MODELLING AND OPTIMISATION OF VUV PHOTOLYSIS FOR ETHYLENE CONTROL: FOR POTENTIAL APPLICATION IN POSTHARVEST MANAGEMENT

by

Bongolwethu Professor Mabusela

Thesis submitted in fulfillment of the requirements for the degree of

DOCTOR OF ENGINEERING: CHEMICAL ENGINEERING

in the

FACULTY OF ENGINEERING

at the

CAPE PENINSULA UNIVERSITY OF TECHNOLOGY

Supervisors: Dr Buntu Godongwana
Dr Zinash A. Belay
Dr Oluwafemi J. Caleb

Bellville
August 2024

DECLARATION

I, **Bongolwethu Professor Mabusela**, declare that the contents of this dissertation reflect my own unaided work and have not been previously submitted for academic examination toward any qualification. Additionally, the opinions expressed herein are solely mine and do not necessarily reflect those of the Cape Peninsula University of Technology, Agricultural Research Council (ARC), or the National Research Foundation (NRF).

B. Mabusela August 2024

ABSTRACT

Fresh horticultural produce faces considerable postharvest losses, ranging from 30 to 44%, primarily due to the highly perishable nature of these goods. Among the various contributors to these losses, ethylene emerges as a key factor, triggering and accelerating fruit ripening, leading to softening, senescence, and an overall decline in quality. Effective control of ethylene during postharvest handling and storage is crucial for extending fruit shelf life, maintaining fruit quality, and promoting sustainable agricultural practices. Various methods, including ozone treatment, low-temperature storage, bio-filtration, and potassium permanganate ($KMnO_4$), have been explored to mitigate ethylene's impact. However, these methods often have limitations that affect their long-term applicability, and their efficacy in maintaining fruit and vegetable quality varies. Additionally, there is a gap in understanding these technologies' effects on microbial activity.

This study aimed to evaluate the efficacy of a vacuum ultraviolet (VUV) photolysis reactor for ethylene removal in fruit storage and its subsequent impact on microbial activity responsible for rapid ripening. Specific objectives included investigating ethylene degradation kinetics using a VUV photolysis reactor, assessing the potential of VUV photolysis for ethylene removal in mixed-fruit storage at room temperature, examining the impact of direct VUV radiation on apples' physiological parameters at 15 °C, and exploring proteomic changes related to ethylene removal by VUV photolysis and its effects on apple ripening during postharvest storage. To achieve these objectives, a VUV photolysis reactor was developed and used in experiments to remove ethylene from fruit storage. The first experiment compared the VUV photolysis reactor with the standard fruit industry adsorbent, potassium permanganate ($KMnO_4$), for ethylene removal from mixed-fruit storage (apples, bananas, and pears) at ambient temperature (16 °C) for 6 days. The second study evaluated the impact of direct VUV radiation on the quality attributes of apples stored at 10 °C for 21 days. Results showed that ethylene levels in mixed-fruit storage were significantly reduced by 86.9 % with the VUV reactor, compared to 25.4 % with potassium permanganate. Direct VUV exposure effectively reduced ethylene and respiration rates but caused some skin damage to the apples. Apples in control storage lost firmness at a rate 2.3 times higher, while VUV photolysis extended apple shelf life by 46 days.

