and no steel wool was flushed  
761 with nitrogen to obtain different O<sub>2</sub> concentrations (21 - <0.1%). For each test 8 µL L<sup>-1</sup> of  
762 ethylene was injected. The system was able to remove ethylene at atmospheres (<5%)  
763 O<sub>2</sub> with < 1 µL L<sup>-1</sup> ozone production. The scrubbing system was found to be equally

effective in ethylene removal in air or nitrogen atmosphere in the study. However, the study did not evaluate the humidity level which could have been responsible for similar ethylene removal in air and nitrogen. A VUV based unit was tested by Lawton (1991) in a fruit store and the conversion efficiency was found to be quite low (7 %). According to the manufacturer of the unit the efficiency of the device decreases at low concentrations. VUV based system in ethylene conversion by VUV radiations (254+185 nm) at different O<sub>2</sub> concentrations (0.2%, 1%, 2%, and 3%) for application in CA storage of apples was investigated by Jozwiak et al. (2001). They reported faster ethylene degradation at higher O<sub>2</sub> concentration than at 0.2% O<sub>2</sub> concentration.

Maneerat et al. (2003) and, Maneerat and Hayata (2006a, 2008) conducted a series of investigations involving the application of UV/UVA on selected F&V in storage. Maneerat et al. (2003) stored unripe green tomatoes in a glass desiccator, with TiO<sub>2</sub> solution in the bottom and the system was exposed to UVA radiation at 25 °C and 90-95% RH, until the tomatoes developed full red colour. Untreated control tomatoes developed the ripening response (colour change) within 2 weeks, whereas the UVA treated tomatoes ripened after 4 weeks. Tomatoes exposed to UVA did not develop any disorder in ripening. Nutritional quality parameters such as lycopene, vitamin A, vitamin C, along with pH and TSS values were found to be similar to that of the control. These findings showed that TiO<sub>2</sub> photocatalytic reaction was capable of delaying the ripening responses, such as colour change, fruit softening and ethylene climacteric peak.

In a study at same storage conditions (25 °C and 90-95% RH) but at varying quantity of TiO<sub>2</sub> and UV intensity, Maneerat and Hayata (2006a) observed that increasing TiO<sub>2</sub> concentration and/or increasing UV intensity delayed fruit ripening in tomatoes, which corresponded to a reduction in ethylene. Change in TiO<sub>2</sub> concentration from 0 to <10 g L<sup>-1</sup> and increasing the UV intensity from 0 to 5 W m<sup>-2</sup> extended the ripening time of green tomatoes as observed by colour change from 11 to 22 days. TiO<sub>2</sub> was also found to be photocatalytically effective in decreasing anaerobic metabolites (acetaldehyde and ethanol) that produce off-odours, but this was dependent on fruit metabolic stage. Additionally, Maneerat and Hayata (2008) investigated the feasibility of TiO<sub>2</sub>-coated films in packaging and storage of red tomatoes. Packaging film with TiO<sub>2</sub> was developed by coating a colloidal suspension of TiO<sub>2</sub> micro- and nano-particles on oriented-polypropylene film. Tomatoes were packaged with and without the coated films and stored at 25 °C for 10 days. At the end of 10 days, ethylene accumulated in the control



797 packages ( $\sim 22 \mu\text{L L}^{-1}$ ), while in packages coated with  $\text{TiO}_2$  ethylene concentration was  
798 significantly reduced. About 88% reduction in ethylene was achieved in the coated  
799 packages in 10 days using black light (UV-A) lamps.

800 The effectiveness of ethylene removal on ripening of green tomatoes was tested by de  
801 Chiara et al. (2015). They treated one batch of tomatoes with  $2 \mu\text{L L}^{-1}$  ethylene at a  
802 flowrate  $2 \text{ mL min}^{-1}$  for 3 days. A second batch of tomatoes was given the same  
803 treatment for same duration except that the ethylene was first passed through a reactor,  
804 consisting of a catalyst ( $\text{TiO}_2$  and  $\text{SiO}_2$  -80:20 wt) irradiated by UVA (315-400 nm) and a  
805 third batch treated with air served as control. The tomatoes were then kept at  $15^\circ\text{C}$  for  
806 14 days. The photocatalytic activity was found to delay the ripening process of tomatoes  
807 which was evident by slower epicarp colour change in the second batch of tomatoes  
808 compared to the first batch and third batch (control) samples. At the end of 7 days of  
809 storage, ethylene treated tomatoes (first batch) showed substantial colour with 10%-  
810 30% surface not green while the ethylene plus photocatalyst treated tomatoes (second  
811 batch) as well as the control (third batch) just had a break in colour from green to  
812 tannish yellow (pink or red  $< 10\%$  of surface). At the end of 14 days of storage, first batch  
813 of tomatoes had reached a uniform 'red' ( $< 90\%$  surface) ripening stage, whereas the  
814 second batch of tomatoes had not reached the 'red' stage and did not show any irregular  
815 ripening behaviour. The authors observed that the changes in the measured colour were  
816 similar in control tomatoes and ethylene plus photocatalyst treated tomatoes. Therefore,  
817 it could be concluded that the photocatalytic activity of the catalyst was effective in  
818 eliminating ethylene from the atmosphere surrounding the tomatoes due to which the  
819 treated tomatoes behaved similar to the control.

820 Another practical application of photocatalysis in F&V storage was reported by  
821 Kartheuser and Boonaert (2007). They developed a photocatalytic reactor (patented)  
822 which included UVA tubes, ventilator ( $30 \text{ m}^3/\text{h}$ ) and commercial  $\text{TiO}_2$  (P25 Degussa).  
823 Laboratory tests were performed with Granny Smith apples kept in 1000 L airtight  
824 boxes at a temperature of  $\sim 28^\circ\text{C}$ . Within 17.7 h, ethylene ( $16 \mu\text{L L}^{-1}$ ) accumulated in the  
825 chamber, and after switching on the reactor, ethylene concentration declined to  $0.25 \mu\text{L}$   
826  $\text{L}^{-1}$  in 10 h. These authors also investigated longer storage duration by installing the  
827 reactor in a refrigerator, hereby referred to as photocatalytic refrigerator. The reactor  
828 occupied 200 mL and required a light intensity of  $13.8 \text{ mW cm}^{-2}$ . Another refrigerator  
829 (standard refrigerator) was used as control. Kiwifruits, three melons and one pineapple

were stored in the lower plastic container of the refrigerators for 22 days with temperature set at 4 °C in both refrigerators. The kiwifruits did not show any significant changes, however, melons and pineapple in photocatalytic refrigerators showed a visibly better outward appearance than those in standard refrigerators. The pineapple in the photocatalytic refrigerator was also firm and had better quality flesh. Avocadoes also showed a visible effect in delayed ripening in the photocatalytic refrigerator after 32 days of storage at 6 °C. The authors also conducted another long term storage experiment by placing seven of such reactors in a kiwi storage facility (200 m<sup>3</sup>) at 0 °C with normal atmospheric gas composition. In previous years, the producer was unable to keep kiwis for more than three months in the storage facility without significant damage to the fruit under the same conditions. However, with the reactors the fruit could be kept in the storage facility for three months longer than usual. This study presented photocatalysis as an inexpensive technique fit for small and medium storage areas.

For potential F&V cold storage applications, Hussain et al. (2010) reported application of novel TiO<sub>2</sub> nanoparticles for ethylene degradation at 3 °C. Feasibility of ethylene photooxidation in fruit shipping containers was assessed in another study (Nielson et al., 2015). They developed a photocatalytic reactor system in which different parameters such as the flow velocity, gaseous concentrations, and relative humidity could be controlled. A model was developed by coupling the ethylene production rate by fruit and photocatalytic decomposition to predict ethylene removal from a 40' shipping container. They estimated that for a fruit load of 20 tons, the system could remove the ethylene produced by fruit, on UV (254 nm) irradiation (37.5 mW cm<sup>-2</sup>) of a few m<sup>-2</sup> of photocatalyst (TiO<sub>2</sub> based). The study also dealt with the issue of heating from the lamps as most of the energy is dissipated as heat. The heat released by the lamps was estimated to be comparable to that generated by fruit. At less ethylene concentrations the respiration of fruits is lowered thereby reducing the heat generated by fruits. So overall the heating by UV lamp was considered to be of less concern in the study. Moreover, the UV lamp could be operated non-continuously. However, catalyst deactivation at high humidity could be problematic in fruit storage.

The various studies summarized above demonstrated that PCO and VUV could offer an effective solution in extending the shelf life of F&V. Critical evaluation of these reports showed that the application of these techniques have been limited to lab scale

applications. Scaling up the techniques for application in practice remains a challenge, due to complexity of the reaction mechanism and variability of reactor design.

## Conclusions

This review presents VUV, PCO, and VUV-PCO techniques for ethylene removal as emerging techniques that could have potential for application in postharvest supply chain. Being low cost, continuous in operation, functional at room temperature and requiring less energy, it can provide a low cost alternative to ethylene removal systems, such as, catalytic oxidisers. However, these techniques have been so far reported in small scale laboratory conditions and studies on scaled-up units for industrial applications are minimal. For successful commercial application the drawbacks associated with these techniques such as low efficiency at low ethylene concentrations need to be improved. For instance, in PCO, deactivation of catalyst and low efficiency especially at high humidity which is generally encountered in F&V storage, still remains a challenge. This requires further research in the development of an efficient catalyst. Similarly, for VUV photolysis application, it is important to remove the by-product ozone which could be harmful for fresh produce in high concentrations. Using the in-process generated ozone in further oxidation of the ethylene with the addition of a catalyst could help improve ethylene removal as well as reduce ozone. Placing such catalyst at the exit stream of VUV photolysis might tackle the problem of excess ozone production and further oxidise the residual ethylene in the presence of limited light radiation.

Furthermore, another alternative to overcome the individual drawbacks of PCO and VUV involves the use of a VUV-PCO hybrid system. This hybrid system has a synergistic effect, and the low efficiency and catalyst deactivation of PCO is eliminated in the presence of VUV. In the hybrid system, the 254 nm as well as 185 nm radiation is utilised. On the other hand, generation of excessive ozone in VUV is reduced in presence of UV/TiO<sub>2</sub>. Thus, the hybrid VUV-PCO system is proposed to be a more viable method in postharvest storage than VUV or PCO alone. A better understanding of the factors influencing the VUV-PCO process and the development of a more efficient catalyst could help in improving the reactor design and thereby increasing ethylene removal efficiency in these systems.

Adequate understanding of the possible impact of the in-process generated reactive oxygen species and intermediates on postharvest nutritional, phytochemical and overall

quality of F&V is essential. From a technological point of view, to develop an optimum, product-specific ethylene removal system for storage and bulk transportation, the metabolic rate of fresh produce (i.e. ethylene production rate) should be taken into consideration. Similarly, practical aspects, such as, durability of lamps, space requirement as well as energy consumption and heat generation by the unit also requires careful consideration in the design. Overall, PCO and VUV showed good results in small scale applications; however, in order to develop a functional up-scaled unit concerted attention from both researchers and the industry is required.

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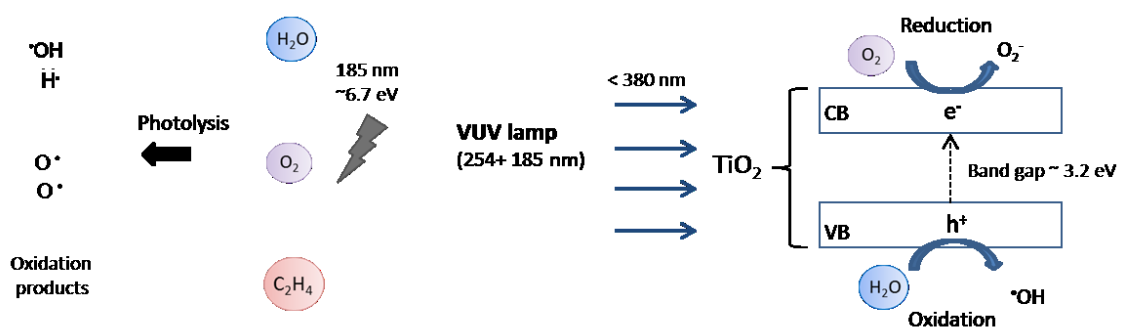


Fig. 1 Schematic of production of reactive oxygen species in ethylene oxidation by combined photochemical and photocatalytic oxidation process (VUV-PCO). CB: conduction band, VB: valence band, PCO: photocatalytic oxidation, VUV: vacuum ultraviolet light

**Table 1** Summary of detrimental effects of ethylene on fruit and vegetables

Ethylene effect	Specific effect		Ethylene exposure level	Commodity	Storage condition and duration	Reference
<i>Abscission</i>	Basal abscission	leaves	-	Cauliflower	-	Rees et al. (2011)
<i>Colour</i>	Yellowing		0.1 $\mu\text{L L}^{-1}$ and $<0.005 \mu\text{L L}^{-1}$	Broccoli, Parsley, Chives	5, 20 °C	Wills et al. (1999)
			1 $\mu\text{L L}^{-1}$	Broccoli	10 °C for 12 days	Fan and Mattheis (2000b)
			$<0.005\text{-}10 \mu\text{L L}^{-1}$	Chinese cabbage	0, 20 °C	Wills et al. (1999)
	Degreening		10 $\mu\text{L L}^{-1}$	Cucumber	15 °C for 12 days	Hur et al.(2009)
		Leaf tip browning	$<0.005\text{-}1 \mu\text{L L}^{-1}$	Lettuce	0 , 20°C	Wills et al. (1999)
	Mesocarp discolouration		50 $\mu\text{L L}^{-1}$ 12-48 hrs	Avocado	5 °C for 3 weeks	Pesis et al. (2002)
	Pulp browning		4 $\mu\text{L L}^{-1}$			
	Increase in hue angle (greenness), reduction in lightness		1 $\mu\text{L L}^{-1}$	Kiwifruit	17 weeks	Pranamornkith et al. (2012)
	Chilling injury		50 $\mu\text{L L}^{-1}$ 12-48 hrs; 4 $\mu\text{L L}^{-1}$	Avocado	5 °C for 3 weeks	Pesis et al. (2002)
			$<0.005\text{-}10 \mu\text{L L}^{-1}$	Orange	5 °C for 56-129 days	Wills et al. (1999)
<i>Physiological disorders</i>	Russet spotting		126 $\mu\text{mol}\cdot\text{m}^{-3}$	Lettuce	6 °C for 9 days	Fan and Mattheis (2000b)
	Superficial scald		0, 1, 5 or 10 $\mu\text{L L}^{-1}$	Pear	2°C for 3 months	Bower et al. (2003)
	Internal browning					
	Rotting and senescence		$<0.005\text{-}1 \mu\text{L L}^{-1}$	Strawberry	0 , 20°C for 8 h - 10 days	Wills and Kim (1995)
	Epidermal sloughing, soaking	water	1 $\mu\text{L L}^{-1}$	Cucumbers	15 °C for 12 days	Hur et al. (2009)
	Water soaking injury	soaking	1 $\mu\text{L L}^{-1}$	Kiwifruit	17 weeks	Pranamornkith et al. (2012)

**Table 1** Summary of detrimental effects of ethylene on fruit and vegetables (continues)

Ethylene effect	Specific effect	Ethylene exposure level	Commodity	Storage condition and duration	Reference
<i>Senescence</i>	Chlorophyll degradation and decline in protein content	10 $\mu\text{L L}^{-1}$	Coriander leaves	20 °C for 8 days	Jiang et al. (2002)
<i>Softening</i>	Loss of Firmness	0.01, 0.1 and 1 $\mu\text{L L}^{-1}$	Kiwifruit	0 °C, 4 weeks	Jabbar and East (2016)
	Softening	0.1–100 $\mu\text{L L}^{-1}$	Peach	-	Hayama et al. (2006)
		<0.005-10 $\mu\text{L L}^{-1}$	Mango, peach, custard apple, Banana, kiwifruit,	0,20 °C	Wills et al. (2001)
<i>Sprouting</i>	Increased sprouting	<0.005-10 $\mu\text{L L}^{-1}$	Potato	20 °C for over 35 days	Wills et al. (2004)
<i>Taste and flavour</i>	Bitterness	42 $\mu\text{mol}\cdot\text{m}^{-3}$	Carrot	10 °C for 4 days	Fan and Mattheis (2000b)
	Bitterness, earthy flavours, green flavours, terpene flavour, aftertaste	1 $\mu\text{L L}^{-1}$	Carrots	15 °C for 3 weeks	Seljåsen et al. (2001)
<i>Toughness</i>	Lignification	1 $\mu\text{L L}^{-1}$	Asparagus	22 °C in air with 80–90% RH for 5 days in the dark	Liu and Jiang (2006)

**Table 2** List of some commercially available products for ethylene management

Mode of action	Product name	Product type	Material/chemical used	Company
<b>Absorption/adsorption</b>	ReTain®	na	Amionoethoxyvinylglycine (AVG)	Valent BioSciences Corporation, USA
	SmartFresh <sup>SM</sup>	Sachets and other	1-Methyl cyclopropane (1-MCP)	AgroFresh, Inc., USA
	It's Fresh!	Sheets	Palladium impregnated zeolite	It's Fresh! Ltd, UK
	PrimePro®	Sheets	na	DeltaTRAK, Inc., USA
	<b>Extend-A-Life<sup>TM</sup></b>	<b>Filters, sachets</b>	na	AgraCo Technologies International LLC, USA
	<b>Produce Saver<sup>TM</sup></b>			
	KEEPPRES H®	Sheets, bags	na	Teck Blue Systems, SL Keepfresh, Spain
	na	Sachets, filters and warehouse systems	na	CJS Ethylene Filters, USA
	Peakfresh	Bags	LDPE film impregnated with a naturally occurring mineral	Peakfresh, Australia
	Green Bags <sup>TM</sup>	na	Clay	Evert-Fresh Corporation, USA
	<b>EC-3+</b>	<b>Sachets, filters, filtration system</b>	Zeolite impregnated with potassium permanganate	Ethylene Control Inc., USA
	Bi-On®, ETHYL STOPPER na	Filtration system, sachets <b>Ethylene filters</b>	Porous clay and potassium permanganate na	Bioconservación S.A, Spain
	Ryan®	Sachets, filters	na	CargoDepot, Mexico Sensitec Co.,USA

na: not available

**Table 2** List of some commercially available products for ethylene management (continues)

Mode of action	Product name	Product type	Material/chemical used	Company
<b>Oxidation</b>	<b>ETI 25, 50</b>	Absorption system	ABSOTIL/purafil-Alumina pellets	<b>Fruit Control Equipments srl, Italy</b>
	na	<b>Sachets, equip. for small to large warehouse</b>	Potassium permanganate	Prodew Water & Air Innovations, USA
	<b>Air repair ethylene absorbers</b>	Packets, blankets, tubes	na	DeltaTRAK, Inc., USA
	na	<b>Filters and sachets</b>	Alumina impregnated with permanganate	Ozeano, Spain
	Bio-Turbo	Air filtration equip.	Ozone	Miatech, Inc., USA
	Purfresh equipment	na	na	Purfresh, Inc., USA
<i>High temperature catalytic oxidation</i>	na	na	na	Ozone solution Inc, USA
	SWINGTHERM-BS	Air filtration equip.	na	Eco Sensors, USA
	na	na	na	<b>Fruit Control Equipments srl, Italy</b>
	na	na	na	Absorger , France
	na	na	na	Besseling Group BV, The Netherlands
	na	na	Platinum aluminium granules	Van Amerongen, The Netherlands
<i>Photocatalytic oxidation</i>	ECOscrub	Air filtration equip.	Titanium dioxide + UV light	Absorger, France
	<i>AiroCide®</i>	na	na	<i>KES Science &amp; Technology, Inc.</i>
	FRESH+™	na	Catalyst + UV light	Fresh Plus International, USA

na: not available, equip: equipment

**Table 3** Summary of possible reaction pathways in combined photochemical and photocatalytic oxidation (VUV-PCO) of ethylene

System	Reaction pathways
PCO (UV <sub>254nm</sub> /TiO <sub>2</sub> )	$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 + h^+ + e^-$ $h^+ + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}^+$ $e^- + \text{O}_2 \rightarrow \bullet\text{O}_2^-$ $\bullet\text{O}_2^- + \text{H}^+ \rightarrow \bullet\text{HO}_2$ $2 \bullet\text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$ $\text{H}_2\text{O}_2 + \bullet\text{O}_2^- \rightarrow \bullet\text{OH} + \text{OH}^- + \text{O}_2$ $h^+ + \text{OH}^- \rightarrow \bullet\text{OH}$
VUV (185 nm)	$\text{O}_2 + h\nu (<243\text{nm}) \rightarrow \text{O}(^1\text{D}) + \text{O}(^3\text{P})$ $\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O}(^3\text{P}) + \text{M} \text{ (M= O}_2 \text{ or N}_2\text{)}$ $\text{O}(^3\text{P}) + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ $\text{H}_2\text{O} + h\nu (185 \text{ nm}) \rightarrow \bullet\text{OH} + \text{H}^+$ $\text{Ethylene} + h\nu (185 \text{ nm}) \rightarrow \text{oxidation products}$
O <sub>3</sub> /TiO <sub>2</sub>	$\text{O}_3 + \text{active sites on TiO}_2 \text{ surface} \rightarrow \text{O}^{\bullet} + \text{O}_2$ $\text{O}^{\bullet} + \text{H}_2\text{O} \rightarrow 2 \bullet\text{OH}$
O <sub>3</sub> /VUV/ UV <sub>254nm</sub>	$\text{O}_3 + h\nu (< 310 \text{ nm}) \rightarrow \text{O}^{\bullet} + \text{O}_2$ $\text{O}^{\bullet} + \text{H}_2\text{O} \rightarrow 2 \bullet\text{OH}$
O <sub>3</sub> /electron-hole pairs	$\text{O}_3 + e^- \rightarrow \text{O}_3^{\bullet-}$ $\text{H}^+ + \text{O}_3^{\bullet-} \rightarrow \text{HO}_3^{\bullet}$ $\text{HO}_3^{\bullet} \rightarrow \text{O}_2 + \bullet\text{OH}$

PCO: photocatalytic oxidation, TiO<sub>2</sub> : titanium dioxide, UV: ultraviolet light, VUV: vacuum ultraviolet light, O<sub>3</sub>:ozone

**Table 4** Studies on ethylene removal via photocatalytic and/ photochemical oxidation

Research scope	TiO <sub>2</sub> form/Type	Light source/wavelength (nm)	Reference
Effect of VUV on Banana storage	-	UV (254+185)	Scott et al. (1971)
Development of scrubber for atmospheric pollutants	-	UV (254+185)	Scott and Wills (1973)
Ethylene removal from low oxygen atmospheres	-	UV (254+185)	Shorter and Scott (1986)
Effect of moisture and temperature	Pt/TiO <sub>2</sub>	UVA	Fu et al. (1996)
Effect of moisture and temperature	-	-	Obee and Hay (1997)
Effect of temperature, humidity, airflow rate and ethylene concentration	Zirconia-Titania pellets	4 W UV fluorescent lamp	Tibbitts et al. (1998)
Presence of water and O <sub>2</sub> on oxidation	Ultrafine TiO <sub>2</sub>	>280	Park et al. (1999)
Kinetic rate studies	Thin films of Titania supported on glass rings	-	Sirisuk et al. (1999)
Kinetic studies of oxidation	TiO <sub>2</sub> Pellets	UVA	Yamazaki et al. (1999)
Model for ethylene decomposition in CA storage of apples	-	UV (254+185)	Jozwiak et al. (2001)
Presence of water and O <sub>2</sub> on oxidation and Pt loading	Ultrafine TiO <sub>2</sub>	>280	Park et al. (2001)
PCO in presence of microwaves	TiO <sub>2</sub> /ZrO <sub>2</sub> films	Fluorescent bulb Emitted UV light via microwave plasma lighting 50-60 C	Kataoka et al. (2002)
Effect of humidity on PCO; impact on ripening of tomatoes	TiO <sub>2</sub> coated glass bead, TiO <sub>2</sub> solution	300 – 400	Maneerat et al. (2003)
Visible light degradation of ethylene	Titanium oxynitride compounds with small quantity of palladium	300 – 700, UV/365	Kumar et al. (2005)

**Table 4** Studies on ethylene removal via photocatalytic and/ photochemical oxidation (continues)

Research scope	TiO <sub>2</sub> form/Type	Light source/wavelength (nm)	Reference
Effect on fruit ripening and off flavors in fruit storage	TiO <sub>2</sub> slurry	315 – 400	Maneerat and Hayata (2006a)
Storage of fruits (apples, avocado, melons, pineapples, kiwi)	Degussa P 25	UVA	Kartheuser and Boonaert (2007)
Optimization of coating and other parameters, study of reaction rate ; Ethylene levels in headspace of tomato packages	TiO <sub>2</sub> coated packaging films	315 – 400	Maneerat and Hayata (2008)
Photocatalytic oxidation on synthesized Au/TiO <sub>2</sub>	TiO <sub>2</sub> and Au/TiO <sub>2</sub> coated on glass tubes	350	Belarapurkar et al. (2010)
PCO at low temperature for potential application in cold storage for fruits	Novel TiO <sub>2</sub> nanoparticles	UVA (320-400) UVB (290-320)	Hussain et al. (2010)
Reaction pathway of PCO, using Fourier transform infrared spectroscopy	Aerolyst 7710 (Evonik)	UV LEDs , 310-400	Hauchecorne et al. (2011)
Catalyst comparative study between novel particles and Degussa, effect of parameters	Novel TiO <sub>2</sub> nano particles	UVA/(320–400); UVB/(290–320)	Hussain et al. (2011)
Photocatalytic and antimicrobial properties	Ultra-thin TiO <sub>2</sub> coating	-	Yao and Yeung (2011)
Effect of high temperature (60 °C- 520°C)	Degussa P 25	-	Westrich et al. (2011)
Process optimization	Evonik Aeroxide (Degussa P25)	254	Tytgat et al. (2012)
VUV-PCO	TiO <sub>2</sub> coated on reactor surface	254 +185, 254, 365	Chang et al. (2013)
Design of fluidized based photoreactor and its evaluation, Development of catalyst	SiO <sub>2</sub> /TiO <sub>2</sub> - coated alumina spores	315 – 400	de Chiara et al. (2014)
Effect of oxygen, moisture and temp. on visible light PCO	N-Doped TiO <sub>2</sub>	400	Lin et al. (2014a)



**Table 4** Studies on ethylene removal via photocatalytic and/ photochemical oxidation (continues)

Research scope	TiO <sub>2</sub> form/Type	Light source/wavelength (nm)	Reference
Parameters affecting visible light PCO	C-Doped TiO <sub>2</sub>	400	Lin et al. (2014b)
Optimisation of catalyst, application on tomatoes	Mesoporous TiO <sub>2</sub> /SiO <sub>2</sub> nanocomposite powder	315 – 400	de Chiara et al. (2015)
Hybrid Microwave/UV/TiO <sub>2</sub> , effect of parameters- microwave intensity, O <sub>2</sub> concentration, flow rate	TiO <sub>2</sub> deposited on aluminium balls by chemical vapor deposition	UVC	Lee et al. (2015)
Model for fruit transportation in 40' shipping container	Quartzel PCO (Saint Gobain)	UV (254)	Nielson et al. (2015)
Photoelectrocatalytic degradation of ethylene	Activated carbon felts supported TiO <sub>2</sub>	254	Ye et al. (2015)

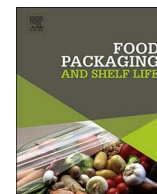
C: carbon, N: nitrogen, PCO: photocatalytic oxidation, TiO<sub>2</sub>: titanium dioxide, SiO<sub>2</sub>: silicone dioxide, UV: ultraviolet light, VUV: vacuum ultraviolet light

### **3. Impacts of mixed fruit loading on postharvest physiological responses and quality of horticultural produce**

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# Impacts of mixed fruit loading on postharvest physiological responses and quality of horticultural produce



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## ABSTRACT

Postharvest supply chain of fresh produce often involves close proximity of fruit with different ethylene sensitivities. Thus, the quality of fruit sensitive to ethylene may be affected due to the exogenous ethylene, produced by other commodities. This study was conducted to assess the impacts of a mixed fruit loading and storage on the physiological and qualitative attributes of fruits. Further on, the effectiveness of ethylene removal using conventional ethylene absorbent sachets as well as an in-house developed ultraviolet light based reactor in such mixed storage was also evaluated. High ethylene producer (apples) was stored along with non-treated green bananas and unripe kiwifruit (highly sensitive to ethylene), at 15 °C for 10 days. Post-storage analysis showed that bananas and kiwifruits stored with apples had significantly elevated respiration and ethylene production rates compared to samples stored alone. Mix loading with apples resulted in a significant decline in tissue strength from 25.01 to 6.44 N for kiwifruits; and a significant increase in total soluble sugars from 2.7 to 21.09% for bananas at the end of storage. The use of ethylene absorbent as well as the reactor reduced ethylene concentration in the storage chamber and slowed down respiration rate in the fruits. However, to preserve fruit quality to a higher extent, further research into development of ethylene removal system with higher ethylene removal rate is suggested. The results obtained also highlight the need of proper separation of fresh produce (based on ethylene sensitivity) during transportation, storage and retail display.

## 1. Introduction

Fruit and vegetables (F & V) are perishable products that along with root crops contribute to 40–50% of the global food waste annually (FAO, 2015). The high perishability of F & V is due to the fact that even after harvest they remain metabolically active and undergo ripening and senescence (Mahajan, Caleb, Singh, Watkins, & Geyer, 2014). Thus, to minimize the postharvest losses, slowing down these physiological and metabolic processes along the value chain is essential. Various postharvest techniques have been successfully used in delaying various physiological and biochemical activities associated with ripening and senescence of F & V. These include the use of cooling, controlled atmosphere storage, modified atmosphere packaging, ethylene management and other techniques (Bapat et al., 2010; Mahajan et al., 2014; Martínez-Romero et al., 2007).

Besides optimal storage conditions, ethylene management is of critical importance along the fresh produce value chain. Ethylene

management has also been suggested as an important measure to reduce fresh produce waste (Blanke, 2014, 2015). Ethylene is a product of plant metabolism, which triggers an autocatalytic and irreversible ripening process in climacteric fruit, and expedites senescence in non-climacteric fruit (Saltveit, 1999; Wills, 2015). It is also a by-product of combustion of petrochemicals (Zagory, 1995). Ethylene concentration in the vicinity of storage facility for fresh produce has been found to be higher than normal (0.001–0.005 ppm). This was associated with ethylene produced by climacteric fruits and to the movements of trucks, tractors, forklifts within the facility (Warton, Wills, & Ku, 2000). Similarly, varying concentrations of ethylene were reported at different points in the supply chain; with 0.017–0.035 ppm at supermarkets outlet, and 0.06 ppm at whole sale markets and distribution centers (Warton et al., 2000). Study reported by Rees et al. (2011) found approximately 0.05 ppm and 3.6 ppm ethylene concentrations in retail outlets and storage facilities, respectively.

Both ethylene sensitive and ethylene-producing commodities are

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often kept together (mixed loading) during storage and transport. This can be highly detrimental as ethylene has nearly the same specific mass ( $0.97\text{--}0.99\text{ kg m}^{-3}$ ) as air ( $1.27\text{ kg m}^{-3}$ ) and can easily diffuse from one part to the other (Blanke, 2014). Ethylene concentrations as low as 0.001 ppm could induce detrimental changes in fresh produce depending on the storage temperature, exposure time and produce sensitivity (Wills, 2015). In a study conducted by (Warton et al., 2000) empty storage room close to avocado storage room was also found to have 0.280 ppm of ethylene. Furthermore, ethylene concentrations in cargo ships prior to and during transport of fresh produce were investigated by Lawton (1991). The authors demonstrated that containers loaded with kiwifruit and apples had ethylene concentration within the range of 0.001–0.008 ppm and 5–15 ppm, respectively. On the other hand, ethylene concentration in the mixed fruit cargo of apples, pears and grapes was about 50 ppm and emanating from apples and pears. Thus, it is generally recommended to assess the compatibility of different produce prior to mixed loading transport or storage, based on their ethylene sensitivity and other factors such as temperature, moisture, and odor (Watkins, 2016). However, often due to high cost, carriers are required to load and stow different produce in the same vessel, hold, or cargo container. Wholesale market maybe poorly designed without separate facilities for loading, unloading, and ripening chamber. While, retail stores may display ethylene sensitive and ethylene producing fruit in close proximity due to space restrictions.

Therefore, this study was undertaken in order to examine the physiological and qualitative changes that may occur in mixed loading of fresh horticultural commodities. To achieve this aim, three different fruit types with varying degree of ethylene production and sensitivity were selected. This included green bananas and unripe kiwifruit (with low ethylene production, high sensitivity) and apples (high ethylene production, moderate sensitivity) (Blanke, 2014; Martínez-Romero et al., 2007). These fruits were stored in different combinations at 15 °C (to mimic average retail temperature) for 10 days. Quality attributes and physiological responses were determined prior to and at the end of storage life. In addition, the effects of ethylene removal using active sachets and an ethylene filtration device (in house developed reactor) in mixed storage of apples, green bananas and unripe kiwifruit were investigated.

## 2. Materials and methods

### 2.1. Plant material and storage

Apples (cv. Jonagold), bananas (cv. Cavendish) and kiwifruit (cv. Harard) were obtained at commercial maturity directly from a local supplier (Frucht Express GmbH, Groß Kreutz, Germany). The fruit were transported in cooled conditions to the Department of Horticultural Engineering (Fresh Lab.), Leibniz institute for Agricultural Engineering and Bioeconomy, Potsdam, Germany. On arrival, the samples were stored overnight at 15 °C prior to the experiments. Two experiments were conducted consecutively in this study. In the first experiment, fruit samples were distributed into seven different combinations as shown in Table 1. Each combination was stored in a closed chamber (190 L) for 10 days at 15 °C (storage temperature was based on average retail

condition) in dark. Gas composition ( $\text{O}_2$  and  $\text{CO}_2$  concentration) was not controlled but monitored by gas analyser (Checkmate 3, PBI Dan-sensor, Ringsted, Denmark) at regular intervals. Ethylene concentrations were measured using ETD-300 (Sensor sense, Nijmegen, The Netherlands), a laser based photoacoustic detector, along with a gas handling system. The system has a detection limit of 0.0003 ppm with a time resolution of 5 s.

The second experiment was based on mixed storage of apples, bananas and kiwifruit in a ratio of 1/3, 1/3, and 1/3, respectively (Total fruit mass 6 kg). In this experiment, the impact of ethylene removal was investigated using commercial ethylene control sachets and an in-house developed reactor based on ultraviolet light. In the first test chamber (190 L), six ethylene removal sachets based on potassium permanganate (Purafil, USA) were placed, while another chamber without any ethylene removal sachets served as the control. For the second test chamber, a stainless steel reactor (diameter = 12 cm, height = 11 cm) which served an ethylene filtration device was placed inside the chamber. The reactor consisted of 3 ultraviolet lamps with maximum power output of 3W each. The major emission from the lamps was at 254 nm with a small emission (5–8%) at 185 nm. The radiation at 185 nm have high energetic photons that are capable of dissociating water and oxygen molecules present in the atmosphere to produce reactive oxygen species as hydroxyl radicals, OH and superoxide ions,  $\text{O}_2^-$ . These reactive species oxidise ethylene into carbon dioxide and water (Haibao et al., 2016). This method is been researched extensively for air purification (Haibao et al., 2016; Huang, Leung, Li, Leung, & Fu, 2011; Jeong et al., 2006). It is effective in ethylene removal (Chang, Sekiguchi, Wang, & Zhao, 2013) and has potential for application in fruit storage (Scott, Wills, & Patterson, 1971). A small air pump was used to draw the air from the chamber and pass it through the reactor. Thus, a continuous circulation of air was maintained through the reactor. In all three storage chambers, the physiological and quality parameters were measured after a storage period of 10 days.

### 2.2. Respiration rate and ethylene production rate measurement

Respiration rate (RR) as well as ethylene production rate of the fruits were determined before and after the 10 d storage experiment. RR was measured using a non-invasive and continuous monitoring closed system respirometer (developed in-house). The respirometer consisting of 9 acrylic glass cuvettes (8.2 L), each fitted with non-dispersive infrared  $\text{CO}_2$  sensor (GMP222, Vaisala GmbH, Bonn, Germany). Measuring capacity of the respirometer is within the range of  $0.1 \times 10^{-3}$  to  $5\text{ g L}^{-1}$ , with an automated gas flush out system to bring in fresh air for each measurement cycle as described by Rux, Caleb, Geyer, and Mahajan (2017). Fruit of the same lot (4 in number) were placed in a cuvette. Hermetic sealing was achieved with O-rings between the lid and cuvette. The respiration rate was calculated as the amount of  $\text{CO}_2$  produced per unit mass of the fruit per unit time ( $\text{mL kg}^{-1}\text{ h}^{-1}$ ).

In order to measure ethylene production rate, fruits were separately stored in small jars and ethylene concentration was measured at regular interval using ETD-300 over a period of 8 h. Ethylene production rate was calculated as the amount of ethylene produced per unit time per unit mass of the fruit ( $\mu\text{L kg}^{-1}\text{ h}^{-1}$ ).

### 2.3. Mass loss

Four fruits of each kind per combination were marked and weighed before and after storage using an electronic balance CPA10035 (Sartorius, Göttingen, Germany). The difference in the weight between the initial and after storage measurement was calculated and averaged.

### 2.4. Light remittance for pigment analysis

The remittance readings can provide good information on pigment

**Table 1**  
Different combinations of fruit in storage.

No.	Fruit combinations	Apples (kg)	Bananas (kg)	Kiwifruit (kg)
1	Banana	–	6	–
2	Apple	6	–	–
3	Kiwifruit	–	–	6
4	Apple + Banana	3	3	–
5	Apple + Kiwifruit	3	–	3
6	Banana + Kiwifruit	–	3	3
7	Apple + Banana + Kiwifruit	2	2	2

(chlorophylls, carotenoids and anthocyanins) analysis (Kuckenberg, Tartachnyk, & Noga, 2008; Zude-Sasse, Truppel, & Herold, 2002). A hand-held photodiode array spectrophotometer device (Pigment Analyzer 1101, CP, Germany) was used for recording remission spectra in the fruits. The light source was provided by a light cup consisting of five light emitting diodes with maximum peaks with full width at half maximum for illumination of the samples. The spectra was detected with a resolution of 3.3 s (Kuckenberg et al., 2008; Zude, Birlouez-Aragon, Paschold, & Rutledge, 2007). Normalized difference vegetation index (NDVI) is directly calculated. NDVI index is commonly used in remote sensing for separation of green vegetation from soil background (Jones et al., 2007). It has been reported to correlate with the chlorophyll content in plant matter (Gitelson & Merzlyak, 1997).

## 2.5. Texture profile of fresh produce

The tissue strength (softness) of fruit samples for apples and kiwifruit were measured as maximum force (N) to penetrate the tissue of peeled fruit using a SMS-P/4 cylinder on the texture analyser (TA-XT Plus, Stable Micro Systems, Surrey, UK). The speed of penetration and depth of penetration was set at 1 mm s<sup>-1</sup> and 8 mm, respectively. For bananas the stiffness was measured using a spherical probe on the unpeeled fruit as the resistance to the maximum force. Five randomly selected fruits from each storage chamber were analysed, and results were presented as mean value.

## 2.6. Total soluble solid content and titratable acidity

Total soluble solid content (TSS) of juice obtained from the individual fruit was measured using a hand refractometer (DR301-95, Krüss Optronic, Hamburg, Germany) and expressed as%. For bananas, 5 g of bananas was smashed and diluted with 10 mL of distilled water and the TSS of the resultant mixture was measured. Total titratable acidity (TTA) of the juice sample was measured potentiometrically by titration with 0.1 mol L<sup>-1</sup> NaOH to end-point of pH 8.2 using an automated T50 M Titrator with Rondo 20 sample changer (Mettler Toledo, Switzerland). The TTA concentration was expressed as g L<sup>-1</sup> of malic acid for apples and citric acid for kiwifruit. The ratio of TSS and TTA of apple juice was calculated and expressed as TSS/TTA.

## 2.7. Statistical analysis

Three different fruit types (green bananas and unripe kiwifruit and apples) were considered as factors and various quality attributes and physiological responses were the measured parameters. The non-linear regression analysis was performed to evaluate the impact of mixing fruits in different proportions on measured parameters using Statistica software. The statistical analysis was carried out using Statistica software (version 10.0, StatSoft Inc., Tulsa, USA) and Microsoft Excel (Office 2010, Microsoft, Germany). All analysis was conducted in triplicate and average was used.

# 3. Results and discussion

## 3.1. Ethylene evolution

Ethylene concentration inside each chamber containing various combinations of fruits was monitored during storage and the concentration at the end of 10 days storage is shown in a contour plot in Fig. 1. This indicated that chambers with apples alone had the highest ethylene concentration. The results obtained in this study are in agreement with various reports, which showed that apples are high ethylene producers compared to green bananas and unripe kiwifruits (Blanke, 2014; Martínez-Romero et al., 2007).

Furthermore, post-storage ethylene production rates were found to be significantly impacted by the mixed loading. A comparison of

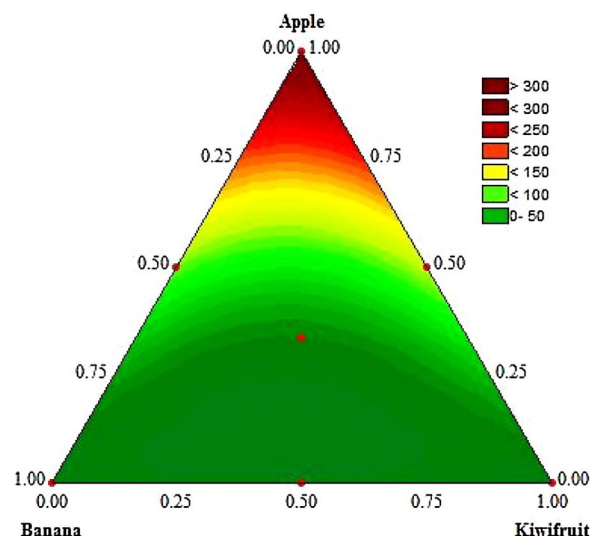


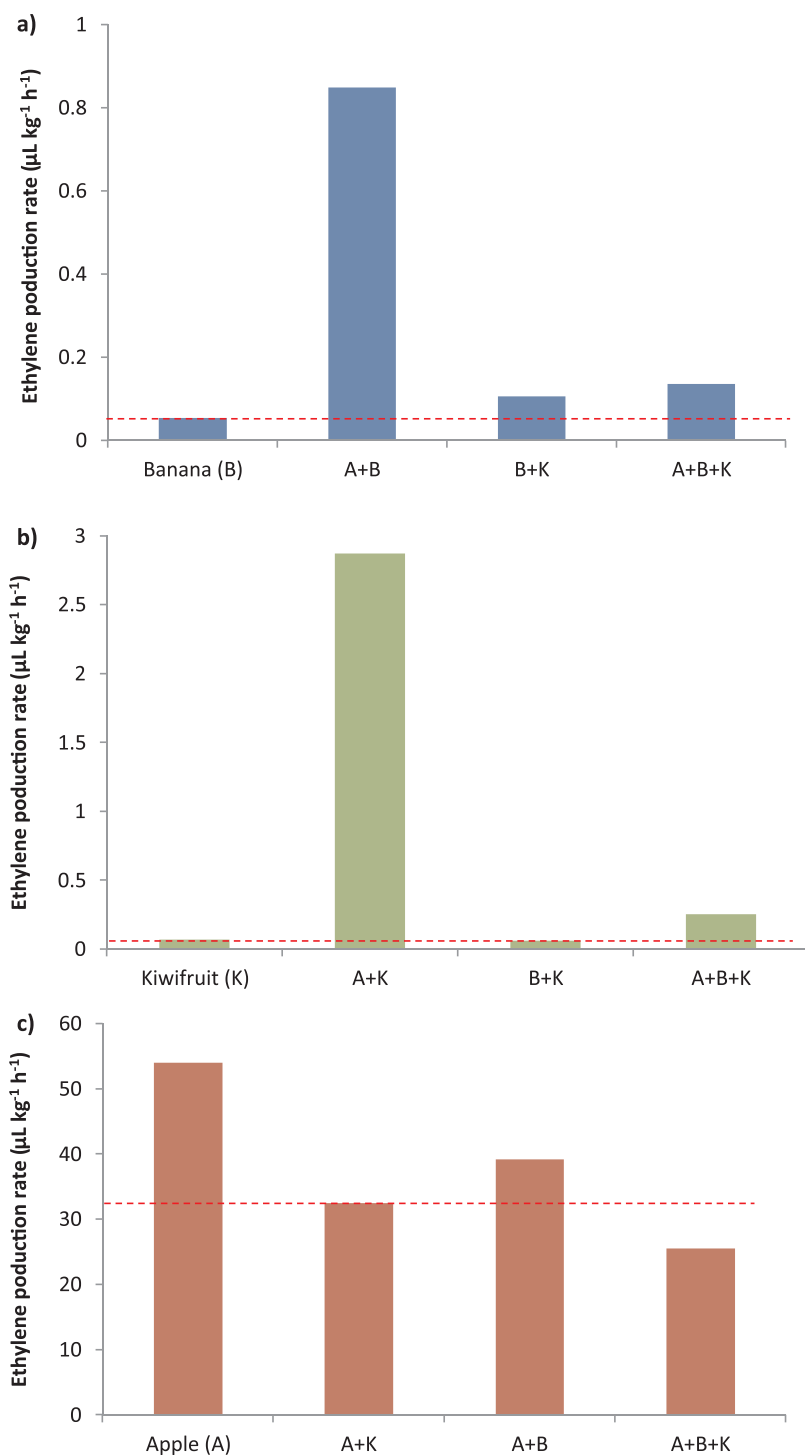
Fig. 1. Contour plot for absolute ethylene concentration (ppm) inside the storage chamber containing mixed fruit load at the end of 10 day storage.

ethylene production rates of apples, bananas and kiwifruits under different mixed storage combinations, to the initial and individual fruit storage showed clear differences (Fig. 2). After day 10, the ethylene production rates increased from 0.03 to 0.84  $\mu\text{L kg}^{-1} \text{h}^{-1}$  for bananas stored with apples (Fig. 2a). Excessive accumulation of ethylene in chamber containing only apples led to increase in ethylene production rate of apples (Fig. 2c) from 32 to 54  $\mu\text{L kg}^{-1} \text{h}^{-1}$ . In climacteric fruits, such as apples and bananas there are two stages in the ripening phases – pre-climacteric and climacteric. In the pre-climacteric phase, there is low respiration and ethylene production but with the onset of climacteric there is a sudden burst in ethylene production and respiration rate (Martínez-Romero et al., 2007; Saltveit, 1999). Exogenous ethylene can trigger this autocatalytic and irreversible ethylene production in fruits (Saltveit, 1999).

In case of kiwifruit, the ethylene production rates increased from 0.023 to 2.8  $\mu\text{L kg}^{-1} \text{h}^{-1}$ . The ethylene production rate of unripe kiwifruit is less than 0.1  $\mu\text{L kg}^{-1} \text{h}^{-1}$  at 0 °C and 0.1–0.5  $\mu\text{L kg}^{-1} \text{h}^{-1}$  at 20 °C, whereas ripened kiwifruit has a higher production rate of 50–100  $\mu\text{L kg}^{-1} \text{h}^{-1}$  at 20 °C (Crisosto, Mitcham, & Kader, 1996). The ethylene production rate of kiwifruit at the end of storage was not very high as expected of ripened kiwifruit as even though kiwifruits are classified as climacteric, however, unlike other climacteric fruits, the ethylene production in kiwifruit occur only after they are fully ripe (Antunes, Pateraki, Kanellis, & Sfakiotakis, 2000).

## 3.2. Respiration rate

A comparison of the RRs of individual fruit from the different storage combinations after 10 days of storage showed that mixed fruit loading had an influence on RR (Fig. 3). For instance, bananas displayed the highest respiration rate when stored in combination with apples and kiwifruit (51.16 mL kg<sup>-1</sup> h<sup>-1</sup>), while least RR was found when stored alone (7.84 mL kg<sup>-1</sup> h<sup>-1</sup>). The observed difference in respective RR for fruit samples under the storage combinations could be associated with the exposure to exogenous ethylene produced by apples (Fig. 3). Ethylene is known to elevate the RR and induce senescence for many horticultural commodities during postharvest storage (Fugate, Suttle, & Campbell, 2010). Higher ethylene concentrations in storage chambers with apples resulted in the enhanced respiration rates of the fruits. Kiwifruit also displayed higher respiration rate when stored with apples (A/K) and in all three fruit mixed storage (A/B/K) compared two storage alone (K) or with bananas (B/K).



**Fig. 2.** Rate of ethylene production from a) Banana b) Kiwifruit (c) Apple after removing them from the mixed fruit load on day 10 of storage. X-axis indicates the type of fruit combinations. The horizontal dashed line indicates the initial ethylene production rate of respective fruits.

### 3.3. Mass loss

At the end of storage, maximum percentage mass loss was observed in the mixture of apples and bananas as shown in the contour plot (Fig. 4). After harvest, the fruit continue the processes of respiration (involving breakdown of carbohydrates and releasing heat, carbon dioxide and water) and transpiration (loss of water vapor from fruit surface to the surrounding) that contribute to mass loss (Bovi, Caleb, Linke, Rauh, & Mahajan, 2016; Flores-López, Cerqueira, de Rodríguez, & Vicente, 2016). Thus, the high mass loss (%) found in the mixture of apples and bananas could be attributed to ripened bananas as indicated by their high rate of respiration (Fig. 3). The major

contributors to mass loss in banana was suggested to be the movement of water from pulp to peel and subsequent evaporation of water from peel during ripening (Opara et al., 2013).

### 3.4. Color change

Colour change associated with the breakdown of chlorophyll content in fruit peel can be monitored using light remission technique (Kuckenberg et al., 2008; Merzlyak, Solovchenko, & Gitelson, 2003). Light remission parameters such as NDVI has been reported to show a good positive correlation with chlorophyll content (Kuckenberg et al., 2008). The NDVI index of the bananas prior to storage and after storage

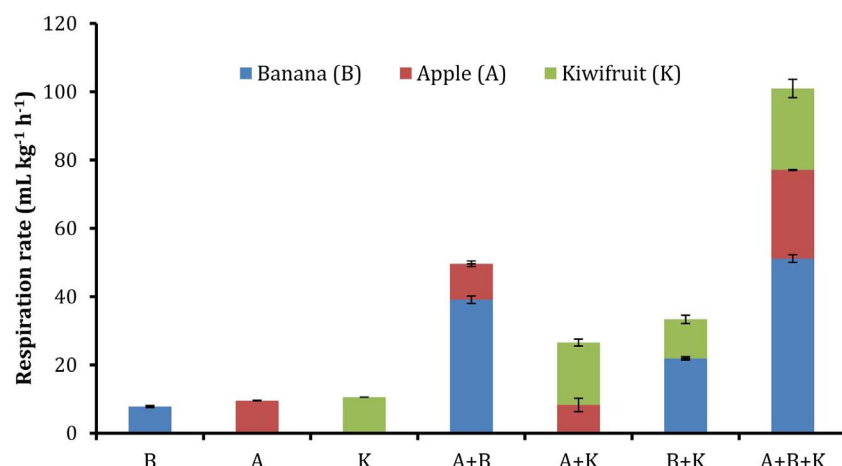


Fig. 3. Post-storage respiration rate of fruit samples taken out from the mixed fruit load at the end of 10 day storage at 15 °C. Error bars represent standard deviation n = 3.