The potential of a VUV photolysis reactor for ethylene removal during postharvest storage and its effect on proteomic changes in apple fruit stored at 15 °C for 28 days was investigated. A total of 441 differentially expressed proteins (DEPs) were identified, with 336 proteins in fresh apple samples (on day 0), and 287 and 396 proteins in the treatment and control groups, respectively, after 28 days of storage. Proteins responsible for cell wall modification and ethylene synthesis were upregulated in the control group, while VUV photolysis significantly downregulated proteins associated with cell wall degradation and ethylene synthesis. The degradation kinetics of ethylene were investigated at different light intensities (0.0005 mW/m^2, 0.0014 mW/m^2, and 0.0021 mW/m^2) and relative humidity (RH) levels (20 % and 80 %), and the economic feasibility of the VUV photolysis system was evaluated. The results showed that ethylene degradation increased with higher light intensity. Additionally, high relative humidity favoured ethylene degradation. Both light intensity and RH significantly influenced the kinetic parameters and degradation of ethylene ($p < 0.05$). At low light intensity, ethylene degradation followed a zero-order kinetic model, while at high intensity, it followed a fractional-order kinetic model, indicating a possible change in the reaction mechanism. The economic feasibility of the VUV photolysis system was evaluated using electrical energy per order (EEO), which remained below 10 kW m^{-3} $order^{-1}$, indicating both energy efficiency and practical applicability.

A mathematical model was developed to optimize the VUV photolysis reactor and simulate the temperature variation inside it. The developed mass balance model successfully predicted the experimental ethylene concentrations with R^2 values above 0.9. Although the energy balance model underestimated the temperature variation inside the reactor, it accurately captured the overall trend in temperature increase, demonstrating the model's feasibility. A sensitivity analysis was performed to investigate critical factors affecting the design and optimization of the VUV photolysis reactor. Light intensity and reactor length were found to have the most significant impact on ethylene degradation. Increasing light intensity and decreasing reactor length improved removal efficiency.

In conclusion, this study highlights the significant potential of VUV photolysis as an innovative technique for ethylene removal during the transportation and storage of fruits and vegetables. The findings suggest that VUV photolysis is a promising tool for postharvest management, offering an effective solution to preserve fruit quality and reduce horticultural supply chain losses. Future research should focus on optimizing exposure conditions, designing ozone scrubbers, and refining kinetic models to enhance the practical implementation of this technology.

Iziqhamo ezilinyiweyo ezitsha ezingankonxwanga emva kwesivuno, ezikumyinge ophakathi ko30% ukuya ku44%, zisengozini ngokungafumaneki ngenxa, lezinga eliphezulu lokutshabalala (lokubola) kwezi mveliso. Ezinye iimpembelelo ezingunobangela woku kutshabalala (kubola), yi-ithelini evela ingoyena nobangela ungundoqo, ethi ichaphazele kwaye ikhawulezise ukubola kweziqhamo, ekhokelela ekuthambeni, ekugqithweni lixesha lokusetyenziswa, kwakunye nokuhla nje kukonke komgangatho wayo. Ukukwazi ukulawula i-ithelini ngexesha lokukhiwa nokugcinwa kwesivuno yeyona nto ibalulekileyo kubomi bokugcina iziqhamo kwishelufa ixesha elide, ukugcina umgangatho wesiqhamo, kunye nokuphucula ukugcinwa kweendlela zolimo. Iindlela ezahlukeneyo eziquka unikezelo ngomoya ococekileyo (iozoni), ugcino lweqondo lobushushu lisezantsi, uhluzo lwebhakhthiriya yokucoca amanzi (ibhayofilthreyishini), kunye nepotaziyamu phemanganeyithi (KMnO4), ebezikhe zalingwa ukuhlangabezana nempembelelo ye-ithelini. Noxa kunjalo, ezi nkqubo amaxesha amaninzi zibanokungazi nazisombululo okuchaphazela ukusetyenziswa kwazo ixesha elide, nokusebenza kwazo ngendlela (imiphumela) kuyashiyana ekugcineni iziqhamo nemifuno isemgangathweni. Kwakhona, kukho ukungaqondi iimpembelelo zeetekhnoloji ezichaphazela ukusebenza kwemayikhrobhu.