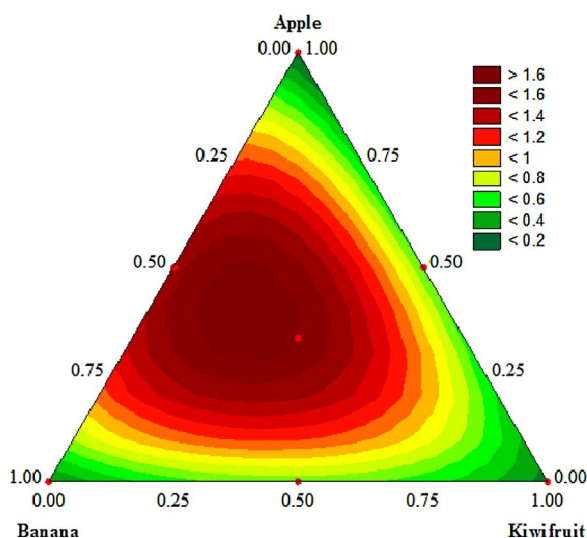


Fig. 4. Contour plot showing the effect of different proportions of fruits on the total percentage mass loss on day 10 of storage at 15 °C.

alone (B) and with kiwifruits (B/K) showed a high NDVI index, whereas, the bananas stored with apples (A/B), and with kiwifruits and apples mixed storage (A/B/K) showed a low NDVI index (Table 2). In bananas, during ripening the peel chlorophyll degrades, and the change in peel color from green to yellow is indicative of the ripening (Turner, 1994). The bananas stored alone and those stored along with kiwifruits retained green color, while the bananas in A/B and A/B/K storage were yellow (Fig. 5). In the case of apples and kiwifruits no visible change in color or change in NDVI index was observed. The non-homogeneous coloring of apples and the short storage duration could account for the insignificant variations in these indices.

### 3.5. Tissue strength

The tissue strength did not show significant change in apples and bananas post storage under different combinations (Table 2). However, in kiwifruits post storage the tissue strength decreased significantly ( $p < 0.05$ ). The initial tissue strength of kiwifruits was measured to be  $25.01 \pm 8.6$  N, which decreased to 11–13 N when stored kiwifruit alone and with bananas. Lowest decline in tissue strength of 5–7 N was found in A/K and A/B/K storage combinations. Kiwifruit is an ethylene sensitive fruit in which even very low ethylene concentrations (0.005–0.01 ppm) leads to fruit softening (Pranamornkith,

Table 2  
Quality parameters of fruits before and after storage in different combinations.

Fruit type	Fruit combination	Quality parameters			
		Tissue strength (N)	Total Soluble solids (% Brix)	Surface colour (NDVI index <sup>a</sup> )	Titrateable acidity (%)
Banana (B)	Initial	$2.01 \pm 0.0^*$	$2.70 \pm 0.2$	$0.96 \pm 0.0$	–
	B	$2.01 \pm 0.0$	$5.89 \pm 0.5$	$0.95 \pm 0.0$	–
	A/B	$2.00 \pm 0.0$	$21.43 \pm 1.6$	$0.20 \pm 0.0$	–
	B/K	$2.01 \pm 0.0$	$5.92 \pm 1.5$	$0.94 \pm 0.0$	–
	A/B/K	$2.00 \pm 0.0$	$21.09 \pm 0.8$	$0.17 \pm 0.0$	–
Apple (A)	Initial	$50.33 \pm 7.8$	$13.39 \pm 0.8$	$0.60 \pm 0.1$	$0.50 \pm 0.1^b$
	A	$43.74 \pm 3.3$	$13.32 \pm 0.7$	$0.37 \pm 0.2$	$0.49 \pm 0.2^b$
	A/B	$42.52 \pm 4.8$	$12.84 \pm 1.0$	$0.40 \pm 0.2$	$0.53 \pm 0.2^b$
	A/K	$47.18 \pm 3.4$	$13.78 \pm 0.9$	$0.33 \pm 0.2$	$0.42 \pm 0.1^b$
	A/B/K	$42.32 \pm 5.2$	$12.64 \pm 0.9$	$0.50 \pm 0.2$	$0.50 \pm 0.1^b$
Kiwifruit (K)	Initial	$25.01 \pm 8.6$	$13.44 \pm 0.5$	$0.94 \pm 0.0$	$0.70 \pm 0.1^c$
	K	$11.50 \pm 2.5$	$13.36 \pm 0.7$	$0.95 \pm 0.0$	$0.66 \pm 0.1^c$
	B/K	$12.83 \pm 1.8$	$13.10 \pm 0.6$	$0.94 \pm 0.0$	$0.56 \pm 0.1^c$
	A/K	$5.00 \pm 0.8$	$14.10 \pm 0.5$	$0.95 \pm 0.0$	$0.28 \pm 0.1^c$
	A/B/K	$6.44 \pm 2.8$	$13.48 \pm 0.6$	$0.94 \pm 0.0$	$0.32 \pm 0.1^c$

\* Mean values (mean  $\pm$  standard deviation, n = 5).

<sup>a</sup> normalized difference vegetation index.

<sup>b</sup> % malic acid and % citric acid, respectively.

<sup>c</sup> % malic acid and % citric acid, respectively.



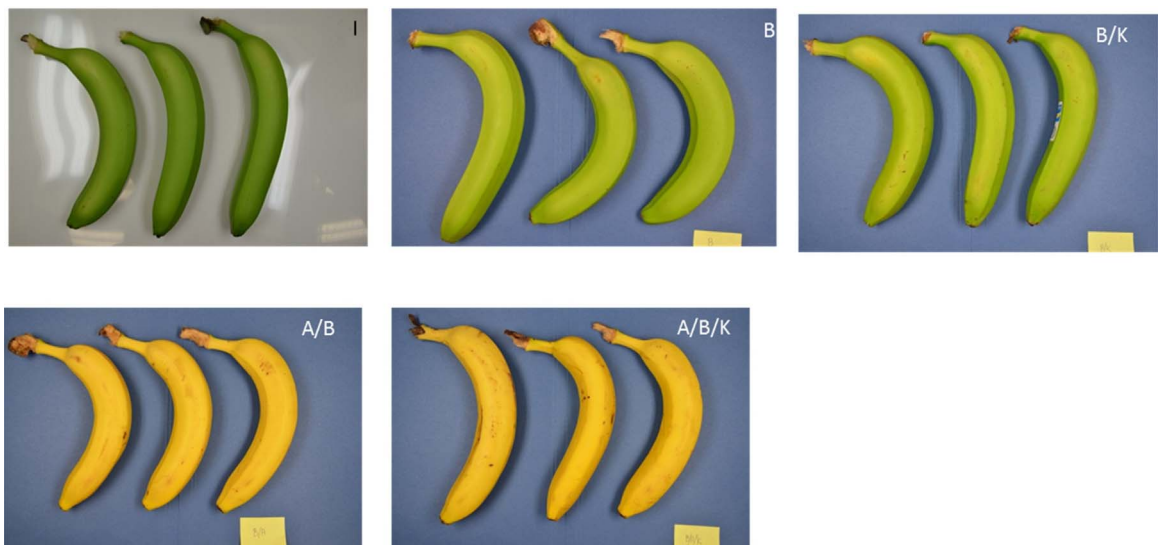


Fig. 5. Visual appearance of banana before and after mixed storage with other fruits at 15 °C for 10 d; I- Before storage, B- Banana alone, B/K – banana with kiwifruit, A/B – banana with apples, A/B/K – banana with apples and kiwifruit.

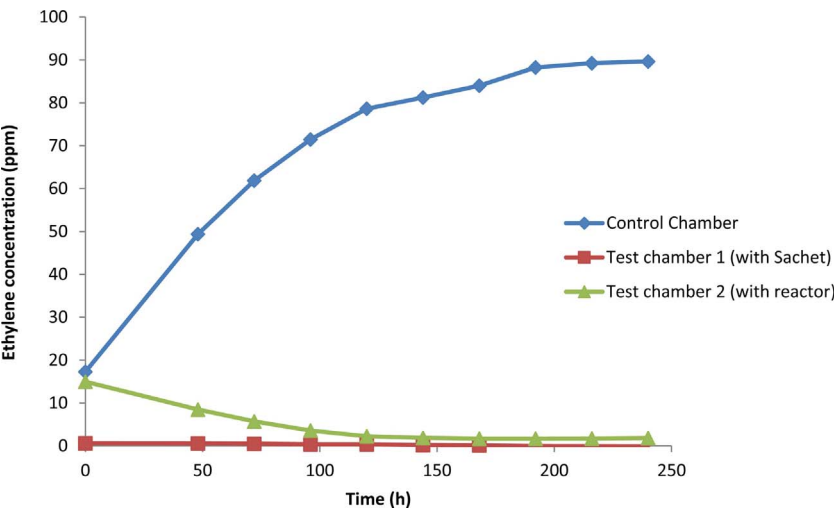


Fig. 6. Ethylene concentration (ppm) inside the storage chambers containing mixed load of apple, banana, kiwifruit at 15 °C. Test chamber 1: with ethylene removal sachet; Test chamber 2: with ethylene removal reactor. Control chamber: without ethylene removal sachet.

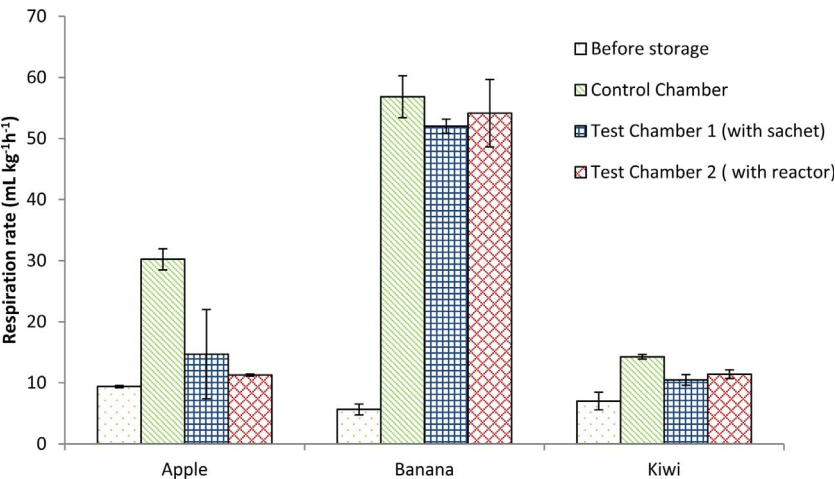


Fig. 7. Post-storage respiration rate for mixed load of banana, apple, and kiwifruit stored with and without active ethylene removal at 15 °C for 10 days. Test chamber 1: with ethylene removal sachet; Test chamber 2: with ethylene removal reactor. Control chamber: without ethylene removal. Error bars represent standard deviation n = 3.



East, & Heyes, 2012). Thus, due to the presence of ethylene the tissue strength of kiwifruit decreased significantly post storage.

### 3.6. Soluble solid content and total titratable acidity

The total soluble solids were determined in pulp samples of all types of fruits in the seven combinations (Table 2). The TSS of bananas initially were  $2.7 \pm 0.2\%$ , which changed after storage of bananas alone ( $5.89 \pm 0.5\%$ ) and along with kiwifruit (B/K) ( $5.92 \pm 1.5\%$ ). On the other hand there was an increase in the TSS content of the bananas stored with apples and in A/B/K storage up to  $21.43 \pm 1.6\%$  and  $21.09 \pm 0.8\%$ , respectively. Kiwifruits stored with apples showed a slightly higher TSS content than other combinations. During ripening several changes occur in the fruit including conversion of starch to sugar (Marriott, Robinson, & Karikari, 1981), which accounts for increased sugar content after storage. The TTA of kiwifruit was measured initially as  $0.7 \pm 0.1\%$  citric acid which decreased when stored with apples ( $0.28 \pm 0.1\%$ ) and in A/B/K storage ( $0.32 \pm 0.1\%$ ) whereas the decrease was less in storage of kiwifruit (K) alone and with bananas (B/K).

### 3.7. Effect of active ethylene removal

Ethylene removal sachets were introduced in the first test chamber containing mixed load of apples, bananas and kiwifruit. Inside another identical test chamber the ethylene removing reactor was installed while the control chamber consisted of similar mixed load of fruits but without any ethylene removal system. Ethylene concentration in the control chamber increased to 90 ppm at the end of 10 d storage period. It was observed that the use of ethylene sachets effectively kept the ethylene concentration to  $< 0.59$  ppm inside the test chamber (Fig. 6) while the reactor was able to reduce it up to 1.8 ppm at the end of 10 days. This led to lower post-storage RR (Fig. 7) and ethylene production rates (data not shown). According to a study on the effect ethylene removal by potassium permanganate on papaya (Corrêa et al., 2005), it was reported that potassium permanganate decreased the ethylene accumulation by direct capture of ethylene molecules. This reduction in ethylene reduced the intensity of climacteric peak thereby reducing autocatalytic production of ethylene in the fruit (papaya). Similar effect in reduction of autocatalytic ethylene production (as evident by lower ethylene production rates) could be accounted for in the present experiment test chambers. In the test chamber with reactor, the ethylene molecules were oxidized by the reactive oxygen species produced by the radiation in presence of oxygen and water (Chang et al., 2013) compared to the direct capture of ethylene molecules in the absorber.

The bananas in control chamber attained fully developed yellow peel color at the end of storage compared to the bananas in test chamber with sachet, which retained about  $< 20\%$  of surface green color. The removal of ethylene increases the green life of bananas (Broughton & Wu, 1979). This was evident by the retained green color for bananas in the test chamber with sachets. This suggests that there could be a time-lapse or delays between ethylene production by the fruit and ethylene absorption by potassium permanganate. In the test chamber with reactor, the bananas turned yellow as in the control chamber in spite of the reduced ethylene levels. This was due to the initial exposure to ethylene as the reactor took a longer time in reducing ethylene levels (Fig. 6). The quality parameters such as TSS, textural properties were retained to a higher extent in the products stored in the test chambers than in control. At the end of storage, the tissue strength in kiwifruit declined in the control chamber, whereas kiwifruits from test chamber with sachets remained comparatively firm even after 10 days of storage. The stiffness of banana also remained same ( $2.00 \pm 0.0$  N) after storage in all chambers. The TSS of banana increased from an initial  $0.825 \pm 0.5\%$  to  $3.43 \pm 1.4\%$  in control chamber. Whereas it increased to  $5.6 \pm 1\%$  and  $3.8 \pm 1.9\%$ , for

samples in test chambers with sachet and with reactor, respectively. Kiwifruits had a slight increase in TSS from an initial of  $12.2 \pm 2.3\%$  to  $14 \pm 1.7\%$  in the control chambers. TSS in test chambers with sachet and reactor were measured to be  $12.8 \pm 0\%$  and  $13.5 \pm 1.2\%$  respectively. TSS and TTA concentration for apples did not show a significant change after storage. Thus, with better ethylene removal, fruit quality can be retained to a greater extent. In this study, it was observed that even though ethylene concentration was low in the test chambers, bananas still turned yellow to some extent. This is due to the initial ethylene exposure before being removed by ethylene control systems. Thus, there is still a need of better ethylene removal systems with higher ethylene removal rate.

## 4. Conclusion

This study showed that mixed storage of apples with bananas and kiwifruits resulted in elevated respiration and ethylene production rates for bananas and kiwifruits, which accelerated their quality degradation. Hence, long-term storage and/or transport of such mix loading would be highly detrimental. This highlights the need to carefully sort fresh produce arrangement along the supply chain and in retail display outlets. This would help to minimize the exposure of ethylene sensitive products to high ethylene emitting commodities. The use of ethylene control sachets reduced the ethylene concentration inside the storage chambers and slowed down respiration and ethylene production rates. Whereas, the ultraviolet light based reactor was able to reduce ethylene, however, ethylene removal rate was slow. Therefore, further research into a more efficient ethylene removal system with proper storage ventilations or ethylene removing filters is needed that can quickly remove ethylene to the lowest possible concentration and without impacting the quality of fruit and vegetables.

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#### **4. Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage**

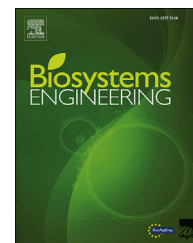
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## Research Paper

# Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage



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Detrimental effects of ethylene on fresh produce make ethylene removal one of the major challenges in storage of horticultural commodities. Novel techniques based on advanced oxidation processes such as photocatalysis and photolysis by vacuum ultraviolet light (VUV) offer good potential for ethylene removal. This study focused on the use of VUV photolysis and the impact of different process variables on the efficiency of this technique. The set objectives of this study were to investigate the combined effects of three process variables; flow rate, initial ethylene concentration, and ultraviolet radiation on the efficiency of VUV photolysis for removal of ethylene at normal atmospheric conditions. Response surface methodology along with Box–Behnken design was applied to determine the combined effect of these variables. Flowrate exerted the most significant effect on the amount of ethylene removed, followed by initial ethylene concentration and ultraviolet lamp power. The combined effect of these three process parameters exerted a significant effect on percentage ethylene removal. Reducing the flowrate and increasing the lamp power as well as the initial ethylene concentration had a positive effect on the amount of ethylene removed. For an initial ethylene concentration of 5 ppm, the percentage ethylene removal (76%) was highest under optimised process variable of 9 W lamp power and 0.5 L/min flowrate. The developed reactor was tested on short term storage of apples and kiwifruit. The reactor effectively reduced ethylene concentrations in storage space of both products. Kiwifruit storage connected to the reactor had higher flesh firmness compared to the control samples.

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## 1. Introduction

Ethylene is a colourless and odourless gas that is naturally produced as a by-product of plant metabolism, and it is also generated during burning of hydrocarbons (Zagory, 1995). It is a plant hormone that plays an important role in the growth and development of fruit and vegetables (Saltveit, 1999). Besides its beneficial effects, ethylene also exerts numerous negative impacts on fruit and vegetables with the most prominent being accelerated ripening and rapid decay of fresh horticultural produce (Mahajan, Caleb, Singh, Watkins, & Geyer, 2014; Saltveit, 1999; Wills, Warton, Mussa, & Chew, 2001). It is estimated that 10–30% of fresh produce is wasted because of undesired ethylene exposure (Warton, Wills, & Ku, 2000). Thus, the removal of ethylene from storage systems is one of the major postharvest challenges in the horticultural industry.

Common methods for removing ethylene in horticultural space involve the use of adsorbers and oxidisers (Arteca, 2014). These methods have several limitations in terms of absorption capacity, the need for continuous replacement and/or additional disposal challenges. Catalytic oxidisers promote oxidation of ethylene in presence of a catalyst at high temperatures, thus, offering better application in terms of continuous ethylene removal, no by-product disposal limitation and no frequent replacement. However, high initial capital and operational cost due to energy consumption are limiting factor for this method. Alternatively, ultraviolet light based equipment/reactors which have lower energy requirement can be used, as they can operate at room temperatures (Huang et al., 2016). The photocatalytic oxidation (PCO) technique based on UV light is an emerging technique that involves the use of a catalyst (e.g.  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZnS}$ ,  $\text{CdS}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ) and UV light (normally ranged between 200 and 380 nm depending on the catalyst).

These techniques have been extensively researched for removal of volatile organic compounds in indoor air purification (Huang et al., 2016; Zhao & Yang, 2003) as well as for oxidation of ethylene (Keller, Ducamp, Robert, & Keller, 2013; Pathak et al., 2017). PCO involves irradiation of a catalyst, such as titanium dioxide by ultraviolet light. The process generates electron–hole pairs at the surface of the catalyst that react with surface adsorbed oxygen and water to produce reactive oxygen species (such as hydroxyl radicals,  $\text{OH}^\bullet$  and superoxide ions,  $\text{O}_2^\bullet$ ) that eventually oxidises ethylene to carbon dioxide and water. This is a cost effective technique that can operate at room temperature and pressure. Literature concerning the utility of PCO for ethylene removal in fresh produce storage is emerging (de Chiara, Pal, Licciulli, Amodio, & Colelli, 2015; Hussain, Bensaid, Geobaldo, Saracco, & Russo, 2011; Kartheuser & Boonaert, 2007; Maneerat & Hayata, 2006; Nielsen, Vesborg, Hansen, & Chorkendorff, 2015). However, this method suffers from catalyst deactivation due to accumulation of intermediate products at catalyst surface and low efficiency due to electron–hole pair recombination (Huang, Leung, Li, Leung, & Fu, 2011). Moreover, at high humidity the ethylene removal efficiency decreases due to the competing effect between water and ethylene molecules to get adsorbed on the catalyst surface (Jeong et al., 2013).

Photolysis based on vacuum ultraviolet (VUV) light, unlike PCO, does not involve the use of a catalyst, instead the VUV irradiation (wavelength  $< 200$  nm) has high energy photons that are self-sufficient in dissociating oxygen and water present in the gaseous state to produce reactive species such as atomic oxygen  $\text{O}(^1\text{D})$ ,  $\text{O}(^3\text{P})$ , hydroxyl radicals ( $\text{OH}^\bullet$ ) and ozone ( $\text{O}_3$ ) which oxidise ethylene (Huang et al., 2016). VUV photolysis has a higher overall efficiency than PCO as photocatalysis is a surface phenomenon occurring on the surface of the catalyst whereas the photolysis occurs in the gas phase and therefore is faster and consequently has a higher efficiency. In a study on toluene removal (Hussain, Russo, & Saracco, 2011), 63.9% removal efficiency was reported with VUV photolysis alone as compared to 14.3% in case of PCO. Unlike PCO, VUV photolytic effect is not diminished at high humidity as water molecules are converted to hydroxyl radicals which are strong oxidising species. In the same study by Hussain, Russo, et al. (2011), toluene removal was observed to be higher in wet air than dry air with the efficiency of removal being 63.9% and 43.3% in respective cases.

Very few studies on the application of VUV on ethylene removal have been reported especially those relating to application in fruit and vegetable storage. The main motivation for this study was to develop an efficient VUV based process for ethylene removal for application in fruit and vegetable storage. In early 70s and 80s, some studies on the application of VUV light on ethylene were reported (Scott & Wills, 1973; Scott, Wills, & Patterson, 1971; Shorter & Scott, 1986). The potential of VUV in ethylene removal for the purpose of fruit storage was demonstrated by Scott et al. (1971). Shorter and Scott (1986) experimented on removal of ethylene using VUV producing lamps at different oxygen concentrations. In those studies, the actual oxidation mechanism was not known; however, atomic  $\text{O}_2$  was proposed to be responsible for the effect. These studies presented the potential of this technique for application in horticultural storage industries, but did not provide the details of mechanism and guidelines for development of an efficient system. For potential application in controlled atmosphere (CA) storage of apples, a static model was developed by Jozwiak, Bartsch, and Aneshansley (2003). In that study, the authors mainly focused on the effect of  $\text{O}_2$  concentration on ethylene removal in presence of VUV light but did not cover the effect of other engineering and process parameters that influence photo-oxidation. Key parameters affecting the photo-oxidation of ethylene include flow rate, the light intensity, feed composition (ethylene, oxygen, and water concentration), and temperature (Lin, Weng, & Chen, 2014; Obee & Hay, 1997). In order to develop a highly efficient ethylene removal process it is important to take into consideration the combined effect of these factors.

Thus, this study was aimed at investigating the combined effects of flow rate, initial ethylene concentration, and UV radiation in VUV photolysis for removal of ethylene at normal atmospheric conditions. For process optimisation, response surface methodology was implemented. Box–Behnken (BB) design with three factors (flow rate, lamp power, and initial ethylene concentration) and 3-levels was applied. The model developed was experimentally validated. The optimised



reactor was thereafter tested in storage application for apples and kiwifruits at 10 °C and 15 °C, respectively.

## 2. Materials and method

### 2.1. Photolysis reactor

In order to carry out the oxidation reaction, a cylindrical stainless steel reactor (diameter = 12 cm, height = 11 cm) was designed with an inlet and outlet port for flushing with the gas of desired concentration. Three ozone producing UV lamps (Dinies, Villingendorf, Germany), with a power input of 3 W each were placed inside the reactor (Fig. 1). The major emission of the irradiation by the lamps was at 254 nm, while minor emission (~5–8%) was at 185 nm. The lid of the reactor had openings for the electric fittings of the UV lamps, and the temperature and humidity sensors (Ahlborn, Holzkirchen, Germany). The annotated experimental setup is shown in Fig. 1. The desired concentration of ethylene was obtained by mixing ethylene from ethylene standard,  $9.88 \pm 0.20$  Mol-ppm or  $105.3 \pm 2.1$  Mol-ppm and rest synthetic air (Air Liquide, Berlin, Germany) with compressed gas using a gas mixer. The reactor was flushed continuously with the desired gas concentration in a flow through system. The outlet port of the reactor was connected to equipment for ethylene measurement.

### 2.2. Ethylene measurement

Ethylene measurements were carried out using ETD-300 (Sensor sense, Nijmegen, The Netherlands), a laser based photoacoustic detector, along with a gas handling system. The ETD-300 detector consists of a high power laser. Ethylene absorbs the laser radiation and the energy is converted into heat that causes pressure changes inside a closed volume. Consequently, periodic waves are generated which are detected by a sensitive microphone. The system has a detection limit of 0.3 ppb with time resolution 5 s. Ethylene concentration was monitored continuously during the entire duration of the experiment. After obtaining a stable desired

configuration of ethylene, the lamps inside the reactors were switched on and data was logged till the drop in ethylene concentration stopped and again a stable value was obtained. The amount of ethylene removed was expressed as percent ethylene removal (Eq. (1)):

$$\text{PER} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where PER = Percent ethylene removal, %;  $C_i$  = Initial ethylene concentration, ppm;  $C_e$  = Ethylene concentration after equilibrium, ppm.

### 2.3. Experimental design

BB design is an independent second order design, which is rotatable or near rotatable. The advantages of BB design are the reduced number of treatments in a three factor system as well as good precision in the predicted response (Lahlali, Massart, Serhini, & Jijakli, 2008). Thus, in this study, BB design was employed to investigate the effect of the three variables, namely, UV lamp power, flow rate and initial ethylene concentration on percent ethylene removal.

The range of values for the independent factors, 3–9 W for UV lamp power, 2–30 ppm for initial ethylene concentration and 0.5–5 L/min for the flow rate was selected on the basis of preliminary experiments. The total power was varied by using multiple numbers of lamps, and each lamp drew a power of 3 W. On the other hand, the flow rate was varied and controlled using a gas mixer. The 3 levels (–1, 0, +1) for each variable were determined by the standard method (Ansorena, Moreira, & Roura, 2014; Lahlali et al., 2008). Total numbers of experiments required in this design were 15 including 3 repetitions of the central points. All experiments were performed in random order and in duplicates. The average value was recorded as the value of the response.

### 2.4. Model fitting and optimisation

A second order equation was used to fit the experimental data using Statistica software (Statistica v. 10.0, StatSoft Inc., Tulsa, OK, USA) as described in Eq. (2):

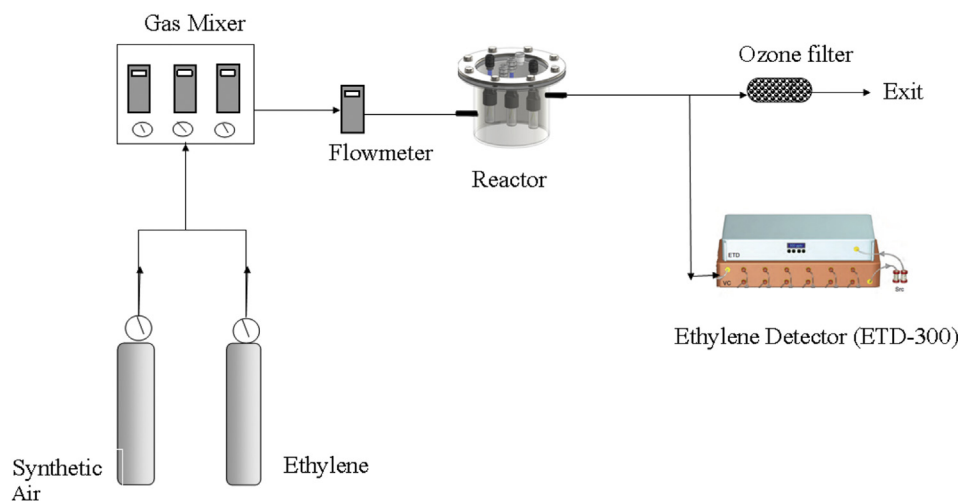


Fig. 1 – Schematic design of the experimental setup for ethylene removal.

$$\begin{aligned} \text{PER} = & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 \\ & + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \end{aligned} \quad (2)$$

where  $X_1$ ,  $X_2$ , and  $X_3$  are the coded values of process variables for lamp power, flow rate and initial ethylene concentration, respectively;  $\beta_0$  is the intercept coefficient;  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  are the linear coefficient terms;  $\beta_{12}$ ,  $\beta_{13}$ ,  $\beta_{23}$  are the interactive coefficient terms;  $\beta_{11}$ ,  $\beta_{22}$ ,  $\beta_{33}$  are the quadratic coefficient terms.

The model was applied for optimisation in order to achieve maximum PER while applying the following constraints: 1) initial ethylene concentration 5 ppm; 2) flow rate 0.5–5 L/min; and 3) lamp power 3–9 W. The validation experiment was carried out under the optimised conditions as predicted by the model at 5 ppm ethylene concentration.

### 2.5. Fruit storage experiments

For fruit storage application, the reactor was connected in closed circuit to a glass jar (4.1 L). A small pump was used to draw in air from the glass jar directly into the reactor via the inlet. In order to prevent ozone produced by the lamps from entering into the fruit storage area, the air at reactor exit was passed through rusted steel wool before returning to the storage chamber again. Rusted steel wool selectively removes ozone without significantly affecting the ethylene removal capacity of the reactor (Shorter & Scott, 1986). The reactor was set at low air flow rate (0.5 L/min) and high lamp power (9 W) for maximum ethylene removal.

Apples (cv. Jonagold) 0.7 kg and kiwifruit (cv. Hayward) 0.4 kg were stored separately in respective glass jars connected to the reactors. Fruits were also stored separately in glass jars not connected to the reactor to serve as control. Apples and kiwifruits were stored for a short-term duration of 7–10 days at 10 °C and 15 °C, respectively, to mimic average retail storage conditions. During the entire storage period ethylene, CO<sub>2</sub> and O<sub>2</sub> concentrations in the glass jars were monitored. In addition, physical and chemical quality attributes of the fruit samples were evaluated prior to and at the end of storage. Soluble solids content (SSC) and total titratable acidity (TTA) values were measured for the juice samples extracted from the fruits before and after the experiments. The SSC was measured using a hand refractometer (DR301-95, Krüss Optronic, Hamburg, Germany) and expressed as %. The TTA of the juice sample was measured potentiometrically by titration with 0.1 mol L<sup>-1</sup> NaOH to end-point of pH 7 using an automated T50M Titrator with Rondo 20 sample changer (Mettler Toledo, Switzerland). The TTA value was expressed as g L<sup>-1</sup> of malic acid and citric acid. The ratio of SSC and TTA of apple juice was calculated and expressed as SSC/TTA. The tissue strength (softness) of fruit samples was measured as maximum force (N) to penetrate the tissue of peeled fruit using a SMS-P/4 cylinder on the texture analyser (TA-XT Plus, Stable Micro Systems, Surrey, UK). The speed of penetration and depth of penetration was set at 1 mm s<sup>-1</sup> and 8 mm, respectively. Five randomly selected fruits from each storage chamber were analysed, and results presented as mean value.

### 2.6. Statistical analysis

The statistical analysis was carried out using Statistica software (version 10.0, StatSoft Inc., Tulsa, USA) and Solver tool in Microsoft Excel (Office 2010, Microsoft, Germany). Pareto analysis and surface plot were used to describe the effects of the 3 factors at 95% confidence interval, and the quality of the fit of the model was determined on the basis of R<sup>2</sup>. Response surface plots were obtained after applying response surface methodology with BB design to the entire data set. The effects of the different process variables on the response as illustrated by the plots are discussed further.

## 3. Results and discussion

### 3.1. Ethylene degradation and effect of flowrate

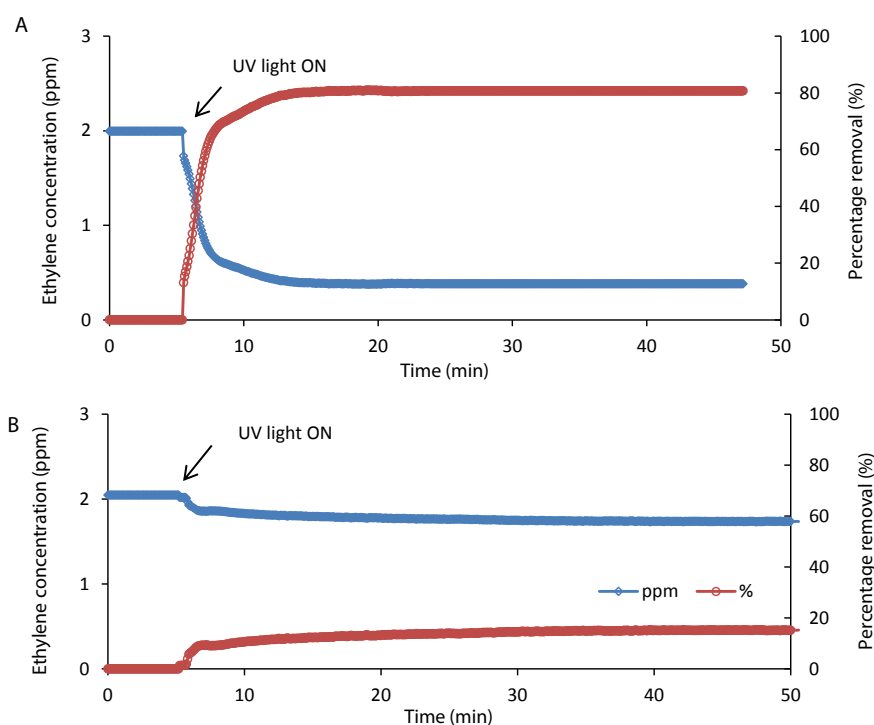
The various experimental combinations according to the BB design with their coded and uncoded values along with the experimental results are presented in Table 1. In addition, the environmental conditions (temperature and humidity) inside the reactor were monitored during the experimental run (Supplementary Table 1). For every experimental run the ethylene concentration dropped immediately after switching on the lamp and equilibrated after sometime depending on the flowrate. Figure 2 describes how the ethylene concentration changed on opening the lamps under two different experimental variables (flowrates 0.5 and 5 L/min, with 2 ppm initial ethylene concentration and 6 W lamp power). Initially, a stable straight line was obtained when the UV lamp was off and reactor was flushed with 2 ppm ethylene concentration. Then the UV lamps were switched on and the ethylene concentration decreased immediately. The measurement was continued till a stable ethylene concentration was obtained as shown in Fig. 2.

In the surface plot (Fig. 4) it can also be observed that in every case decreasing the flowrate increased the amount of ethylene removed. A decrease in the flowrate from 5 L/min to below 1 L/min increased the percentage ethylene removal to >60% from <20%. However, the degree of influence i.e. the extent of ethylene removal was dependent on other two variables namely initial ethylene concentration and lamp power. Flowrate determines the residence time for which the reactant gas (ethylene) remains inside the reactor from the point of entry to exit (Lee, Park, Kim, Lee, & Jung, 2015). Hence, decreasing the flow rate increased the residence time, which implies that the time of contact between ethylene molecules and the reactive species in the reactor is increased, consequently, increasing the ethylene removal. Previous studies on effect of flowrate on percentage ethylene removal in a photocatalytic reactor also reported similar observations (Hussain, Russo, et al., 2011; Tibbitts, Cushman, Fu, Anderson, & Bula, 1998). A decrease in percentage ethylene removal from 75 to 30% was reported with increase in flowrate from 0.1 L/min to 2 L/min by Tibbitts et al. (1998). Hussain, Bensaid, et al. (2011) and Hussain, Russo, et al. (2011) observed a decrease from >60 to <40% on increasing flowrate from 0.1 to 0.3 L/min. The increase in the residence time may increase

**Table 1 – Box–Behnken experimental design for studying the effect of various combinations of process variables on ethylene removal by vacuum ultraviolet radiation.**

Exp. no.	Process variables			Experimental response	
	Flowrate (L/min)	Initial [C <sub>2</sub> H <sub>4</sub> ] (ppm)	Lamp power (W)	Absolute removal (ppm)	Percent removal (%)
1	0.5 (–1) <sup>a</sup>	2 (–1)	6 (0)	1.49 ± 0.2d	79.01 ± 2.7a
2	0.5 (–1)	30 (1)	6 (0)	11.18 ± 0.7a	36.68 ± 1.7c
3	5 (1)	2 (–1)	6 (0)	0.34 ± 0.0f	15.03 ± 0.3d
4	5 (1)	30 (1)	6 (0)	0.28 ± 0.0g	0.91f
5	0.5 (–1)	16 (0)	3 (–1)	6.35 ± 2.0b	36.06 ± 7.5c
6	0.5 (–1)	16 (0)	9 (1)	8.76 ± 0.4b	57.02 ± 6.3b
7	5 (1)	16 (0)	3 (–1)	0.21 ± 0.0h	1.25 ± 0.1c
8	5 (1)	16 (0)	9 (1)	0.93 ± 0.5de	5.78 ± 3.1e
9	2.75 (0)	2 (–1)	3 (–1)	0.42 ± 0.1ef	17.93 ± 5.7d
10	2.75 (0)	2 (–1)	9 (1)	0.91 ± 0.2d	41.18 ± 10.4bc
11	2.75 (0)	30 (1)	3 (–1)	0.49 ± 0.0e	1.62 ± 0.0f
12	2.75 (0)	30 (1)	9 (1)	1.90 ± 0.5c	5.91 ± 1.1e
13	2.75 (0)	16 (0)	6 (0)	0.99 ± 0.3d	5.67 ± 1.0e
14	2.75 (0)	16 (0)	6 (0)	1.12 ± 0.1d	6.38 ± 0.0e
15	2.75 (0)	16 (0)	6 (0)	0.85 ± 0.5d	4.76 ± 2.3e

<sup>a</sup> Coded values of process variables. Values represent mean ( $n = 2$ ) ± standard deviation, and different lower case letters are significantly different at 95% confident interval.



**Fig. 2 – Time course for conversion of ethylene at initial ethylene concentration 2 ppm, UV lamp power 6 W, and flow rate: A) 0.5 L min<sup>-1</sup>, and B) 5 L min<sup>-1</sup>.**

the percentage of ethylene removed, but as the amount of ethylene treated per unit time decreases this may lead to inefficient energy utilisation (Lee et al., 2015). Therefore, an optimised flow rate is required for an efficient PCO process.

### 3.2. Effect of initial ethylene concentration

The general trend observed in the surface plots is that the quantity of ethylene removed (in ppm) increased with

increase in initial ethylene concentration, while the percentage ethylene removal decreased (Fig. 4). It has been reported that with respect to the initial VOC such as chloroform, carbon tetrachloride, trichloroethylene concentration the kinetic reaction for primary photolysis is a first order reaction (except Cl<sup>•</sup> sensitised reactions) (Feiyan, Pehkonen, & Ray, 2002). A separate experiment was conducted (in a non flow-through system) to test if first order kinetics also applies to ethylene photooxidation with respect to initial ethylene concentration.



This experiment was conducted in a closed reactor without air flow, where a known ethylene concentration was introduced into the closed reactor and allowed to mix well. After this, the UV lamps were put on and the ethylene concentration inside the reactor was monitored with time. The experimental data from this experiments was fitted to first order reaction kinetics according to the equation  $C = C_0 e^{-kt}$ , where  $C$  is concentration (ppm) at any time  $t$ ;  $C_0$  is initial concentration (ppm);  $k$ : first order reaction constant ( $\text{min}^{-1}$ );  $t$ : time (min). A good fit ( $r^2 = 94.71\%$ ) was observed (Fig. 3). The  $k$  value obtained was  $0.056 \text{ min}^{-1}$ . Thus, considering that ethylene oxidation follows a first order reaction kinetics with respect to initial ethylene concentration, the reaction rate should be higher at higher initial ethylene concentrations.

However, even though actual amount of ethylene removed increased with increasing initial ethylene concentration; the percentage of ethylene removed compared to the initial ethylene concentration decreased. This can be observed by comparing the respective figures between percentage removal and absolute removal (Fig. 4). In Fig. 4A, as percentage ethylene removal decreased from 82 to 50% (Fig. 4[A1]) with increase in initial ethylene concentration, the actual amount of ethylene removed increased from 2 to 12 ppm (Fig. 3[A2]). These results are in accordance with previous studies by Chang, Sekiguchi, Wang, and Zhao (2013) and Yang et al. (2007). Chang et al. (2013) reported that in VUV–PCO of ethylene on increasing the initial ethylene concentration from approximately 20 to 100 ppm percentage ethylene removal decreased from 63% to 40%. However, the total amount of ethylene removed increased from ~13 ppm to 40 ppm.

The combined effect of initial ethylene concentration and flowrate on the absolute ethylene removal at a fixed lamp power was also adequately illustrated by the fitted surface plots (Fig. 4). Lowering the flow rate and simultaneously increasing the ethylene concentration increased the possibility of more ethylene molecules coming in contact with the

reactive species, resulting in higher ethylene removal. At the lowest flow rate (0.5 L/min) and highest initial ethylene concentration (30 ppm) a total 36.7% (11.12 ppm) ethylene was removed in comparison to 15.1% (0.344 ppm) at highest flow-rate (5 L/min) and lowest initial ethylene concentration (2 ppm) at fixed lamp power 6 W.

### 3.3. Effect of UV lamp power

The overall percentage ethylene removal and absolute ethylene removal was slightly higher at 6 and 9 W (Fig. 4). The presence of UV lamp is essential as in the absence of the lamp no reactive species are produced and hence there is no ethylene removed. Also, decreasing the lamp power resulted in a decreased light intensity. Since at lower intensities the number of photons emitted is less, consequently, the number of radiation generated reactive species is also small resulting in lesser ethylene removal. The reaction rate of degradation of pollutants through photooxidation (VUV or PCO) has been reported to be light intensity dependent with higher intensity favouring more pollutant degradation (Feiyan et al., 2002). Yang et al. (2007) also reported a linear decrease in the conversion of formaldehyde in VUV process with decrease in photon flux, i.e., photons generated per second per unit area.

Observing the interactive effect of process variables, it can be seen that at high flowrates changing the lamp power does not strongly affect the amount of ethylene removed compared to low flowrates. At fixed initial ethylene concentration of 30 ppm, at high flowrates >4 L/min the amount of ethylene removed has no significant change even on increasing lamp power. On the contrary, at low flowrates <1 L/min the amount of ethylene removed changed from <12 ppm at 3 W to >14 ppm at 9 W. This could be because at lower flowrate, the number of photons absorbed per unit air increased so the reactive oxygen species generated by VUV increased causing a rise in ethylene removal (Yang et al., 2007).

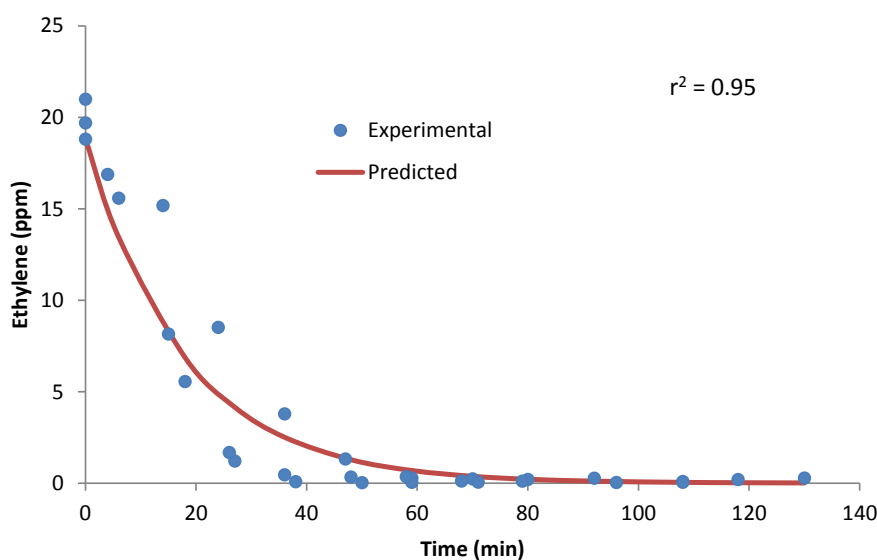
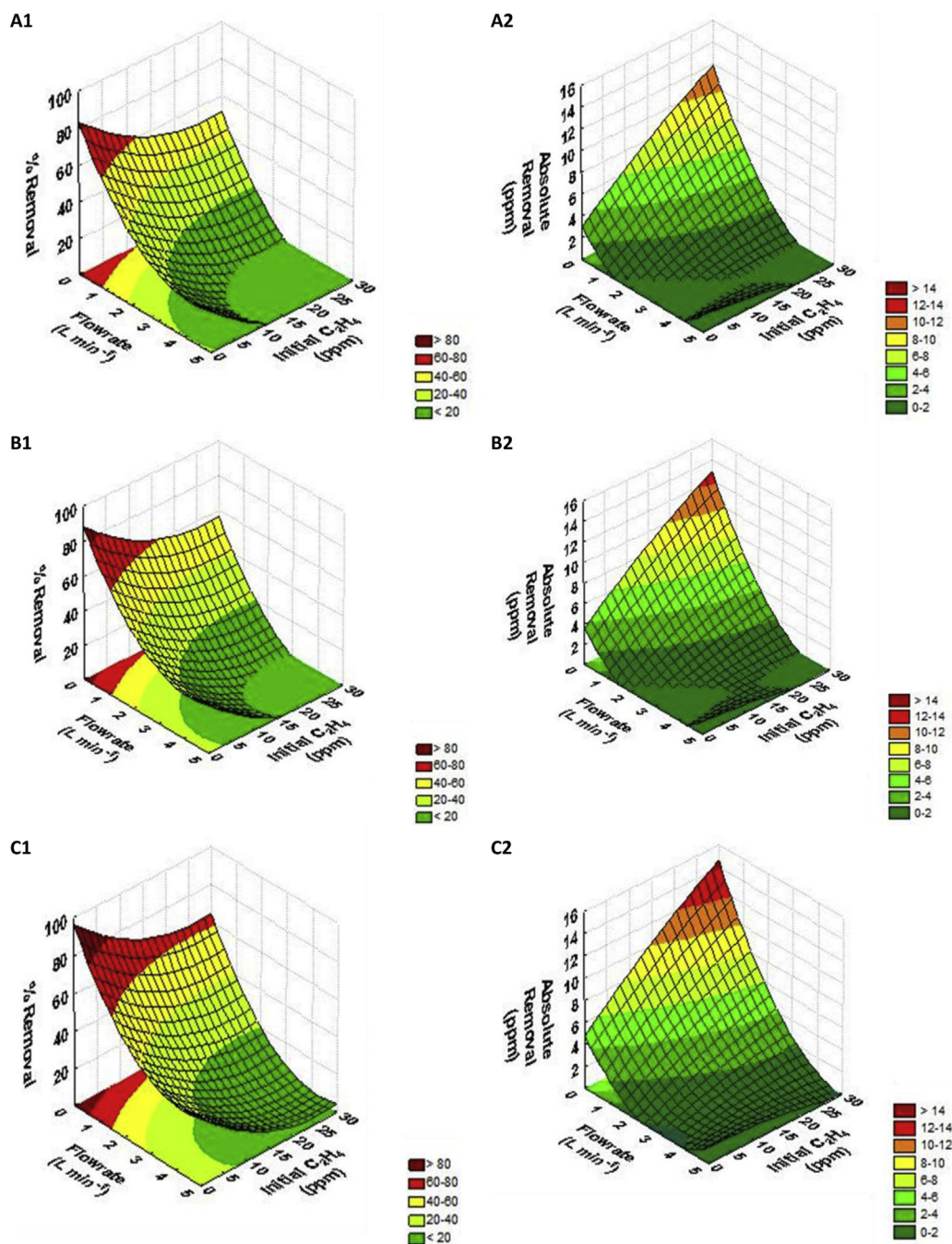


Fig. 3 – Ethylene concentration inside the closed reactor after opening the lamps (initial ethylene concentration injected  $20 \pm 1$  ppm). Dotted symbols indicate experimentally observed data and continuous line represents the predicted ethylene concentration according to the first order reaction kinetics.



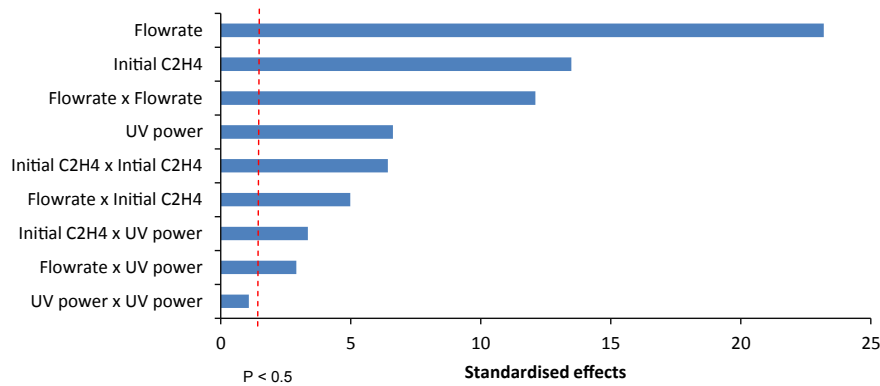
**Fig. 4** – Effect of process variables on percentage and absolute ethylene removal. Letters A, B, C denote UV lamp power at 3, 6 and 9 W respectively. Numbers 1 and 2 denote percentage and absolute ethylene removal, respectively.

Pareto analysis chart showed the effects of different process variables and their interactive effects on the percentage ethylene removed (Fig. 5). All experimental factors/process variables investigated had a significant influence on ethylene removal ( $p < 0.05$ ). Flowrate was identified to have the most dominant and significant impact on ethylene removal, followed by initial ethylene concentration and lamp power. In previous studies also these parameters have been reported to influence the photodecomposition of VOCs (Chang et al., 2013; Feiyan et al., 2002; Yang et al., 2007). The interaction between different process variables were also significant, indicating

that process variables influenced each other's effect and exert a combined effect on ethylene removal.