Esi sifundo sijonge ukuvavanya ukusebenza kwesixhobo sevatyhumu althravayolethi fotolayisisi (VUV) ukususa i-ithelini kugcino lweziqhamo kwakunye nempembelelo eya kuvela kumsebenzi wemayikhrobhu enoxanduva lokukhawulezisa ukuvuthisa (iziqhamo/imifuno). Iinjongo ezikhethekileyo ziquka ukuphanda iikhayinethikhi zokuphelisa (zokususa) i-ithelini ngokusebenzisa isixhobo iVUV fotolayisisi, ukuhlola amathuba eVUV photolayisisi ekususeni i-ithelini kugcino lomxube weziqhamo ngokweqondo lobushushu eliqhelekileyo (legumbi), ukuhlola impembelelo yemitha engqamene neVUV kwii-apile ezihleli kwiqonda elingu15 °C, kwakunye nokuhlola

iinguqu zeprothiyo ezibhekiselele ekususeni iVUV fotolayisisi kunye nempembelelo yayo ekuvuthweni kwee-apile ezikugcino lwesivuno.

Ukuphumeza ezi njongo, isixhobo iVUV fotolayisisi siye sayilwa saze sasetyenziswa kuhlolo lokususa i-ithelini ekugcino lweziqhamo. Uhlolo lokuqala luthelekise isixhobo iVuV fotolayisisi nesifunxi seemoletyhuli emgangathweni wezoshishino lweziqhamo oluqhelekileyo, ipotaziyamu phemanganeyithi ($KMnO_4$), ukususa i-ithelini kwisigcini somxube weziqhamo (ii-apile, iibhanana, kunye namapere) kwiqondo lobushushu elizingqongileyo u(16 °C) iintsuku eziyi6. Isifundo sesibini sihlole impembelelo yemitha yeVUV engqalileyo ngokweempawu zomgangatho onee-apile ezigcinwe ku10 °C iintsuku eziyi21. Iziphumo zibonakalise ukuba amazinga e-ithelini kugcino lomxube weziqhamo ebethotywe ngamandla kangange 86.9% ngesixhobo seVUV, xa kuthelekiswa no25.4% ngepotaziyamu phemanganeyithi. Ukungakhuseleki kweVUV engqalileyo kunciphise izinga le-ithelini kunye nelokuphefumla kwade kwadala umonakalo kufele lwee-apile. Ii-apile ebezikugcino olulawuliweyo (olucwangcisiweyo) zilahlekelwe kukuqina ngokwezinga elingu2.3 ukuphindana, ngeli lixa iVUV fotolayisisi yongeze ubomi be-apile ekwishelufu ngeentsuku eziyi46.

Amathuba esixhobo seVUV fotolayisisi okususa i-ithelini ngexesha lokugcinwa kwesivuno kunye nempembelelo yayo kwiinguqu zeprothiyomi kwisiqhamo i-apile egcinwe ku15 °C iintsuku eziyi28 iye yaphandwa. Kuye kwaqatshelwa inani eliyi441 lilonke leeproteni (DEPs) ezahlukeneyo, eline336 yeeproteni kwisampuli ye-apile entsha (kusuku 0), kunye ne287 kwakunye ne397 yeeproteni kumaqela ohlaziyo nolawulo ngokufanayo, emva kogcino iintsuku eziyi28. Iiproteni ezinoxanduva lokuguqula udonga lweseli nokuxutywa kwe-ithelini ziye zonyuselwa kwizinga eliphezulu kwiqela elilawulwayo, kwangelo xesha iVUV fotolayisisi ithotyelwe kwelona qondo lisezantsi iiproteni ezinxulumene nodonga lweseli enolawulo oluthotyiweyo kwakunye nokuxutywa kwe-ithelini.