### 3.4. Model fitting and optimisation

Regression coefficients of the coded data as obtained are presented in Table 2. A high  $R^2$  value (0.98) obtained in this study suggests a good fit of the quadratic model to the experimental values. Furthermore, experimental data obtained was correlated to the modelled values as shown in Fig. 6. The scatter plot shows a good relationship between



**Fig. 5 – Pareto analysis showing the effect of process variables on percentage ethylene removal. Vertical line shows the t-student value at  $p = 0.05$ .**

experimental and the modelled values of ethylene removal. Thus, the developed model satisfactorily describes the percentage ethylene removal and was further used for optimisation of process variables.

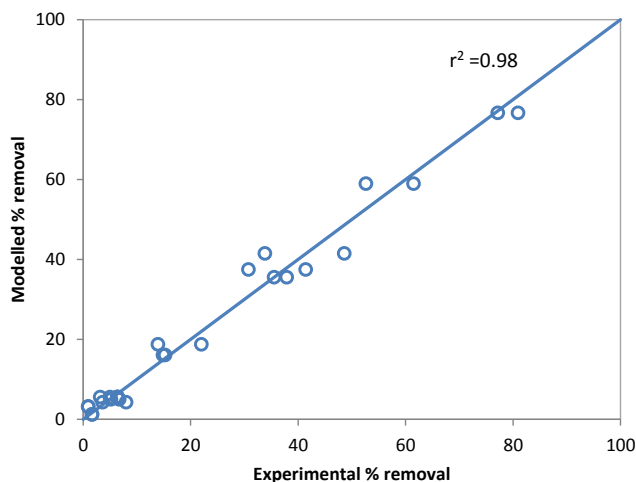
In order to optimise the process variables the initial ethylene concentration of 5 ppm was used and the following

**Table 2 – Regression coefficients (coded data) and  $R^2$  of the response surface models for percentage ethylene removal.**

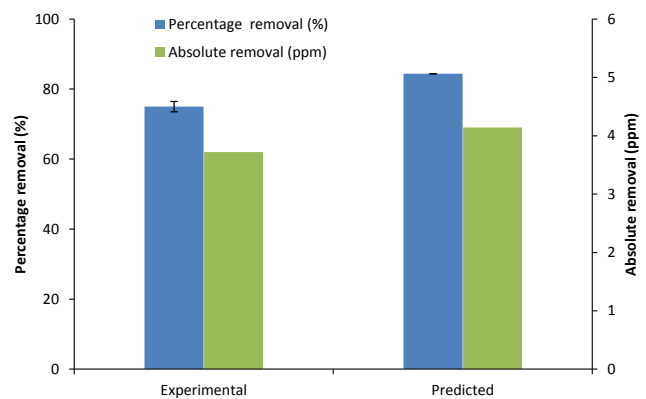
Regression coefficients	Values
$\beta_0$	5.6
$\beta_1$	−23.2
$\beta_2$	−13.5
$\beta_3$	6.6
$\beta_{11}$	17.8
$\beta_{22}$	9.5
$\beta_{33}$	1.6
$\beta_{12}$	7.1
$\beta_{13}$	−4.1
$\beta_{23}$	−4.7
$R^2$	0.98

constraints were imposed: 1) Lamp power (3–9 W) and 2) flowrate (0.5–5 L/min). This value of initial ethylene concentration was selected since the application was aimed towards storage of fruit and vegetables and <5 ppm was described as a relevant range of ethylene concentration for studies involving fruit storage applications by [Nielsen et al. \(2015\)](#). [Blanke \(2014\)](#) reported the ethylene concentration in cold storage to be 4.5 ppm. For optimisation, the Solver function in MS Excel was used which aimed at maximising percentage ethylene removal. The optimised values of the other two variables for maximum percentage ethylene removal obtained were at 0.5 L/min flowrate and 3 lamps.

For validation, independent experiment was performed at the optimised conditions namely, flowrate 0.5 L/min; lamp power 9 W and 5 ppm initial ethylene concentration. The predicted value of ethylene removal by the model was 84.7% while 76% percentage ethylene removal was obtained in the validation experiments ([Fig. 7](#)). In this study, the percentage deviation between the experimental and the theoretical value in percentage removal was 9%. This deviation could be due to the fluctuations in temperatures and humidity during the experimental period ([Supplementary Table 1](#)). Temperature and relative humidity are also known to influence the VUV photolysis of VOCs ([Chang et al., 2013](#); [Yang et al., 2007](#)). The



**Fig. 6 – Variation between the experimental and the predicted modelled values of percentage ethylene removal.**



**Fig. 7 – Validation experiment (initial ethylene concentration 5 ppm; flowrate 0.5 L/min; UV lamp power 9 W): model predicted values versus experimental values.**

VUV–PCO system developed by Chang et al. (2013) was able to achieve over 90% ethylene removal at a flowrate of 0.5 L/min and initial ethylene concentration (34 ppm). The difference between the ethylene removal (%) reported by Chang et al. (2013) and this current study could be due to different designs of the reactor in terms of geometry of reactor, positioning and type of lamp.

It can be deduced from the results that ethylene removal was higher at high initial ethylene concentration. In low ethylene systems, such as, in fruit and vegetables storage where the ethylene concentration is low (ppm to ppb), the addition of TiO<sub>2</sub> to the system (VUV–PCO) could also be explored for higher ethylene removal. Moreover, for application of VUV photolysis of ethylene in CA storage of fruits and vegetables, further experiments with the optimised system for exploring the effect of the temperature, humidity and varying oxygen concentration on the amount of ethylene removed are also needed.

### 3.5. Experimental validation with apples and kiwifruits

#### 3.5.1. Change in ethylene, O<sub>2</sub>, and CO<sub>2</sub> concentrations

The continuous change in ethylene, O<sub>2</sub> and CO<sub>2</sub> concentrations during the storage period for apples and kiwifruits is presented in Fig. 8. The humidity as measured during the storage period inside the chambers quickly saturated to 100%. Prior to switching on the UV light, ethylene was allowed to accumulate inside the storage chambers with apples for 2 h. In storage chambers with kiwifruit, a concentration of 2.5 ppm of ethylene was introduced manually into the chambers to mimic external ethylene present in supply chains. In a report by Rees, Hipps, Colgan, and Thurston (2011), ethylene concentrations were measured along the fresh produce handling chain and were reported to be in the range of 0.5–3.6 ppm, with the lowest concentration reported in retail areas and back of shop stores while highest concentration was recorded in storage facilities. The ethylene concentration inside the storage chamber connected with reactor immediately decreased as the UV lamp was on in the storage chamber and reached below 0.7 ppm for apples and <0.2 ppm for kiwifruit towards the end of storage. On the other hand, in the control chamber (not connected to reactor) for apples a continuous increase in the ethylene concentration was observed throughout the storage period. Ethylene concentration was >400 ppm at the end of day 7 for apples. Ethylene is a natural product of plant metabolism so the outcome in the control chamber with apples was quite expected showing continuous increase in ethylene with time. In the storage chambers connected to the reactor, ethylene concentration declined from 30 ppm to 0.64 ppm but was not completely removed (Fig. 8a). This observation could be attributed to a slightly higher rate of ethylene production by the apples than the rate of ethylene removal (RER) by the reactor.

The ethylene production rate by the apples was measured to be 30.5  $\mu\text{L kg}^{-1} \text{h}^{-1}$  and for 0.7 kg of apples, the calculated ethylene production was about 21.35  $\mu\text{L h}^{-1}$  or 0.355  $\mu\text{L min}^{-1}$ . The RER ( $\mu\text{L min}^{-1}$ ) was calculated as:

$$\text{RER} = \dot{Q}(C_{\text{in}} - C_{\text{out}}) \quad (3)$$

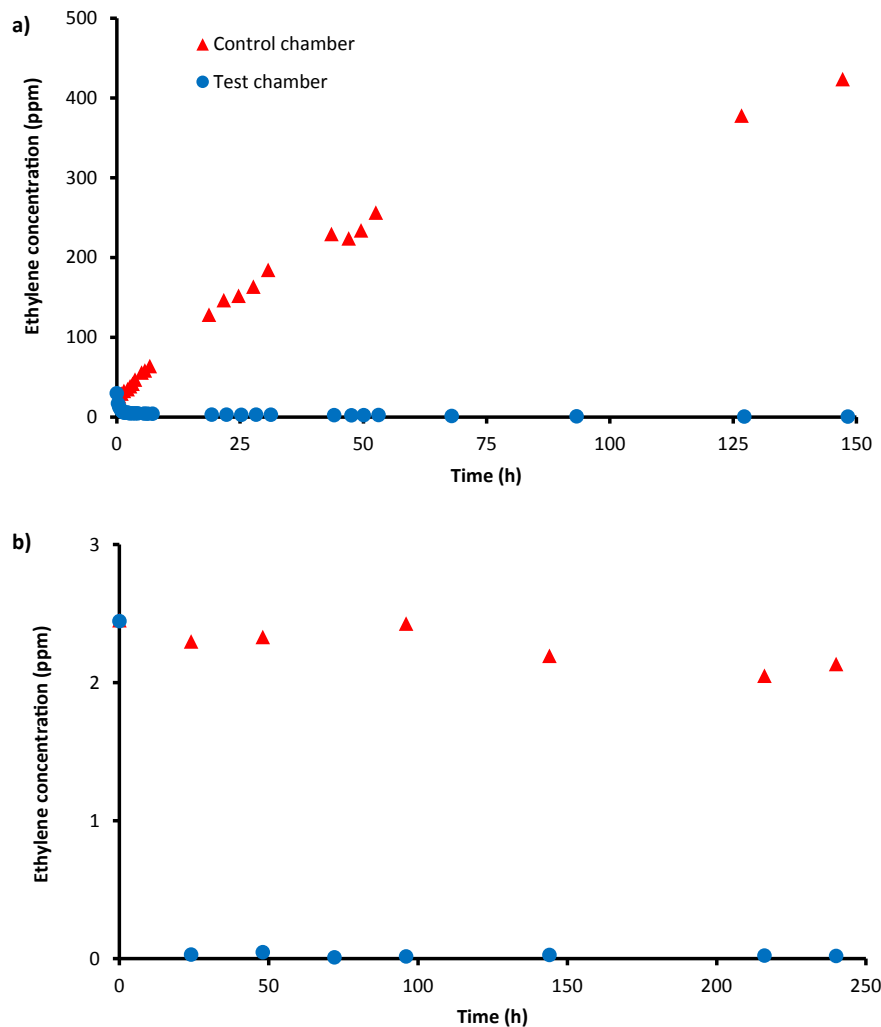
where  $\dot{Q}$  is the flowrate (L/min);  $C_{\text{in}}$  is the ethylene concentration at the inlet (ppm); and  $C_{\text{out}}$  is the ethylene concentration at the outlet (ppm) after equilibrium was established (Nielsen et al., 2015).

The absolute amount of ethylene removed by the reactor ( $C_{\text{in}} - C_{\text{out}}$ ) was dependent on initial ethylene concentration and was higher at high initial ethylene concentration (Section 3.2), therefore, the RER by the reactor should also be higher at high initial ethylene concentration for same flowrate and lamp power. This can be explained by quantifying the RER by the reactor at different initial ethylene concentrations. At 30 ppm initial ethylene concentration (0.5 L/min flow rate; 9 W lamp power), the RER was calculated using Eq. (3) as 6.47  $\mu\text{L min}^{-1}$  whereas at 5 ppm initial ethylene concentration it was 1.85  $\mu\text{L min}^{-1}$  (based on validation experiment data). Over the storage period, the ethylene concentration reached to 0.6 ppm. At this concentration, the calculated RER was 0.245  $\mu\text{L min}^{-1}$  which was less than the rate of ethylene production by the apples (0.355  $\mu\text{L min}^{-1}$ ). Hence, when low ethylene concentration was achieved in the chamber, the ethylene removal rate decreased than the ethylene production rate by apples. Therefore, ethylene concentration did not reach zero even at the end of 7 days. This can be observed in Fig. 8 where the ethylene was removed rapidly in the beginning in the test chamber but later the removal rate slowed down. This observation corroborates the findings reported by Chang et al. (2013) and Yang et al. (2007) that the initial ethylene concentration has a significant impact on ethylene decomposition.

In the case of kiwifruit, which had an initial induction of ethylene (2.5 ppm) at the start of the experiment, the ethylene concentration remained > 2 ppm at the end of storage in the control (Fig. 8b). In contrast, storage chamber connected to the reactor, ethylene concentration dropped to <0.2 ppm in the first 24 h and remained <0.2 ppm until the end of storage period. Kiwifruits have been classified as climacteric fruit as their ripening is accompanied with a period of autocatalytic ethylene production (Pratt & Reid, 1974). However, unlike other climacteric fruits in kiwifruits, the ethylene production occurs only after they are full ripe (Antunes, Pateraki, Kanellis, & Sfakiotakis, 2000). Unripe kiwifruit has a very ethylene low production rate (Less than 0.1  $\mu\text{L/kg h}$  at 0 °C; 0.1–0.5  $\mu\text{L/kg h}$  at 20 °C) (Crisosto, Mitcham, & Kader, 1996). Therefore, the ethylene in the control chamber with unripe kiwifruits did not increase at all, and samples stored in storage chamber connected to the reactor remained relatively below 0.2 ppm.

The concentrations of O<sub>2</sub> and CO<sub>2</sub> declined continuously during the storage for apples and kiwifruits (Fig. 9). The O<sub>2</sub> concentration decreased with a corresponding increase in CO<sub>2</sub> concentration in both test and control chamber. However, the rate of decline in O<sub>2</sub> and increase in CO<sub>2</sub> concentration was higher in the control chamber compared to the chambers connected to the reactor. Ethylene accelerates ripening and induces respiratory burst of CO<sub>2</sub> production in climacteric fruits (Zagory, 1995). Kiwifruits displayed high sensitivity to ethylene, which was evident in the higher CO<sub>2</sub> production as observed in this current study in the control chamber (Fig. 9b). This result is consistent with literature where application of ethylene has been associated with





**Fig. 8 – Change in ethylene concentration over time in storage chamber connected with (Test chamber) and without ethylene reactor (Control chamber): (a) Storage chamber with apples stored at 10 °C for 7 days and (b) chamber with kiwifruits stored at 15 °C for 10 days.**

increased respiration rate (Agar, Biasi, & Mitcham, 1999; Fugate, Suttle, & Campbell, 2010).

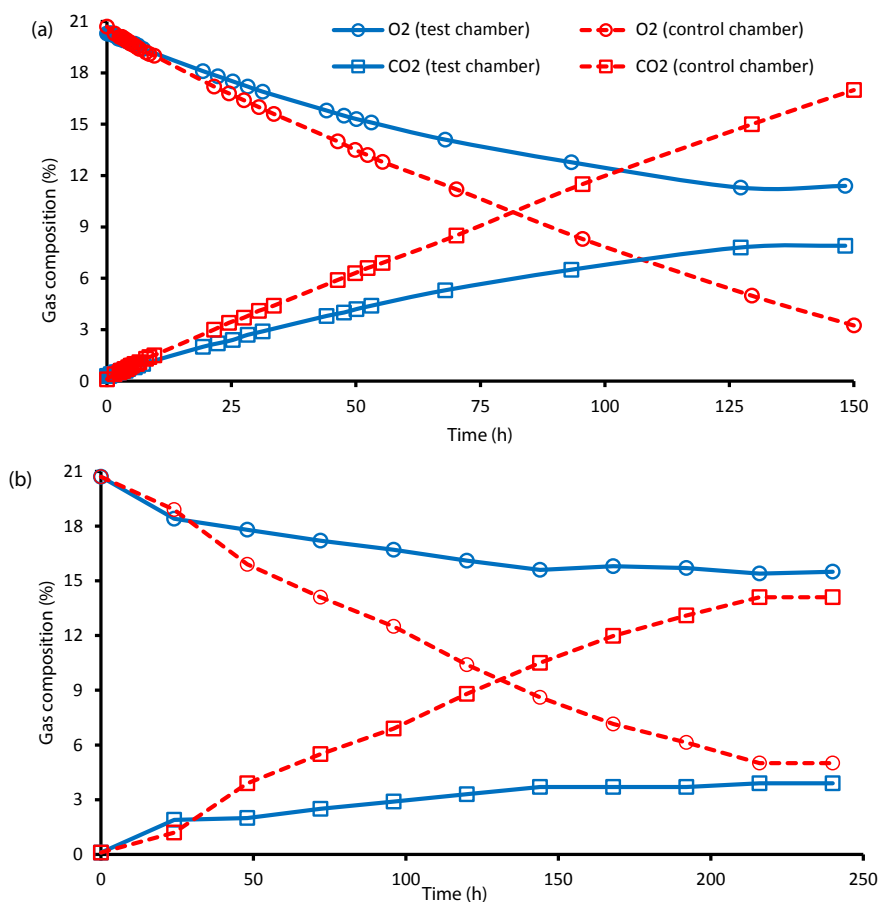
### 3.5.2. Change in quality attributes

Storage treatments had no significant ( $p > 0.05$ ) impact on the SSC and TTA concentrations for both apples and kiwifruits. For apples the SSC and TTA concentration were within the range of 12.9–13.8% and 0.51–0.64 g 100 mL<sup>-1</sup>, respectively, while, kiwifruits ranged from 13.4 to 13.6% and 0.8–1.2 g 100 mL<sup>-1</sup>, for SSC and TTA concentrations, respectively. Limited changes observed for these quality parameters could be due to the short-term storage period. A slight increase in SSC and decrease in acidity was observed in the control treatment for kiwifruits. However, the storage treatments had a significant effect on softness/tissue strength of kiwifruits ( $p < 0.05$ ). The measured tissue strength declined from initial  $38.5 \pm 5.9$  N on day 0 (prior to storage) to  $20.1 \pm 0.9$  N and  $10.3 \pm 3.5$  N, for samples stored connected with and without the reactor, respectively, after day 10. Kiwifruit response to ethylene has been shown to increase fruit softening (Lallu, Searle, & Macrae, 1989; Park, Jung, & Gorinstein, 2006). In addition, the gradual

softening or loss of firmness for kiwifruits in storage chamber connected with the reactor could be attributed to increased sensitivity to low endogenous ethylene. Kiwifruit is very susceptible to ethylene, even at concentration as low as 0.1  $\mu\text{L L}^{-1}$  at 0 °C fruit softening can be induced (McDonald & Harman, 1982). Therefore, it is critically important that ethylene is reduced or scrubbed to zero concentration in order to extend storage life. The use of PCO reactor under VUV irradiation helped in slowing down the ripening of kiwifruit by removal of ethylene.

## 4. Conclusion

In this study, the response surface methodology along with BB design was applied to determine the effect of flowrate, UV lamp power and initial ethylene concentration. Flow rate was observed to have the most significant effect on the amount of ethylene removed followed by initial ethylene concentration and the lamp power. The combined effect of various process parameters exerted a significant effect ( $p < 0.5$ ) on percentage



**Fig. 9 – Change in gas composition in storage chamber connected with (test chamber) and without ethylene reactor (control chamber): (a) Storage chamber with apples stored at 10 °C for 7 days and (b) chamber with kiwifruits stored at 15 °C for 10 days.**

ethylene removal. In general, reducing the flowrate, increasing the lamp power and the initial ethylene concentration led to an increase in ethylene removal. The model showed a good fit to the data. At an initial ethylene concentration of 5 ppm, the optimised conditions were obtained as lamp power 9 W and flowrate 0.5 L/min. The ethylene removal was observed to be 76% at the optimised conditions. Furthermore, this study showed the potential of photooxidation reactor via VUV irradiation as a good alternative for ethylene removal in storage based on the case study of apples and kiwifruits. The VUV reactor effectively reduced the ethylene concentration in the storage chambers of apples and kiwifruits. In high ethylene producing commodities such as apples the RER by the reactor versus the rate of ethylene production of the commodity played an important role. Thus, the use of appropriate number of reactors in the storage space according to the commodity can aid in effective ethylene removal. Future studies on impact of other variables such as temperature, humidity and different oxygen concentration (in modified and CA storages) could be valuable for fruit storage applications. In addition, the reactor had lower efficiency in the removal of ethylene when the initial concentration was low. Further studies based on the

combination of VUV with other oxidation processes could be investigated for total ethylene removal. This include approaches such as VUV photolysis-ozone catalytic oxidation combination, and/or PCO under VUV irradiation, which involves the use of a catalyst e.g. TiO<sub>2</sub> along with VUV light.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.biosystemseng.2017.04.008>.

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## **5. Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions**

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# Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions

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Fruit and vegetables

## ABSTRACT

Most fresh horticultural commodities are highly perishable and ethylene often plays an important role in their ripening and senescence process. Reduction of ethylene concentrations around these commodities may lead to the slowing down of metabolic processes, which could potentially extend their storage or shelf life. The objective of this work was to investigate photocatalytic oxidation (PCO) and vacuum ultraviolet light (VUV) photolysis for ethylene removal in fruit storage. The efficacy of both techniques for ethylene removal was analyzed under different storage conditions (initial ethylene concentration, oxygen, relative humidity and temperature). Ethylene removal in VUV photolysis was much faster than PCO with the reaction mechanism followed by Langmuir-Hinshelwood and first-order equations, respectively. Higher O<sub>2</sub> concentration in the reactor favored both ethylene removal processes. However, high relative humidity impeded PCO and enhanced VUV photolysis efficacy of ethylene oxidation. Lowering the temperature from 21 °C to 1 °C showed no consistent trend of temperature effects on ethylene removal in the PCO process, whereas in VUV photolysis, reducing the temperature decreased ethylene removal significantly ( $p \leq 0.05$ ). Ethylene removal in a gas stream with a single pass through VUV photolysis reactor was 84.8% whereas it was only 14.9% in PCO reactor. Apple storage revealed that the ethylene concentration increased to 70  $\mu\text{L L}^{-1}$  in 8 days at 1 °C. This concentration was brought down to 24 and 2.6  $\mu\text{L L}^{-1}$  in storage chambers connected to PCO and VUV reactors, respectively. Further research efforts are needed to improve the performance of the reactors for the complete removal of ethylene in postharvest storage of fresh produce.

## 1. Introduction

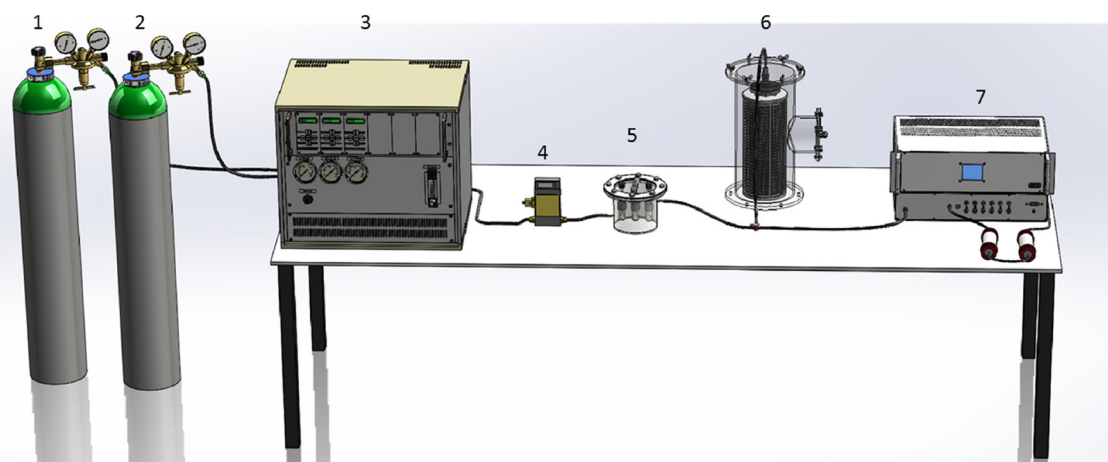
Most fresh fruit and vegetables are highly perishable commodities and for the products to reach the consumer in good quality it is often essential to slow down ethylene-induced ripening in the supply chain. Ethylene has been known to play a pivotal role in accelerating ripening and senescence in fresh produce (Saltveit, 1999). The benefits of reducing ethylene levels in slowing down ripening and senescence, and increase in shelf life of some climacteric and non-climacteric horticultural commodities have been widely studied (Ku et al., 1999; Wills et al., 2001; Pathak et al., 2017c). Therefore, ethylene management is of importance along the supply chain. Generally, most fruit handling companies and storage facilities rely on various traditional methods such as air ventilation, the use of ethylene adsorbers and oxidizers, or the use of air filtration equipment based on catalytic oxidation/ photocatalysis and ozone generators (Wills, 2015; Martínez-Romero et al.,

2007; Zagory, 1995).

The suitability of a method for ethylene management depends on the type of storage and product. For instance, in packaged fresh produce ethylene adsorbent/absorbent-packages, -sachets, -sheets and/or -pads could be used. These materials may include, potassium permanganate, activated carbons, clay, zeolite and palladium based scrubbing material (Álvarez-Hernández et al., 2018; Terry et al., 2007). They suffer limitations in terms of the absorption/adsorption capacity as over time they may get saturated and require replacement, which may not be ideal in case of long-term storage and distant shipping (Martínez-Romero et al., 2007; Pathak et al., 2017a). Air ventilation can be an inexpensive technique, however, it is not suitable for all regions due to unsuitable environmental conditions and cannot be applied in case of controlled atmosphere storage (Thompson, 1998). For continuous ethylene removal in closed storage units there are equipment available, such as, ozone generators and filtration units based on catalytic

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**Fig. 1.** Schematic of the experimental setup used for studying ethylene removal in photocatalytic (PCO) and photolysis (VUV) reactor. 1 - Synthetic air cylinder, 2 - ethylene cylinder, 3 - Gas mixer, 4 - Flow controller, 5 - Reactor (PCO/VUV), 6 - Activated carbon for ozone absorption (only in case of VUV reactor), 7 - Ethylene detector.

oxidation/photocatalysis (Keller et al., 2013; Martínez-Romero et al., 2009). In usage of ozone generators, it is important to control ozone concentrations, as ozone is hazardous to human health and recommended exposure limit is  $0.1 \mu\text{L L}^{-1}$  for 8 h by United States occupational safety and health administration (US-OSHA). Similarly, high concentrations of ozone can also cause injury in plant tissues (Smilanick, 2003). The catalytic oxidation based filters require high temperatures as oxidation of ethylene occurs at temperatures above  $100^\circ\text{C}$  (El Blidi et al., 1993).

Photocatalytic oxidation (PCO) is another technique that can be used for ethylene removal. It is based on the use of ultraviolet light and catalysts, such as titanium dioxide ( $\text{TiO}_2$ ), which is most popularly used. The technique can be described in principle as a 'green' technique as it does not leave behind any residue (Gonzalez et al., 1999). Ethylene is oxidized into carbon dioxide ( $\text{CO}_2$ ) and water in a complete oxidation reaction. The application of photocatalytic oxidation has been widely studied for the removal of volatile organic compounds in gaseous as well as aqueous state (Ibhadon and Fitzpatrick, 2013). There is also an emerging research on development of PCO for ethylene removal in fruit and vegetables storage rooms (Maneerat and Hayata, 2006; de Chiara et al., 2015; Hussain et al., 2011a; Nielsen et al., 2015). Another technique reported in literature for removal of ethylene is vacuum ultraviolet light photolysis (VUV), which is based on the use of shortwave ( $\approx 185 \text{ nm}$ ) UV irradiation. The potential of this technique to oxidize ethylene has been demonstrated using lab scale reactors (Pathak et al., 2017b, c; Scott and Wills, 1973). The lab scale reactor developed by Pathak et al. (2017b) displayed an ethylene removal efficiency of 76% in a flow through system in which  $5 \mu\text{L L}^{-1}$  ethylene concentration was supplied at a flow rate of  $0.5 \text{ L min}^{-1}$ . Additionally, the reactor was able to reduce ethylene concentration to  $1.8 \mu\text{L L}^{-1}$  inside a storage chamber consisting of mixed fruits (apple, banana, kiwifruit) stored at  $15^\circ\text{C}$  for 10 d, while under same conditions the control storage chamber had  $90 \mu\text{L L}^{-1}$  of ethylene accumulation (Pathak et al., 2017c).

Both PCO and VUV photolysis have some similarities in the working principles as reactive oxygen species (ROS) are generated in both techniques that eventually oxidize ethylene. In PCO, on irradiation with ultraviolet light electron-hole pair generation takes place on the catalyst surface that react with surface adsorbed oxygen and water molecules to produce ROS. On the other hand, in VUV photolysis, oxygen and water molecules in gaseous state are dissociated under VUV irradiation to produce reactive oxygen species. In spite of the similarities, the overall working and efficiency of both processes in oxidation of gaseous impurities is different (Jiang et al., 2015). The objectives of this study were to investigate the efficacy (the performance) of the two

techniques (PCO and VUV photolysis) in terms of the amount and rate of ethylene removal; and to assess their potential for application in actual fruit storage. To understand the ethylene removal efficiency of these two techniques, experiments were conducted at varying ethylene concentrations  $2 \mu\text{L L}^{-1}$  to  $35 \mu\text{L L}^{-1}$  and the kinetics of the two techniques was analyzed.

In addition, storage of fruit and vegetable requires optimum refrigerated conditions, modified or controlled atmosphere with low  $\text{O}_2$  and/or high  $\text{CO}_2$ , which are well established and commercially adopted (Watkins, 2016; Gross et al., 2016). These conditions involve low temperature, high relative humidity (RH), low  $\text{O}_2$  and high  $\text{CO}_2$  atmospheres, which vary depending on the type and condition of fresh produce. Thus, for application of ethylene removal techniques in fruit storage, it is important to evaluate the performance of the ethylene removal techniques under similar storage conditions. Hence, another objective in this study was to investigate the efficiency of PCO and VUV photolysis in the removal of ethylene under different storage conditions: temperatures ( $0, 6, 14$ , and  $21^\circ\text{C}$ ), and  $\text{O}_2$  concentrations (low and high) and RH (low and high). A case study experiment based on the application of PCO and VUV photolysis techniques to assess ethylene removal in apple storage at  $1^\circ\text{C}$  was also conducted.

## 2. Materials and method

### 2.1. Photocatalytic and photolysis reactor

Two steel reactors (diameter 12 cm, height = 11 cm each) developed in-house (Fig. 1), were used to carry out the experiments for PCO and VUV photolysis experiments, respectively. The PCO reactor consisted of three UV lamps (3 W each) irradiating at 254 nm and  $\text{TiO}_2$ -coated glass slides, while, the VUV photolysis reactor consisted of three UV lamps (3 W each) with irradiation at 254 nm and also a small percent at 185 nm. Lamps were supplied by Dinies (Germany). No  $\text{TiO}_2$ -coated plates were used for VUV photolysis. The lid of both reactors was provided with a rubber septum for gas sampling and electrical fittings for the UV lamps as well as temperature and humidity sensors (FHA 646-R, Ahlborn, Holzkirchen, Germany). The instrumental error of sensors is  $\pm 0.1 \text{ K}$  for temperature, and  $\pm 2\%$  for relative humidity. To enable flushing of the reactor with a gas of desired concentration, inlet and outlet ports were provided on diagonally opposite sides of the reactor.

### 2.2. Optimizing $\text{TiO}_2$ coated area

To carry out the PCO reactions, titanium dioxide ( $\text{TiO}_2$ ) Degussa

P25 based FN3 solution (Advanced Materials, Kamenne Zehrovice, Czech Republic) was used as a catalyst. Titanium dioxide was chosen as a photocatalyst as it is a low cost, stable, and biologically and chemically inert (Nakata et al., 2012). Glass slides (76 × 26 mm) were used as a support for TiO<sub>2</sub> as glass is low cost and inert. Glass slides were dipped into FN3 solution and then dried in an oven at 50 °C for 1 h. The procedure was repeated one more time to obtain a two-layered coating on the glass slides. Advantages of coating the catalyst onto a support are better light distribution and reduction in hydrodynamic pressure problems which may arise in using unsupported particulate catalyst (Zorn et al., 2000; de Chiara et al., 2014). To optimize the TiO<sub>2</sub> coated area in PCO reactions, experiments were performed in a closed steel reactor with fixed initial ethylene concentration (5 μL L<sup>-1</sup>) and varying surface areas of TiO<sub>2</sub>, 59.3, 177.8 and 296.4 cm<sup>2</sup>, obtained by changing the number of TiO<sub>2</sub>-coated glass slides (cm<sup>2</sup>/slide). Lamps were switched on once stable initial ethylene concentration inside the reactor was attained. To avoid any discrepancy in the results due to possible catalyst deactivation only freshly TiO<sub>2</sub>-coated glass slides were used in subsequent experiments.

### 2.3. Experiments at different initial ethylene concentrations

Ethylene production rates in fresh produce varies greatly and may range from very high (> 100 μL kg<sup>-1</sup> h<sup>-1</sup>) in passion fruit; high (10–100 μL kg<sup>-1</sup> h<sup>-1</sup>) in apples, pear, avocado; intermediate (1–10 μL kg<sup>-1</sup> h<sup>-1</sup>) in bananas, fig, tomato; low (< 10 μL kg<sup>-1</sup> h<sup>-1</sup>) in strawberries to very low (< 1 μL kg<sup>-1</sup> h<sup>-1</sup>) in carrots and citrus fruits (Blanke, 2014; Saltveit, 1999). Thus, ethylene accumulation inside a closed storage chamber may vary depending on the type and amount of product, storage conditions and on the dimensions of the storage room. Therefore, the performance of the two ethylene removal processes was studied at different initial ethylene concentrations (2, 5, 10, 22, 35 μL L<sup>-1</sup>) at room temperature (21 °C) and RH < 10%. A static system (closed reactor) was used and the PCO and VUV photolysis were carried out simultaneously in two different reactors. Before carrying out any experiment, the reactors (with or without TiO<sub>2</sub>-coated glass plates) were flushed for 20 min with compressed air (20.5 ± 0.5% O<sub>2</sub> in N<sub>2</sub>, Air Liquide, Berlin, Germany) to remove any impurities or gaseous products remaining from previous experiments.

In order to create different initial ethylene concentrations, calculated amount of ethylene with a concentration of 10 and 100 μL L<sup>-1</sup> was injected into the reactors using a syringe of 5 mL capacity. Ethylene concentration was verified by drawing gas samples (5 mL) from the rubber septum provided in the lid of the reactor. A photoacoustic system based ethylene detector, ETD-300 (Sensor sense, Nijmegen, The Netherlands), which has a detection limit of 0.3 nL L<sup>-1</sup> with a time resolution of 5 s, was used for analyzing the gas samples for ethylene measurements. The ethylene detector was operated in sample mode under a continuous supply of air flow at a flowrate of 0.04 L min<sup>-1</sup>. When the ethylene concentration reached equilibrium inside the reactor, the lamps were switched on. Ethylene concentration were measured at regular intervals till the concentration decreased to < 0.04 μL L<sup>-1</sup>.

### 2.4. Kinetics

#### 2.4.1. Photocatalytic oxidation (PCO)

In PCO kinetic studies, Langmuir-Hinshelwood (L-H) equations are widely accepted (Yamazaki et al., 1999; Ibhaden et al., 2007) as they encompass various steps in a PCO process including absorption of the compound on the catalyst surface (Debono et al., 2017). In a basic L-H equation the reaction rate (R) is proportional to the surface coverage by the reactant, θ (Ibhaden et al., 2007) and R is a function of initial concentration of reactant (C) as described in equation below:

$$R = \frac{dC}{dt} = k\theta = \frac{kKC}{1 + KC} \quad (1)$$

where  $k$  is the reaction rate constant (min<sup>-1</sup>),  $K$  is the adsorption coefficient of the reactant (μL L<sup>-1</sup>) and  $C$  is the reactant concentration (μL L<sup>-1</sup>) and  $t$  is time (min). When reactant concentration is low, the term  $KC$  can be neglected and Eq. (1) can be described as a pseudo first order reaction as shown below:

$$R = k'C \quad (2)$$

where  $k'$  is the apparent first order kinetic constant (min<sup>-1</sup>). It is the rate constant for pseudo first order reaction to describe later part of the ethylene degradation curves when ethylene concentration becomes very small (Batault et al., 2017). Few studies have reported PCO reactions following pseudo first order kinetics (Ye et al., 2013; Batault et al., 2017). Ethylene oxidation using a plasma photocatalytic process was described as a first order reaction by Ye et al. (2013). Contrastingly, Batault et al. (2017) reported a good fit of L-H equation for PCO degradation of toluene compared to first order kinetics. The following analytical solution to Eq. (1), obtained by integrating Eq. (1) was used in their study for fitting experimental data.

$$t = A \cdot \left[ B(C - C_0) + \ln \frac{C}{C_0} \right] \quad (3)$$

where  $C_0$  is initial ethylene concentration (μL L<sup>-1</sup>), and  $A$  (min) and  $B$  (μL L<sup>-1</sup>)<sup>-1</sup> are kinetic descriptors.

Eq. (3) relates the time  $t$  (min) needed for the reactant degradation to the concentration  $C$  (μL L<sup>-1</sup>). In the present study, the ethylene degradation data was fitted to L-H equation using the same analytical solution Eq. (3). The constants,  $C_0$ ,  $A$  and  $B$  were estimated from the least squares regression fitting (Solver function, Microsoft Excel) and are shown in Table 1.

From the estimated values ( $C_0$ ,  $A$  and  $B$ ), the initial reaction rate ( $R_0$ ) and the apparent first order kinetic constant ( $k'$ ) were calculated. As initial reaction rate is the instantaneous reaction rate at the start of the reaction ( $t = 0$ ),  $R_0$  (μL L<sup>-1</sup> min<sup>-1</sup>) was determined at  $t = 0$  and  $C = C_0$  using Eq. (4).

$$R_0 = -\frac{1}{A} \cdot \frac{C_0}{1 + B \cdot C_0} \quad (4)$$

When concentration becomes very low, term ( $B \cdot C_0$ ) in Eq. (4) can be neglected, thus

$$R_0 = -\frac{1}{A} \cdot C_0 \quad (5)$$

The above equation becomes a first order reaction which can be represented by the general equation Eq. (2). Comparing Eqs. (2) and (5),  $k'$  (min<sup>-1</sup>), the apparent first order kinetic constant, is calculated as  $-1/A$ .

**Table 1**

Reaction kinetic descriptors of the Langmuir-Hinshelwood model applied to photocatalytic oxidation (PCO).

Initial ethylene concentration, $C_0$ (μL L <sup>-1</sup> )	Estimated coefficients and reaction rates <sup>a</sup>			
	A (min)	B (μL L <sup>-1</sup> ) <sup>-1</sup>	$R_0$ (μL L <sup>-1</sup> min <sup>-1</sup> )	$k'$ (min <sup>-1</sup> )
2.1	-7.28	0.44	0.15	0.14
6.6	-7.64	0.18	0.38	0.13
11.2	-16.68	0.02	0.55	0.06
22.3	-7.73	0.04	1.53	0.13
36.6	-50.00	-0.02	4.53	0.02

<sup>a</sup> A and B: Kinetic constants;  $R_0$ : Initial reaction rate;  $k'$ : Apparent first order kinetic constant.

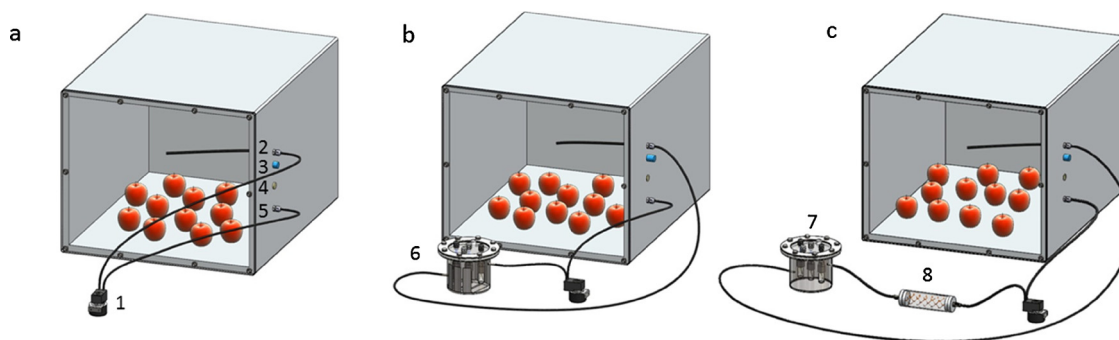


Fig. 2. Experimental setup for fruit storage. a) Control chamber, b) Photocatalytic oxidation (PCO) chamber, c) Vacuum ultraviolet light (VUV) photolysis chamber. 1- pump, 2 -inlet, 3 - temperature/humidity sensors, 4 -rubber septum, 5 -outlet, 6 - PCO reactor, 7 - VUV photolysis reactor and 8-ozone filter.

#### 2.4.2. Vacuum ultraviolet light (VUV) photolysis

Primary photolysis has been generally found to follow the first order kinetics (Feiyan et al., 2002) and was described by the following equation;

$$C = C_0 e^{-kt} \quad (6)$$

where  $C$  is reactant concentration ( $\mu\text{L L}^{-1}$ ) at any time ( $t$ , min),  $C_0$  is initial concentration ( $\mu\text{L L}^{-1}$ ), and,  $k$  is first order reaction constant ( $\text{min}^{-1}$ ). The ethylene degradation curves were fitted to first order equation using Eq. (6) and  $k$  was determined using solver function in Microsoft excel. Initial reaction rate,  $R_0$  ( $\mu\text{L L}^{-1} \text{min}^{-1}$ ) was determined by integrating Eq. (6) at initial conditions,  $C = C_0$  and  $t = 0$ .

$$R_0 = kC_0 \quad (7)$$

#### 2.5. Experiments at different storage conditions

First set of experiments were aimed at understanding the role of different storage temperature (0, 6, 14, and 21 °C) and duration of irradiation time on the efficacy of the PCO and VUV techniques. These experiments were conducted simultaneously in the PCO and VUV photolysis batch reactors. The experimental procedure followed was similar to as described in Section 2.3. The initial ethylene concentration injected into the reactors was fixed at  $10 \mu\text{L L}^{-1}$ . The temperature was varied (0, 6, 14, and 21 °C) whereas RH and  $\text{O}_2$  concentration were kept constant at 10% and 21%, respectively. The RH and temperature inside the reactor was monitored over time using data logger specifications given in Section 2.1.

The second sets of experiments were conducted to determine the effects of RH and  $\text{O}_2$  concentrations. The experimental conditions were RH [low ( $10.7 \pm 1.8\%$ )/ high ( $84.9 \pm 6\%$ )] and  $\text{O}_2$  concentration [low ( $0.67 \pm 0.16\%$ )/ high ( $20.8 \pm 0.08\%$ )] at 21 °C. All experiments were conducted inside a temperature controlled room and at fixed initial ethylene concentration of  $10 \mu\text{L L}^{-1}$ . Both reactors (PCO and VUV) were initially flushed with a gas of desired  $\text{O}_2$  concentration obtained by mixing nitrogen (99%) and compressed air ( $20.5 \pm 0.5\% \text{O}_2$ ) supplied by Air liquid, Berlin Germany. The mixed gas stream was passed through water or silica gel before entering the reactor in order to get desired RH levels. After obtaining desired RH and  $\text{O}_2$  concentration, the inlet and the outlet of the reactors were closed and further procedure similar to Section 2.3 was followed.  $\text{O}_2$  concentrations were measured using a gas analyser (Checkmate 3, PBI Dansensor, Ringsted, Denmark). For the second set of experiments, half time of the reaction was determined based on data obtained from continuous measurements. Half time of the reaction is described as the time taken for a reaction to reach half completion i.e. for the initial reactant concentration to reduce to 50% was determined (Wharton and Szawelski, 1982).

#### 2.6. Experiments with PCO and VUV reactors in actual storage chamber

##### 2.6.1. Single pass – flow through system

Prior to testing the reactors in an actual storage, the amount of ethylene removed in a single pass through the reactor was experimentally measured. An annotated diagram of the experimental setup that was used for this investigation is shown in Fig. 1. Air with desired ethylene concentration was continuously flushed ( $0.24 \text{ L min}^{-1}$ ) through the reactor. The desired ethylene concentration was obtained by mixing ethylene from ethylene standard,  $9.88 \pm 0.20 \mu\text{L L}^{-1}$  or  $105.3 \pm 2.1 \mu\text{L L}^{-1}$  and rest synthetic air (Air Liquide, Berlin, Germany).

The ethylene concentrations at the outlet of the reactor were continuously measured using ETD-300 (in continuous mode) and recorded. Once a stable ethylene concentration was established at the outlet, the lamps were switched on. The percentage ethylene removal (PER) was calculated as percentage of the initial stable ethylene concentration,  $C_i$  (before switching on the lamps) and final stable ethylene concentration,  $C_e$  (after switching on the lamps).

$$PER = \frac{C_i - C_e}{C_i} \times 100 \quad (8)$$

##### 2.6.2. Storage chamber test with apples

Storage with apples was carried out for a short storage period of 8 d to evaluate the effectiveness of PCO and VUV ethylene removal processes. Storage experiments were carried out using air-tight chambers (190 L each) housed in a walk-in cold room set at 1 °C. Apples ‘Gala’ harvested from the experimental farm (Marquart, Potsdam, Germany) were stored inside each of the chambers (6 kg per chamber). The VUV and PCO reactors were connected separately to two of the storage chambers via pre-fitted inlets, while the third chamber served as control. The storage chamber connected to PCO is hereafter referred to as PCO chamber while the chamber connected to VUV reactor is referred to as VUV chamber. A schematic of reactors connected to the respective storage chambers is shown in Fig. 2. All chambers had an external pump connecting the inlet and outlet of the chamber to make a closed air circulation loop in each chamber. Another inlet was fitted with a rubber septum to facilitate air sampling for ethylene,  $\text{O}_2$  and  $\text{CO}_2$  measurements.  $\text{O}_2$  and  $\text{CO}_2$  concentrations were regularly monitored using a gas analyser (Checkmate 3, PBI Dansensor, Ringsted, Denmark) throughout the storage period. The pressure differences due to temperature fluctuations and sampling of air was not taken into account.

Respiration rate (RR) and ethylene production rate were measured at 1 °C and under normal atmospheric conditions before and after storage of fruits using a closed system. Other quality aspects were not measured, because of short storage period and focus was on ethylene removal. RR was measured using an in-house developed respirometer consisting of 9 acrylic glass cuvettes (Rux et al., 2017). Each cuvette consists of a non-dispersive infra-red  $\text{CO}_2$  sensor (GMP222, Vaisala



GmbH, Bonn, Germany), with a measuring capacity up to  $5000 \mu\text{L L}^{-1}$  of  $\text{CO}_2$ . Twelve apples were randomly selected from each storage chamber and distributed equally in three cuvettes.  $\text{CO}_2$  production was recorded over a period of six hours and RR was calculated and expressed in  $\text{nmol kg}^{-1} \text{s}^{-1}$ .

For ethylene production rate, nine apples were randomly selected from each storage treatment chamber, and divided into batches (three apples per batch). Each batch was placed inside hermetically sealed small steel chambers (2.5 L). Air samples from the chambers were periodically drawn using a syringe from the rubber septum provided on top of the lid of chambers and analyzed for ethylene concentration. Ethylene production rate was calculated as the amount of ethylene produced per unit time per unit mass of the fruit ( $\text{nmol kg}^{-1} \text{s}^{-1}$ ).

## 2.7. Statistical analysis

Factorial experimental designs were used in this study. The effects of total surface area exposed to  $\text{TiO}_2$  and duration (exposure time or the irradiation time), and of their interactions were investigated on ethylene removal (%). In another experimental setup, the efficacy of ethylene removal systems as function of the storage temperature (0, 6, 14, and  $21^\circ\text{C}$ ) and duration was investigated using normalized ethylene concentration. Furthermore, the efficiency of ethylene removal the two systems was investigated as function of the storage humidity, and oxygen concentration and of their interactions at a constant temperature  $21^\circ\text{C}$ . Data obtained were subjected to factorial analysis of variance (ANOVA) using Statistical software (Statistica 10.0, StatSoft Inc., Tulsa, OK, USA). Fisher Least significant differences test was used to test the statistical significant differences at  $p \leq 0.05$ . All the results obtained were presented as mean ( $n = 4$  or  $n = 3$  depending on the experimental setup)  $\pm$  standard deviation (SD).

## 3. Results and discussion

### 3.1. Effect of titanium dioxide surface area on PCO

The individual factors ( $\text{TiO}_2$  coated surface area and the duration of exposure or the irradiation time) and their interactions were found to have a significant impact ( $p \leq 0.05$ ) on percentage ethylene removal (Fig. 3). In all PCO experiments conducted with  $5 \mu\text{L L}^{-1}$  initial ethylene concentration using different  $\text{TiO}_2$ -coated area, ethylene removal percentage was  $\geq 99.9\%$ . However, the time required for  $\geq 99.9\%$  ethylene removal was dependent on the exposed surface area of  $\text{TiO}_2$ . It took 150, 120 and 60 min for ethylene removal to reach to  $\geq 99.9\%$  in the PCO reactor with 59.3, 177.8 and  $296.4 \text{ cm}^2$   $\text{TiO}_2$  coated area, respectively. A continuous reduction in ethylene concentration was observed over time, and, higher the  $\text{TiO}_2$ -coated surface area the faster was ethylene oxidation rate. These results are consistent with literature as Chang et al. (2013) in their experiments involving photocatalyst, reported an increase in percentage removal of ethylene from 22.4% to 39% on increasing  $\text{TiO}_2$  area inside the reactor from 83.4 to  $259 \text{ cm}^2$ .

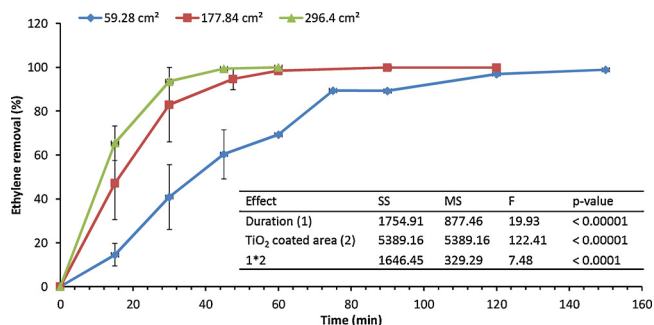


Fig. 3. Effect of titanium dioxide coated area on percentage ethylene removal. Error bars indicate standard deviation from mean values ( $n = 4$ ).

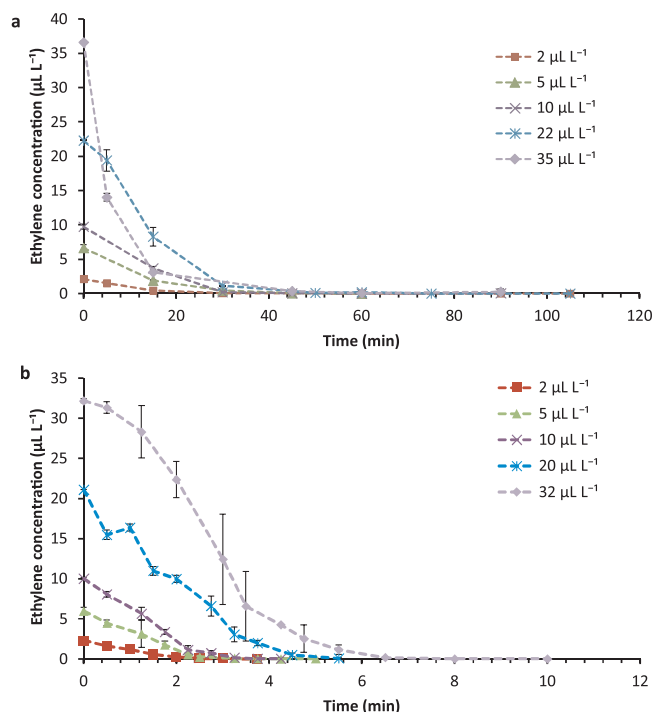


Fig. 4. Ethylene concentration as a function of irradiation time a) Photocatalytic oxidation (PCO) and b) Vacuum ultraviolet photolysis (VUV). The legends denote different initial ethylene concentration. Error bars indicate standard deviation from mean values ( $n = 3$ ).