Ukuthotywa kweekhayinethikhi ze-ithelini kuphandwe ngokwezinga lokuqaqamba kokukhanya (0.0005 mW/m^2, 0.0014 mW/m^2, kunye no- 0.0021 mW/m^2) kunye nokufuma okukhoyo (RH) namanqanaba ako (20% kunye no80%), kwaze kwaphandwa nokubonakala ngokwezoshishino kwinkqubo yeVUV fotolayisisi. Iziphumo zibonise ukuba ukuthotywa kwe-ithelini kuye kwenyuka xa kunyuswe kakhulu ukuqaqamba kokukhanya. Kwakhona, ufukuma okukhoyo okukwizinga eliphezulu kubenefuthe elihle ekuthobeni i-ithelini. Omabini la maqondo okuqaqamba kokukhanya kunye nokufuma abenempembelelo enkulu kwiipharamitha zekhayinethi nasekuthotyweni kwe-ithelini ($p < 0.05$). Xa ukuqaqamba kokukhanya kusezantsi, ukuthotywa kwe-ithelini kulandele imodeli (umzekelo) yekhayinethi enguziro-oda (elandelelana ngeqanda/ngento engekhoyo), ngeli xesha xa ukuqaqamba kokukhanya kuphezulu, ilandela imodeli yekhayinethi yokulandelelana ngokweefrekhshini, okubonisa ukutshintsha okuthile kwinkqubo. Ukubonakala ngokwezoshishino kwenkqubo yeVUV fotolayisisi iye yaphandwa kusetyenziswa amandla ombane ngokokulandelelana (EEO), eye yahlala ingaphantsi ko10 kW m^{-3} $order^{-1}$, ibonakalisa ukusebenza kwamandla ngokufanelekileyo nangokubonakalayo.

Imodeli (umfuziselo) yezibalo iye yayilwa ukunika inkxaso kwisixhobo seVUV fotolayisisi nokukhuthaza ukunyuka nokuhla kwamaqondo obushushu ngaphakathi kuyo. Imodeli yokulinganisa umthamo omkhulu eyiliweyo ithekelele ngokuyimpumelelo ukuxinana kwe-ithelini enamaxabiso ayiR^2 ngaphezulu ko0.9. Nangona imodeli yokulingana kwamandla ithekelele ukuguquka kweqondo lobushushu ngokusezantsi ngaphakathi kwesixhobo, kodwa iyifumene ngokuchanekileyo iyonke indlela yokunyuka kweqondo lobushushu, ibonisa ubukho nokusebenza kwemodeli. Uhlalutyo olubuthathaka lwenzelwe ukuphanda iimpawu ezibalulekileyo ezichaphazela uyilo kunye nokusetyenziswa ngokugqibeleleyo kwesixhobo seVUV fotolayisisi. Ukuqaqamba kokukhanya kunye nobude besixhobo bufunyaniswe ibobona bunempembelelo ekuthotyweni kwe-ithelini. Ukwandiswa kokuqaqamba kokukhanya kunye nokuthotywa kobude besixhobo kuphucule ukususwa okufanelekileyo.

Ukuququmbela, esi sifundo sicacisa ngamathuba abalulekileyo eVUV fotolayisisi njengoyilo lobuchule bokususa i-ithelini ngexesha lokuhanjiswa nokugcinwa kweziqhamo nemifuno. Okufumanekileyo koluphando kucebisa ukuba iVUV fotolayisisi sisixhobo esithembisayo ekulawuleni isivuno, ikwanika necebo elisebenzayo lokugcina iziqhamo ezisemgangathweni kunye nokunciphisa ilahleko kwiintengiso zezilimo. Uphando lwexesha elizayo kufuneka luqwalasele kwiindlela zokukhusela iimeko zemingcipheko, ukuyila izixhobo zokuguqulela iokhsijini ibe ngumoya ococekileyo (ii-ozoni skrayibha), nokucocwa kweemodeli zekhayinethi ukuphucula ukusetyenziswa nokuphunyezwa kwale tekhnoloji.