Photocatalysis is a surface dependent phenomenon and the surface area of the catalyst exposed to the radiation influences ethylene oxidation (Chang et al., 2013; Tytgat et al., 2012). According to Ibhaden and Fitzpatrick (2013) photocatalytic process involves diffusion and adsorption of reactant to the surface of semiconductor, reaction on the surface of semiconductor and subsequent desorption and diffusion of the products from the surface of the semiconductor. Thus, the more the UV irradiated  $\text{TiO}_2$ -coated surface area, the greater is the ethylene removal. Therefore, further study was conducted using  $296.4 \text{ cm}^2$  of  $\text{TiO}_2$ -coated surface area.

### 3.2. Effect of ethylene concentration and kinetics of ethylene degradation

Ethylene concentration as a function of time is presented in Fig. 4. The initial maximum ethylene concentrations of  $35 \mu\text{L L}^{-1}$  and  $32 \mu\text{L L}^{-1}$  were reduced to  $< 0.04 \mu\text{L L}^{-1}$  within  $< 50$  min and  $< 7$  min in PCO and VUV processes, respectively. It was evident that the VUV technique was much faster compared to PCO process. This was due to the fact that VUV technique relies on ethylene oxidation in the gaseous phase whereas; PCO is a surface phenomenon, which mainly occurs at the irradiated surface of the photocatalyst (Huang et al., 2011). Comparing two processes for toluene removal, Huang et al. (2011) reported a much higher toluene removal efficiency for VUV photolysis (63.9%) compared to PCO (14.3%) at a flow rate  $1 \text{ L min}^{-1}$  and initial toluene concentration  $50 \mu\text{L L}^{-1}$ . Further in this study, the reaction kinetics of the two processes was investigated separately.

#### 3.2.1. Photocatalytic oxidation (PCO)

A very good degree of fit was obtained ( $R^2 > 99\%$ ) on fitting ethylene degradation curve to L-H equation (Eq. (3)).

The calculated initial reaction rate ( $R_0$ ) (using Eq. (4)) was found to be dependent on the initial ethylene concentration. A lower reaction rate was obtained at low ethylene concentrations. In PCO studies, the reaction rate has been found to be dependent on the initial reactant concentration. Yamazaki et al. (1999) observed that the PCO reaction

rate follows L-H kinetics with respect to ethylene concentration and reported a linear relationship between the reciprocal of reaction rate and that of initial ethylene concentration. In other related studies, increasing reaction rate with inlet ethylene concentration was reported to stabilize/decrease after a certain threshold ethylene concentration is reached. In a study of ethylene photocatalytic oxidation using C-doped  $\text{TiO}_2$ , Lin et al. (2014a) observed an increase in reaction rate on increasing ethylene concentration from  $55 \mu\text{L L}^{-1}$  to  $459 \mu\text{L L}^{-1}$ . However, the authors observed that beyond  $459 \mu\text{L L}^{-1}$  ethylene concentrations, the reaction rate decreased. In another similar study, using N-doped  $\text{TiO}_2$  and increasing ethylene concentration from  $100 \mu\text{L L}^{-1}$  to  $900 \mu\text{L L}^{-1}$ , reaction rate increased initially and then stabilized. This behavior can be explained on the basis of L-H kinetics (Lin et al., 2014b). In Eq. (1), it can be observed that the reaction rate (R) is proportional to the fraction of the catalyst surface ( $\theta$ ) covered by ethylene (Lin et al., 2014a). It is assumed that there are a limited number of active sites for ethylene adsorption on the catalyst surface. Initially at low ethylene concentrations, the number of active sites was much more with respect to that of ethylene molecules. When the ethylene concentration further increased, ethylene molecules occupied more number of active sites on the catalyst surface, resulting in a greater coverage of the catalyst surface and increased reaction rate. However, once all active sites on the catalyst surface get occupied by ethylene molecules, a further increase in ethylene concentration would no longer increase the reaction rate. According to Hay et al. (2015), this limiting ethylene concentration beyond which reaction rate stabilizes/decreases, is dependent on the light intensity, the nature of the catalyst as well as on the reactant.

### 3.2.2. Vacuum ultraviolet light (VUV) photolysis

The estimated reaction constants ( $k$ ,  $R_0$ ) using Eqs. (6) and (7) are shown in Table 2. The initial reaction rate showed a good first order dependence on initial ethylene concentration. In a VUV photolysis study (Chang et al., 2013), the amount of ethylene removed increased on increasing the initial ethylene concentration, at the same flow rate, that evidently showed that reaction rate increases with increase in initial ethylene concentration. Similar results were observed in degradation of formaldehyde using VUV photolysis (Yang et al., 2007). Overall, the reaction rates were higher for the VUV photolysis compared to PCO. Thus, ethylene removal using VUV photolysis can be advantageous in terms of higher efficiency.

## 3.3. Ethylene degradation under different storage conditions

### 3.3.1. Storage temperature

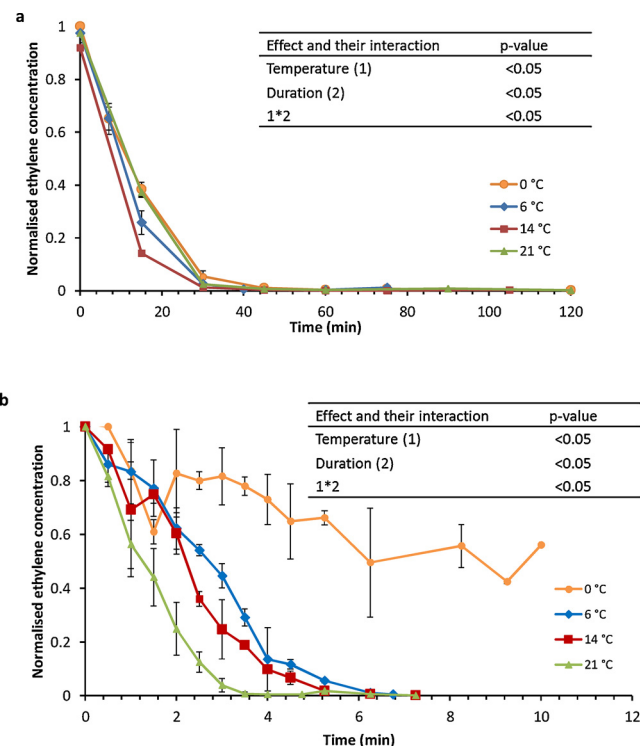
Fig. 5 presents the normalized ethylene concentration (obtained by dividing the measured ethylene concentration value with that of initial ethylene concentration) with respect to temperature. From the statistical analysis, the interactive effect of temperature and duration (or irradiation time) as well as individual effects of temperature and irradiation time significantly ( $p \leq 0.05$ ) affected percentage ethylene removal in both PCO and VUV photolysis. However, a consistent trend of

**Table 2**

Reaction kinetic descriptors of the first order kinetics applied to vacuum ultraviolet light (VUV) photolysis.

Initial ethylene concentration, $C_0$ ( $\mu\text{L L}^{-1}$ )	Estimated coefficient and reaction rate <sup>a</sup>	
	K ( $\text{min}^{-1}$ )	$R_0$ ( $\mu\text{L L}^{-1} \text{min}^{-1}$ )
2.3	1.02	2.05
6.0	0.88	4.38
10.0	0.88	8.80
21.1	0.47	9.36
32.2	0.47	14.14

<sup>a</sup>  $R_0$ : initial reaction rate; K: first order kinetic constant.



**Fig. 5.** Effect of temperature on ethylene removal in a) Photocatalytic oxidation (PCO) b) Vacuum ultraviolet photolysis (VUV). All experiments were carried out at 10% relative humidity, and 21%  $\text{O}_2$ . Error bars indicate standard deviation from mean values ( $n = 3$ ). Statistical analysis on the effect and interaction is presented for percentage ethylene removal.

the effect of temperature on ethylene removal in PCO was not observed (Fig. 5a). PCO process has been reported to be less sensitive to temperature (Mills et al., 1993) however, there are contradicting reports available in the literature (Yamazaki et al., 1999; Fu et al., 1996; Westrich et al., 2011). Ethylene oxidation was found to increase on increasing temperature from 30 to  $110^\circ\text{C}$  by Fu et al. (1996). Effect of very high temperatures  $65\text{--}500^\circ\text{C}$  have been reported by (Westrich et al., 2011; Yamazaki et al., 1999). Hussain et al. (2011b) also reported a slight increase in percentage ethylene removal on increasing temperature from  $30^\circ\text{C}$  to  $35^\circ\text{C}$ , however, at temperatures  $> 35^\circ\text{C}$  the percentage removal decreased. Small increase ( $< 10\%$ ) in ethylene oxidation was reported on increasing the temperature from  $5^\circ\text{C}$  to  $25^\circ\text{C}$ , by Maneerat et al. (2003). Similar effect of temperature on ethylene oxidation was reported by Obee and Hay (1997), who conducted experiments at three temperatures (2, 27 and  $48^\circ\text{C}$ ) and ethylene oxidation rate was found to be higher at elevated temperatures. The results and responses were attributed to the change in adsorption energies of water and ethylene molecules. At high temperatures, water is desorbed to a higher extent leaving active sites vacant for ethylene molecules to get adsorbed, thereby increasing the ethylene oxidation. In present study, similar effect of temperature could not be observed which may be due to the small range of the selected temperatures ( $0\text{--}21^\circ\text{C}$ ).

Under the VUV photolysis (Fig. 5b), ethylene removal was faster when temperature was higher. The ethylene concentration dropped below  $< 0.02 \mu\text{L L}^{-1}$  within 3.5, 5, 6.25 min at 21, 14, and  $6^\circ\text{C}$ , respectively. This was in agreement with Bhowmick and Semmens (1994) who reported a small increase in reaction rate on increasing inside reactor temperature from 45 to  $65^\circ\text{C}$ . In the present study, almost complete ethylene removal ( $0.0007 \mu\text{L L}^{-1}$ ) was achieved in 7.25 min at  $21^\circ\text{C}$ , however, at  $0^\circ\text{C}$  ethylene removal was slow and  $5.6 \mu\text{L L}^{-1}$  of ethylene remained at the end of 10 min. Due to its reduced efficiency at low temperature, VUV photolysis may not be as advantageous in cold

**Table 3**

Effects of varying oxygen concentrations, relative humidity and ethylene removal techniques (photocatalytic oxidation and vacuum ultraviolet photolysis) on the half time (min) of ethylene concentration at 21 °C.

Ethylene removal technique	Storage parameters	Half time (min)
PCO	Low RH* Low O <sub>2</sub>	27.5 ± 0.7
	Low RH* high O <sub>2</sub>	15.75 ± 1.8
	High RH* Low O <sub>2</sub>	28.75 ± 0.4
	High RH* High O <sub>2</sub>	27.25 ± 0.4
VUV	Low RH* Low O <sub>2</sub>	1.35 ± 0.1
	Low RH* high O <sub>2</sub>	1.95 ± 0.8
	High RH* Low O <sub>2</sub>	0.9 ± 0.4
	High RH* High O <sub>2</sub>	0.63 ± 0.0
Effects and their interactions		P values
Ethylene removal technique		0.000000
RH		0.000094
O <sub>2</sub>		0.000029
Ethylene removal technique*RH		0.000012
Ethylene removal technique*O <sub>2</sub>		0.000020
RH*O <sub>2</sub>		0.000278
Ethylene removal technique*RH*O <sub>2</sub>		0.000085

Mean values (n = 3) ± standard deviation of half time (min). RH: relative humidity - low (10.7 ± 1.8%); high (84.9 ± 6%), and O<sub>2</sub> concentration - low (0.67 ± 0.16%); high (20.8 ± 0.08%). Initial ethylene concentration of 10 µL L<sup>-1</sup>.

storages as in higher temperatures storage (> 13 °C) of tropical fruits. However, investigation of up-scaled VUV photolysis reactor system is recommended to confirm this observation.

### 3.3.2. Oxygen concentration and relative humidity

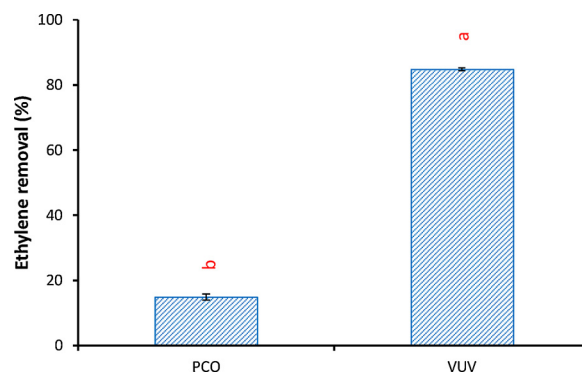
Individual factors O<sub>2</sub> concentration, relative humidity and the type of ethylene technique (PCO and VUV photolysis) and their interactions had a significant impact ( $p \leq 0.05$ ) on total ethylene removed. Table 3 presents the half-time of the ethylene oxidation under different O<sub>2</sub> and RH conditions in PCO and VUV photolysis reactors, respectively. A smaller half-time indicates a faster reaction. Relative humidity and O<sub>2</sub> clearly showed an effect on half-time of both the processes. The PCO reactor had the shortest half-time, and, the fastest ethylene removal was observed at higher O<sub>2</sub> concentration and low RH (Table 3). Higher O<sub>2</sub> has been reported to have a beneficial effect on photocatalytic oxidation (Lin et al., 2014a, b). On the other hand, high RH was unfavorable for PCO as it was evident that in both O<sub>2</sub> concentrations (low O<sub>2</sub> and high O<sub>2</sub>) with high RH the reaction was found to be slower than that of low RH. This is in agreement with Tytgat et al. (2012) and Obee and Hay (1997) who reported negative impact of RH on ethylene oxidation. In contrast, other studies reported that a small quantity of water vapor favored oxidation efficiency of ethylene in PCO (Hussain et al., 2011b; Park et al., 1999; Westrich et al., 2011). In photocatalysis, the trapping of electron-hole pairs is by surface adsorption of O<sub>2</sub> and water molecules on the surface that leads to the formation of hydroxyl radicals and superoxide ions. These reactive oxygen species (ROS) then oxidize the ethylene on the catalyst surface. Thus, in theory, the presence of water vapor and O<sub>2</sub> should produce more ROS, which should lead to higher ethylene removal. However, presence of water molecules may not necessarily lead to increased ethylene removal efficacy as both water vapor and ethylene molecules compete for the same adsorption sites on the catalyst surface (Yamazaki et al., 1999). Although excess accumulation of water vapor may produce more ROS but water molecules equally compete with ethylene molecules for adsorption onto the active sites on catalysts surface. Water having higher absorption affinity limits the number of active sites for ethylene adsorption, consequently, decreasing the ethylene oxidation in PCO (Obee and Hay, 1997). Furthermore, the active sites for O<sub>2</sub> adsorption are separate hence O<sub>2</sub> concentration does not interfere with ethylene adsorption, and thus presence of O<sub>2</sub> favor PCO process. This was evident from Table 3 that

higher ethylene removal occurred at high O<sub>2</sub> concentration and low RH. Thus, the application of this PCO system could be limited under cold storage since high relative humidity is required, however, investigation of up-scaled PCO reactor system is recommended to confirm this observation.

In the case of VUV photolysis, the favorable impact of RH on ethylene oxidation was observed (Table 3). Lower half-time was obtained at high RH conditions compared to low RH conditions. This is agreement with literature that presence of water enhances the VUV photolysis of ethylene (Chang et al., 2013; Jeong et al., 2004). Moreover, since no catalyst is involved, there is no competing adsorption effect as in PCO. The lowest half-time was achieved at high O<sub>2</sub> concentration and high RH (Table 3). Both, water vapor and O<sub>2</sub> molecules absorb the photon energy to produce ROS that oxidize ethylene. As a result both high O<sub>2</sub> and high water vapor favor ethylene oxidation. Overall, the impact of RH was more prominent with faster reaction rate at higher RH irrespective of the O<sub>2</sub> concentration (Table 3). In a study by Jeong et al. (2004), oxidation of toluene under VUV photolysis increased from 10% to 91% on increasing the RH from < 1% to 40%. Chang et al. (2013) also reported increase in ethylene oxidation from 22.4 to 41.9% by increasing RH from < 1% to > 86%. It can be concluded that hydroxyl radicals are the dominant oxidizing species in VUV photolysis.

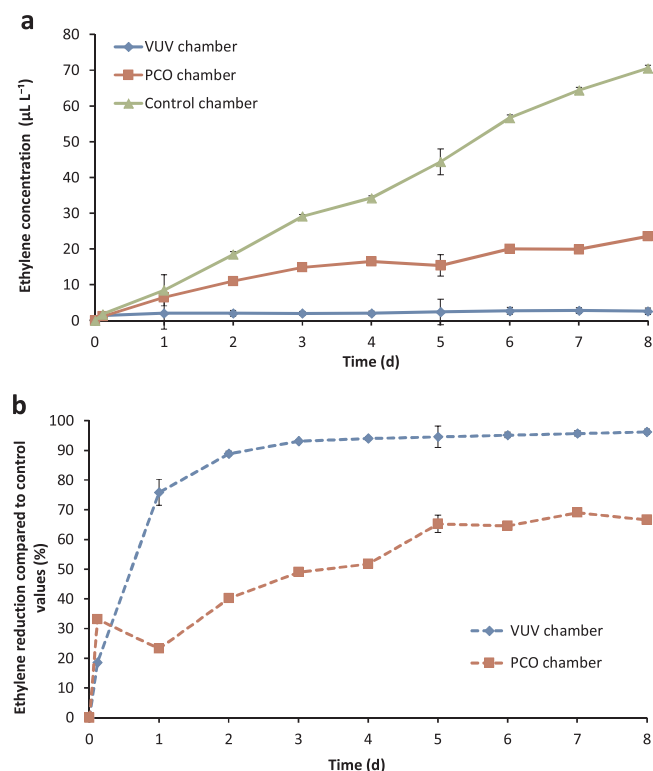
### 3.4. Single pass efficiency and storage experiment

Fig. 6 shows the difference in percentage ethylene removal (PER) in a single pass in a flow through system connected to PCO and VUV reactors. Calculated PER in VUV photolysis reactor was 84.8% whereas it was < 14.86% in PCO reactor. This difference was due to PCO being a surface process whereas VUV photolysis occurs in the gaseous medium, therefore, in VUV photolysis reaction occurs on the bulk phase and is faster whereas in PCO efficiency is limited by mass transfer to the surface of the catalyst (Yang et al., 2007). For the storage experiment with apples, change in ethylene concentration during the storage period in all three chambers is presented in Fig. 7a. Ethylene concentration in the control chamber continued to increase reaching 70 µL L<sup>-1</sup> at the end of 8 d whereas it was 24 µL L<sup>-1</sup> and 2.6 µL L<sup>-1</sup> for PCO and VUV photolysis chambers, respectively. Compared to the ethylene accumulated in the control, the percentage ethylene reduction achieved in VUV photolysis and PCO chamber was 96.28% and 66.58% as shown in Fig. 7b. O<sub>2</sub> and CO<sub>2</sub> concentrations reached 18.9% and 1.10%, respectively in all the three chambers, at the end of 8 d from initial concentration of 20.3% and 0%, respectively. The RH was 97 ± 1%



**Fig. 6.** Comparative percentage ethylene removal in photocatalytic oxidation (PCO) reactor and vacuum ultraviolet light (VUV) photolysis reactor in a flow through system (flowrate 0.24 L/min, initial ethylene concentration 10 µL L<sup>-1</sup>). The experiments were conducted at a temperature 21 °C and relative humidity 40%. Error bars indicate standard deviation from mean values (n = 3). Different lower case letters indicate significant differences at 95% confidence interval.





**Fig. 7.** (a) Ethylene concentration in different apple storage chambers stored at 1 °C during 8 d, and (b) describes the percentage ethylene reduction compared to control values. Error bars indicate standard deviation from mean values (n = 3).

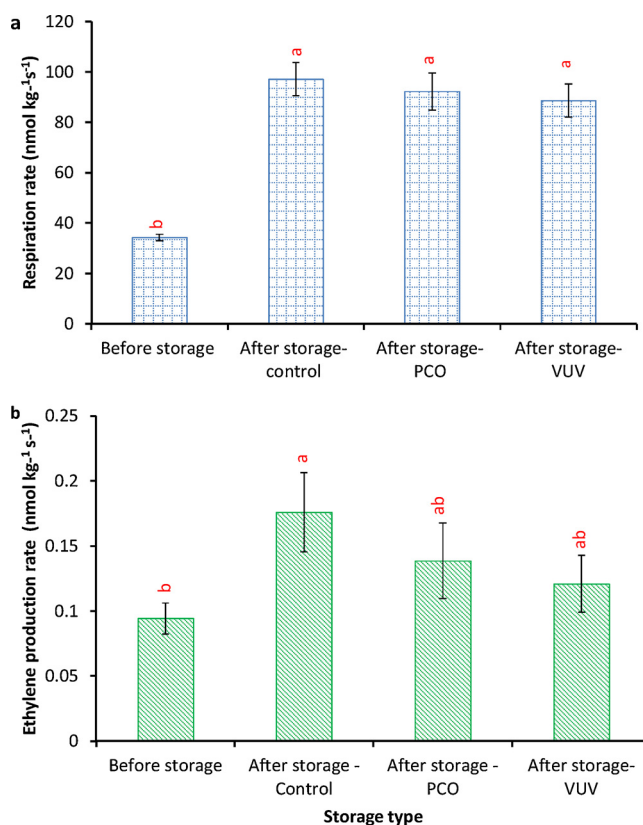
during the 8 days.

Respiration rate (RR) and ethylene production rate, as measured before and after storage, are shown in Fig. 8. There was no significant difference in RR of apples which had been stored in the three different chambers. However, a significant increase in overall respiration rate of apples was observed after 8 d of storage compared to pre-storage which corroborates to the observations that ethylene exposure elevates respiration in many fruits and vegetables (Fugate et al., 2010; Agar et al., 1999). Furthermore, exogenous ethylene also enhances endogenous ethylene production (Park et al., 2006). The ethylene production rate of apples was significantly higher after storage for control samples compared to pre-storage. However, there were no significant differences between the pre-storage ethylene production rate and ethylene production rate after storage treatment for apples stored in PCO and VUV chambers as exogenous ethylene concentrations was less in these two chambers compared to that in control (Fig. 8b).

Both VUV and PCO reactors reduced the ethylene concentration of chambers but could not bring it down to zero even after 10 d of continuous operation of the reactor. The importance of maintaining low ethylene concentrations (< 0.1 μL L<sup>-1</sup>) in postharvest handling of fruits and vegetables is well known (Wills et al., 2001, 2004), thus, further research efforts are needed to improve the performance of the reactors for an effective ethylene removal in postharvest storage of fresh produce.

#### 4. Conclusion

This study investigated two techniques namely, PCO and VUV photolysis for ethylene removal. Both techniques were able to remove ethylene and could be considered as a potential technology for application in postharvest storage of ethylene sensitive fruit and vegetables. The kinetic study of the two techniques clearly showed that both techniques were highly dependent on initial ethylene concentration



**Fig. 8.** Quantified respiration rate (a) and ethylene production rate (b) in apples before and after 8 day storage at 1 °C in different storage chambers. Error bars indicate standard deviation from mean values (n = 3) and bars with different letters are significantly different at 95% confidence interval.

with their ethylene removal efficiency being reduced at low initial ethylene concentrations. Thus, it is important to increase the efficiency of these techniques at low ethylene concentrations to avoid triggering physiological response in fresh produce. The storage parameters (oxygen concentration, humidity and temperature) were found to significantly affect the ethylene removal efficiency of PCO as well as VUV photolysis. Oxygen concentrations favored both the techniques. However, humidity impeded PCO while it enhanced VUV photolysis of ethylene. Also in VUV photolysis, the effect of humidity was dominant compared to oxygen. Temperature effect on PCO did not show any consistent trend, however, in VUV photolysis, low temperatures decreased ethylene removal efficiency. Thus, the application of VUV photolysis at low temperatures may not be fully advantageous, nevertheless, VUV photolysis has an application in storage temperature > 13 °C. In the case study experiment involving apple storage, VUV photolysis effectively lowered the ethylene concentration to 2.6 μL L<sup>-1</sup> compared to 24 μL L<sup>-1</sup> in PCO chambers, whereas in control chamber the ethylene concentration soared up to 70 μL L<sup>-1</sup> at the end of storage day 10. Overall VUV photolysis showed higher ethylene removal efficiency than PCO. However, an additional ozone filter coupled with VUV photolysis is needed, to prevent ozone from reaching the plant tissues and damaging them. PCO does not involve ozone generation, therefore, does not require any additional filtration mechanism. It was also observed in this study that in PCO, the higher TiO<sub>2</sub> surface area increased efficiency of the technique. Thus, increasing the ratio of the TiO<sub>2</sub> coated surface area to the volume of the reactor could effectively increase the efficiency of the process. For VUV photolysis, coupling with multifunctional catalysts (MnO<sub>2</sub>, palladium, and cobalt) which can decompose ozone and additionally enhance ethylene degradation using the residual ozone, could be investigated. Moreover, a combination of PCO-VUV could be explored to tap the advantages of

both the processes and at the same time address the individual disadvantages of the techniques.

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## 6. Conclusions and future perspectives

### 6.1 Conclusions

This study adequately answered all the four research questions raised on the application of PCO and VUV photolysis on ethylene management. The entire hypothesis on the efficiency of PCO and VUV photolysis on ethylene removal were tested and confirmed.

The first hypothesis for this work was that the PCO and VUV photolysis can remove ethylene from realistic fruit storage. This was affirmed in mixed loading storage experiments. The VUV reactor was able to reduce ethylene concentration to  $1.8 \mu\text{L L}^{-1}$  inside a storage chamber (190 L) consisting of 18 kg of mixed-loaded fruit types consisting of apple, banana and kiwifruit in equal quantity (on mass basis) and stored at  $15^\circ\text{C}$  for 10 d. On the other hand, the control storage chamber had  $90 \mu\text{L L}^{-1}$  of ethylene accumulation. The quality parameters were retained to a higher degree in the chamber connected to VUV reactor as compared to control. In another fruit storage experiment, ‘Gala’ apples (6 kg) at  $1^\circ\text{C}$  were placed inside chambers with a 190 L capacity for 8 d. In the storage chamber connected to PCO reactor ethylene concentration declined to  $24 \mu\text{L L}^{-1}$ , whereas in, second chamber connected to VUV reactor ethylene dropped to  $2.6 \mu\text{L L}^{-1}$  after 8 d. In contrast, ethylene concentration in the control chamber was  $70 \mu\text{L L}^{-1}$  at the end of the storage period. Thus, the reactors were able to lower the ethylene concentration in fruit storage chambers although the concentration could not be reduced completely. This could be attributed to the difference in ethylene production rate from the fruit compared to the ethylene removal by the reactors. From these results the following outlook can be presented:

- i) PCO and VUV photolysis techniques reduce ethylene generated by fruits; however, in-order to achieve an overall decrease in the ethylene concentration in fruit storage areas, it needs to be ensured that the ethylene reduction rate of these techniques is higher than the ethylene production rate of the fruits. Thus, it is important to study the product characteristics in terms of ethylene production rates as the dynamic balance between the rate of ethylene production by fruits and the rate of ethylene removal by the reactor is important.
- ii) Commercial ethylene removal sachets (Purafil, USA) showed a slightly higher edge in ethylene removal from the mixed load compared to VUV reactor. The ethylene reduction by sachets was  $> 99\%$ , while with VUV reactor it was  $98\%$  with respect to ethylene concentration

accumulate in the control at the end of 10 d storage. However, unlike the sachets, which had to be disposed of later, VUV reactor did not involve any solid waste generation. To assess the advantages of PCO and VUV photolysis ethylene removal techniques over conventional techniques, a comparative analysis in longer storage duration as well as a cost analysis is needed.

Second hypothesis for the study was that the process parameters affect the ethylene removal efficiency. This hypothesis was found to be correct through this research work. Flowrate of the air passing through the reactor, the initial ethylene concentration and the lamp power showed a significant individual as well as interactive effect. Higher initial ethylene concentrations, higher lamp power and a low flowrate ensured more time for interaction of reactive oxygen species, resulting in more ethylene removal. In case of PCO reactor, the  $\text{TiO}_2$  area exposed to irradiation was found to be an important factor to be considered. Larger  $\text{TiO}_2$  coated area increased ethylene removal, which corroborates to the fact that PCO is a surface phenomenon. The larger the irradiated catalyst surface, the higher the area available for reaction to occur. From these results and findings certain insights for the industrial applications can be obtained.

i) As flowrate of the air, irradiation and initial ethylene concentration affect ethylene removal significantly; an optimized reactor is essential. The flowrate needs to be adjusted according to the storage volume. Reactor design should be optimized for the maximum ethylene removal in the desired flowrate. In practical application to bring down ethylene concentration to desired level from the initial, first it should be estimated how much time is needed for a complete cycle to filter all the air of the storage space. Subsequently, it needs to be ensured that the flowrate of the air passing through the reactor is as high as possible to get desired cycles of air filtration and at the same time it should be slow enough to give maximum ethylene removal per pass.

ii) Air flow distribution is thus important in the storage. On installation of PCO and VUV photolysis based ethylene removal devices, proper air movement through the storage space should be ensured. Installation of more than one unit of such ethylene removing devices or additional fans in the storage space to prevent stagnation of ethylene is important.

iii) PCO is a catalyst-dependent technique. Thus, research into developing a more efficient catalyst as well as into increasing irradiated catalyst surface area, is essential to enhance the ethylene removing efficiency of PCO based processes.

iv) Another experimental observation in this study was that heat is generated due to the lamps involved in both processes. The heat may adversely affect the fruit and vegetable. Thus, the amount of heat generation also needs to be taken into consideration in upscaling of the reactors.

The third hypothesis was that the storage conditions of the products affect the ethylene removal efficiency and it was affirmed through the results of this thesis. Low temperature, low oxygen concentration and high relative humidity are important considerations in postharvest storage of fresh produce. Relative humidity and O<sub>2</sub> clearly showed an effect on ethylene removal in both processes. Obtained results on the effect of storage parameters can contribute to understanding the applicability of a particular technique for product specific storage.

i) Oxygen favourably influenced PCO; high humidity (> 80 %), however, reduced the efficiency of ethylene removal. Thus, presence of water molecules decreased the ethylene removal efficacy of PCO reactor as both water vapour and ethylene molecules compete for the same adsorption sites on the catalyst surface. Thus, to maximize efficiency of PCO based filter there is a need to have a desiccant or water absorber to ensure a flow of dry air through the reactor. In CA storage with low oxygen concentrations or in ultra-low oxygen storage, PCO may have a decreased performance. Thus increasing ethylene efficiency through higher catalyst area or higher irradiation intensity could be advantageous. Temperature did not seem to have any consistent effect on ethylene removal efficiency of PCO.

ii) Irrespective of O<sub>2</sub> concentration, high humidity had a favourable impact on ethylene removal in the VUV reactor. This positive role of high relative humidity on VUV process makes it more advantageous for fruit and vegetable storage as high humidity is often essential for storage of fresh produce to reduce transpiration losses. Although reduced O<sub>2</sub> concentrations have a negative effect, the presence of high water concentration can compensate the reduction. Low temperatures also decreased ethylene removal efficiency of VUV, which could possibly limit the VUV photolysis application in cold storages. This would imply that additional units or a reactor with higher capacity (e.g. higher irradiation intensity) should be installed at low temperatures. Thus, VUV reactors would be advantageous for storage of tropical fruits (which require optimum storage temperature above 13 °C) or could also be implemented in ripening chambers where the excess ethylene needs to be removed after ripening the fruits.

Another highlight of this study is that it presented a comparative insight into the two processes of PCO and VUV photolysis. The ethylene degradation kinetics obtained with both PCO and VUV reactor were best fitted with the reaction rate law based on Langmuir Hinshelwood mechanism and first-order reaction kinetics, respectively.

Langmuir Hinshelwood mechanism for PCO process:  $\frac{dC}{dt} = \frac{k KC}{1+KC}$

First-order reaction mechanism for VUV process:  $\frac{dC}{dt} = k C$

where  $k$  is the reaction rate constant ( $\text{min}^{-1}$ ),  $K$  is the adsorption coefficient of the reactant ( $\mu\text{L L}^{-1}$ ) and  $C$  is the reactant concentration ( $\mu\text{L L}^{-1}$ ) and  $t$  is time (min).

As evident from the governing reaction rates, both processes were highly dependent on initial ethylene concentration. Ethylene concentrations may largely vary in storage facilities (e.g. 0.15-180  $\mu\text{L L}^{-1}$  as observed in this work). Hence, for the designing of the reactor, the product and type of storage need to be identified. VUV process was much faster than PCO, the estimated initial reaction rates were 0.55 and 8.8  $\mu\text{L L}^{-1} \text{ min}^{-1}$ , respectively, for PCO and VUV photolysis, respectively. This could be due to the fact that the former process occurred in the gaseous phase, whereas the latter occurred on the catalyst surface. This was further confirmed by the result from single-pass experiment of gas stream through the reactors, which showed the percentage ethylene removal of 84.8 % in VUV and 14.86 % in PCO reactor (initial ethylene concentration 10  $\mu\text{L L}^{-1}$ , flowrate 0.24  $\text{L min}^{-1}$ ). Even though PCO was a relatively slower process in the current setup, an important observation was that there was no ozone generation. Whereas in VUV, small quantities of ozone was generated, thus requiring additional ozone filter.

According the findings of this study, summarized above, the various parameters to be considered before designing PCO or VUV photolysis based process are collectively illustrated in Figure 6-1.

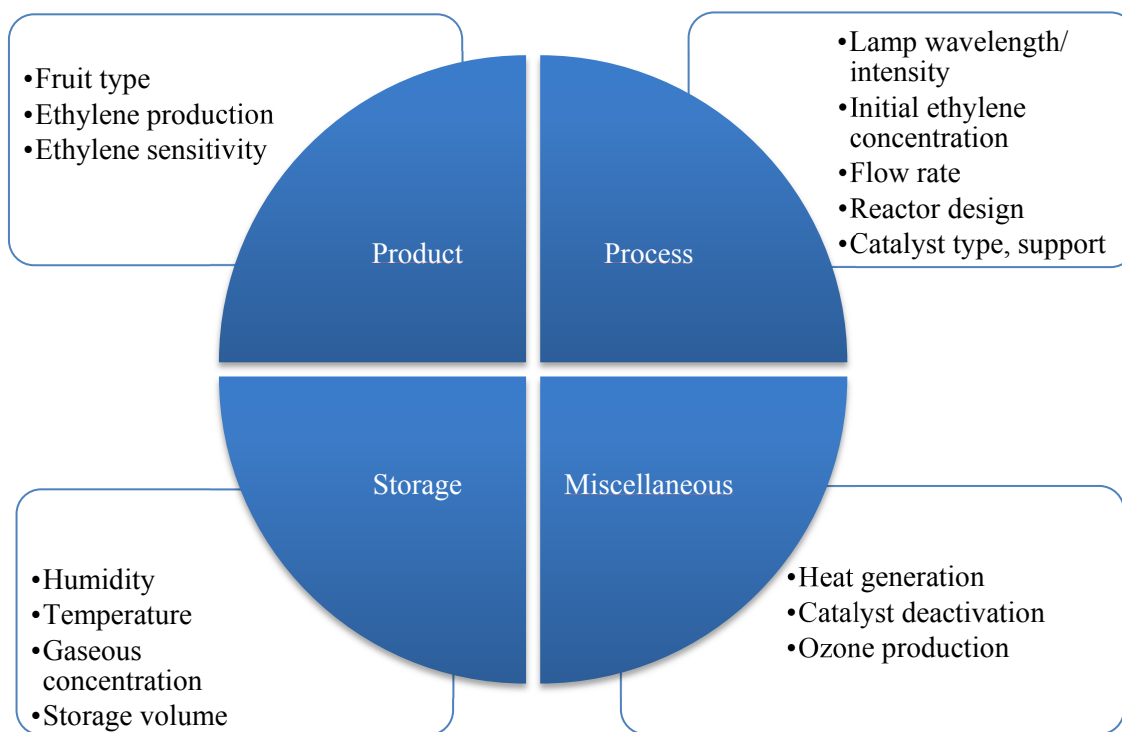


Figure 6-1: Different parameters to be considered while designing filter for ethylene removal based on photocatalytic oxidation (PCO) and vacuum ultraviolet light photolysis (VUV).

## 6.2 Perspectives of future research

*“We keep moving forward, opening new doors and doing new things, because we’re curious and curiosity keeps leading us down to new paths”- Walt Disney*

The various research findings and outcomes from this study have paved way for new ideas for future research. In this study, ethylene removing efficiency along with effects of different entities on the two techniques, PCO and VUV photolysis were analysed. A lot of information on the fundamental aspects of these processes as well as their impact on quality and safety of fruit and vegetables in long term is still lacking. Moreover, ways to overcome the identified drawbacks with these techniques also need attention. These ideas for future outlook have been further elaborated below:

**a) Comprehensive understanding of the reaction mechanism:** A basic study on a fundamental understanding of their reaction mechanisms is needed. This includes type and amount of active species generated, and their properties and roles in ethylene oxidation. The term



reactive oxygen species refers to a broad range of chemically distinct, reactive species such as superoxide anion ( $\text{O}_2^{\bullet-}$ ), hydroxyl radical ( $\text{OH}^\bullet$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), singlet oxygen ( $^1\text{O}_2$ ).

Detection of reactive oxygen species is difficult as they are often short-lived (Figure 6-2). The most frequently used indirect methods of measuring reactive oxygen species are chemiluminescence and fluorescence. Chemiluminescent assays can measure  $\text{OH}^\bullet$ ,  $\text{O}_2^{\bullet-}$  and  $\text{H}_2\text{O}_2$  concentrations but cannot distinguish these species. Fluorescent probes can be easily used to detect  $\text{O}_2^{\bullet-}$ ,  $\text{OH}^\bullet$ , and  $^1\text{O}_2$ , but interference from other oxidants frequently requires additional HPLC analyses to definitively identify the reactive oxygen species. For a direct identification and quantification of these short-lived reactive species, electron spin resonance spectroscopy together with spin trapping could be used.

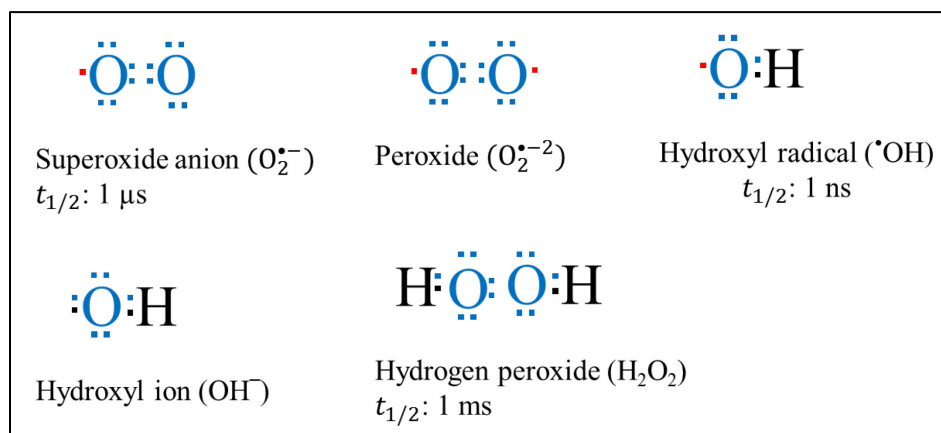
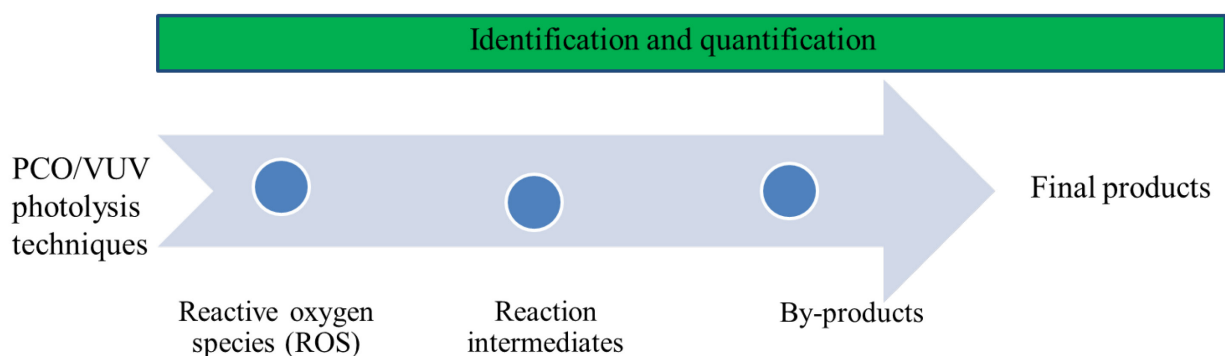


Figure 6-2: Some reactive oxygen species with their electronic structure ( $t_{1/2}$ : Half-life).

Apart from the reactive oxygen species, identification and detection of the intermediate compounds and by-products are also important as an incomplete oxidation in PCO and VUV photolysis may result in formation of by-products, which may be toxic or could potentially harm the product. Thus, along with the identification and quantification of reactive oxygen species, reaction intermediates, products and by-products generated also need to be studied (Figure 6-3).



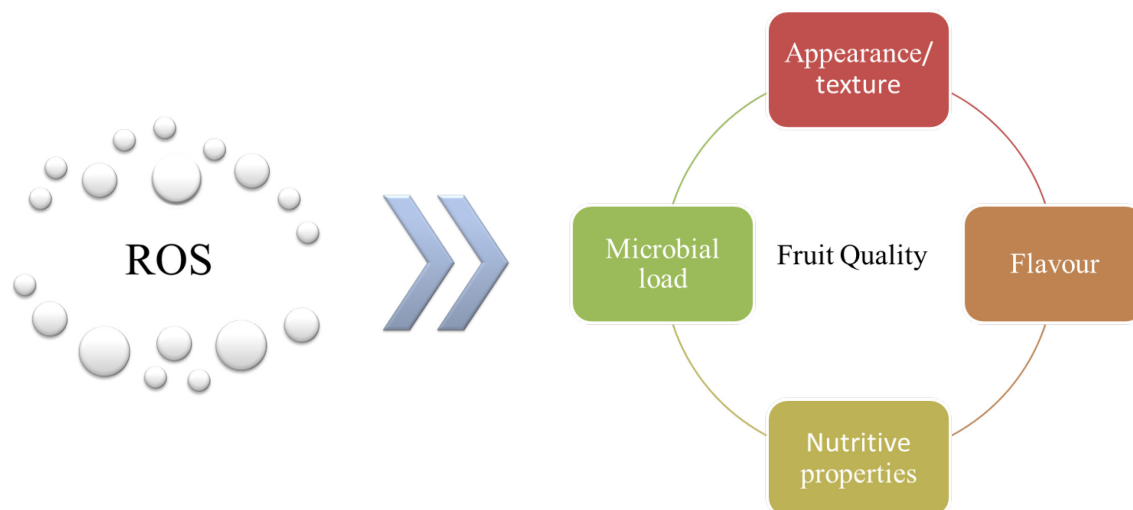
*Figure 6-3: Steps for future research to understand fundamental reaction mechanism in photocatalysis and vacuum ultraviolet light photolysis.*

**b) Impact on quality of horticultural commodities:** From the various fruit storage experiments conducted in this study, a direct effect of PCO and VUV photolysis on ethylene removal was observed, which subsequently reduced respiration and ethylene production rates. The processes did not induce any adverse effect on the visual fruit quality in short-term storage of fruits up to 10 d. However, the quality of fruit also entails other parameters such as textural qualities, flavour and nutritional qualities (Figure 6-4). Visual qualities include general appearance such as colour, size, shape, any visible injuries and/or defects. Textural quantities relate to firmness, crispiness, juiciness, mealiness etc., while flavour quality involves perception of taste and aroma which is affected by sugars, acidity, phenolic compounds and volatile organic compounds. Lastly, the nutritional quality depends on the vitamins, minerals and dietary fibres provided by the product. Retaining good quality parameters is essential for consumer acceptance of the products.

There is a major research gap on the impact of PCO and VUV photolysis on the fruit quality especially under long-term storage. From the results obtained in this study it is obvious that ethylene removal by PCO and VUV photolysis in fruit storage resulted in reduced ethylene concentrations around the fruit, thereby declining their respiration and ethylene production rates. As reported in this thesis, in kiwifruit and banana storage, ethylene removal also helped in retaining quality parameters such as total soluble sugar, acidity and firmness. However, the impact of PCO or VUV photolysis on other fruit quality aspects still needs to be investigated. Among these aspects, the effect on volatile organic compounds and on microbial load could be of

special interest as PCO and VUV photolysis result in oxidation of organic compounds and are also known to inactivate microorganisms. Fruit and vegetables produce a wide range of volatile organic compounds (VOCs), such as esters, alcohols and ketones. These VOCs impart the characteristic aroma and thereby contribute to the flavour of these commodities. (Kader, 2003). Use of oxidation processes, such as PCO and VUV photolysis, may change the VOC balance around these products, which may change their flavour. The oxidation of VOCs may also lead to the generation of other compounds, which may or may not affect the aroma and consequently the fruit quality. Thus, analysis of the impact of these processes on the VOCs in the fresh produce is an important criterion to be considered.

Spoilage of fruit and vegetables often results from microbial activity. The oxidation processes of PCO and VUV photolysis, along with removal of volatile organic compounds can also inactivate microorganisms. The photogenerated reactive oxygen species in the PCO and VUV photolysis may damage the bacterial cell wall and cell membrane, and eventually result in leakage of ions and small molecules from the bacterial cells irreversibly disrupting cell functions. This can be an added advantage for application in fruit and vegetable storage as by inactivating microorganism, the microbial spoilage can be arrested in fresh commodities. Thus, assessing the impact of the oxidation processes on the microbial load of the fresh produce also needs attention.



*Figure 6-4: Different fruit quality parameters potentially affected by reactive oxygen species (ROS) generated in PCO and VUV photolysis processes.*

**c) Combination and/or coupling with other process:** In the application of PCO and VUV photolysis certain drawbacks are also associated. PCO was a relatively slow process, which may involve deactivation of catalyst after some time. High humidity impeded its performance. In VUV photolysis, ozone production was a limitation and, therefore, required an additional filter. Few drawbacks associated with PCO and VUV photolysis could be addressed by combination of the two techniques together or with other oxidation techniques.

i) A combination of PCO and VUV involves the use of  $\text{TiO}_2$  and non-ozone producing lamps as well as ozone producing lamps (254 nm + 185 nm). The combined process could have added advantages of both the processes and at the same time address the individual disadvantages of the processes. Non-ozone producing lamps can reduce the ozone evolution in the VUV process by 185 nm radiation. Irradiation at 254 nm reduces ozone. The combined process can function better at high humidity because VUV photolysis is quite effective at high humidity. Moreover, in VUV photolysis, only 185 nm radiations are useful, while the major emission at 254 nm is not used. In a combined process, the total radiation at 185nm as well as 254 nm can be utilized.

ii) In the VUV process, ozone is a by-product which could be utilized in further ethylene removal. Ozone can produce reactive  $\text{O}_2$  species (ROS) on the surface of certain catalysts such as  $\text{TiO}_2/\text{SiO}_2$  with an active element such as  $\text{MnO}_2$ . This can decompose volatile organic compounds to CO and  $\text{CO}_2$ . Using such catalysts in combination with VUV technique can decompose ozone and, at the same time, enhance ethylene degradation by oxidation of residual ethylene using ROS generated from ozone. On coupling such catalysts with PCO-VUV can provide multiple pathways for ethylene decomposition, such as by VUV photolysis in the gaseous phase, photocatalysis and further fostered by the production of ROS from ozone.

Overall for the future perspectives it could be concluded that, fundamental studies of PCO and VUV photolysis, as well as their interaction and impact on the biological products is essential before these technologies can be practically implemented in postharvest supply chains as efficient and reliable technologies for ethylene control. An in-depth study of the basic process mechanism will provide critical information on ethylene oxidation, intermittent products and impact on product quality. Their exact values or relations could put a strong constraint on designing and optimizing the reactor performance. Further studies, therefore, should aim at improving our understanding of this relation, both from observational and theoretical perspectives. Additionally,

research on the combination of these techniques, or coupling them with other oxidation techniques could enhance ethylene removal efficiency.

Based on the various findings and results of this study, it can be concluded that PCO and VUV photolysis both have a good ethylene removal potential in postharvest. Furthermore, the results from this thesis present valuable insights from scientific as well as industrial point of view, which could help in establishing PCO and VUV photolysis as effective ethylene removal techniques in postharvest.

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## Annex

### Supplementary information supporting chapter 4:

**S. Table 1.** Temperature and humidity measured inside the reactor

No.	Flowrate, (L/min)	C <sub>2</sub> H <sub>4</sub> , (ppm)	Lamp power, (W)	Temperature (°C)		Relative humidity (%)	
				Initial	Final	initial	final
1	0.5	2	6	23.04	28.90	35.03	30.06
2	0.5	30	6	22.73	29.08	29.1	20.6
3	5	2	6	22.3	31.49	29.1	17.5
4	5	30	6	22.58	27.10	19.8	15.0
5	0.5	16	3	23.06	25.06	22.8	18
6	0.5	16	9	21.22	34.22	18	7.8
7	5	16	3	21.79	23.90	22.7	20.9
8	5	16	9	21.63	27.95	24.4	20
9	2.75	2	3	22.84	25.46	37.2	36.5
10	2.75	2	9	24.26	32.87	37	24.8
11	2.75	30	3	21.28	23.27	25.7	22.9
12	2.75	30	9	22.54	30.48	20.5	18.8
13	2.75	16	6	21.65	27.75	24.6	21.4
14	2.75	16	6	22.49	32.25	23.9	23.4
15	2.75	16	6	21.52	26.43	25.6	22.4
16*	0.5	5	9	22.03	29.03	26.6	18.6
17*	0.5	5	9	23.06	30.04	28.8	20.02

\* Refers to the validation experiments.

## **Declaration**

I hereby declare that the work presented in this dissertation is an authentic record of my own work. All used resources and sources are cited. All published parts of this dissertation are listed in the publication list.

Namrata Pathak

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