Amagama angundoqo: Isivuno; iFotolayisisi; uLawulo lwe-Ithelini; UkuYekiswa kokusebenza kweMayikhrobhiyali; Ukuboniswa kweKhayinethikhi

ACKNOWLEDGEMENTS

‘Ndinokuzenza izinto zonke ndikulowo undomelezayo uKristu’ ***Kwabasefilipi 4:13***

I extend my heartfelt gratitude and appreciation to the following individuals, without whom this study would not have been possible:

- I extend my profound gratitude to my supervisor, Dr. Buntu Godongwana, for demonstrating faith in my abilities and bestowing upon me the remarkable opportunity to undertake this academic journey. I am deeply appreciative of the invaluable guidance and mentorship you have provided. Thank you for being a source of inspiration and for instilling confidence in my academic pursuits.
- I am profoundly indebted to Dr. Oluwafemi J. Caleb for providing me with the invaluable opportunity to contribute to this project. Words cannot adequately express my gratitude for the unwavering faith you placed in me, your constant guidance, and the motivation you instilled throughout this study. I will forever be thankful for your warm welcome into your research group and for creating an environment that fostered my growth. Your immeasurable contribution to this work is truly appreciated. Thank you for maintaining an open-door policy and always being available when I needed your support. Your mentorship has been instrumental in my academic journey. It is because of your encouragement and leadership that I am inspired to 'Keep walking' toward further accomplishments and academic excellence.
- I extend my sincere gratitude to Dr. Zinash A. Belay for her unwavering support throughout this study. Dr. Belay, you were my go-to person whenever I sought clarity, and your ability to simplify complex concepts was invaluable. I deeply appreciate your input, critical comments, and corrections on all the manuscripts generated during the course of this project. Your guidance has been instrumental in shaping the outcomes of this research. Enkosi sisi!
- I extend my sincere appreciation to my co-authors, whose significant contributions greatly enriched this project. A special thank you is reserved for Dr. Patricia Mathabe from the Royal Agricultural University, England, who has been an integral part of this project since its inception. My deepest gratitude goes to Dr. Pramod Mahajan and Dr. Namrata Pathak from the Leibniz Institute for Agricultural Engineering and Bioeconomy (ATB), Potsdam, Germany, for their invaluable contributions. Their expertise and commitment have played a pivotal role in the success of this collaborative endeavor.

- Dr. Myalelo Nomnqa, your assistance, guidance, and friendship were instrumental throughout this journey. Your expertise and unwavering support provided the answers I needed at every step.
- I express my heartfelt gratitude to the members of my research group, the 'Agri-Food Systems and Omics Laboratory' at the Agricultural Research Council (ARC) Infruitec-Nietvoorbij, Stellenbosch, for their unwavering support and friendship. The RRTF weekly meetings were instrumental in advancing this project, and I am thankful for the collective effort that significantly contributed to its successful completion. Indeed, it is true when they say ‘If you want to go fast, go alone. If you want to go far, go together.’
- My appreciation also extends to the lab technicians, Mrs. V. Combrinck, Ms. V. Fortuin, and Mr. H. Ruiters at the Postharvest iQ1 Lab, Agricultural Research Council, Infruitec-Nietvoorbij (PHATs), for their assistance with the analyses.
- I would like to thank the technical staff at the Department of Chemical Engineering at CPUT, Mrs. Hannelene Small and Mr. Alwyn Bester, for their assistance in acquiring the materials and design necessary for this project. Mr Bester, you are the Best!
- Special thanks to my parents, Xolani Ngwane and Weziwe Mabusela, who walked barefoot and wore ragged clothes, sacrificing so much that I could have the foundation essential to realize my dream. Your unwavering dedication and sacrifices have laid the bedrock for my journey. Your resilience, selflessness, and enduring love have shaped me into the person I am today. I am grateful for the sacrifices you made to provide me with the opportunities and support necessary to pursue my dreams. Your legacy of perseverance will forever inspire and guide me. Thank you for being the pillars of strength in my life.

DEDICATION

This thesis is dedicated to my unwavering support system—my parents, Xolani Ngwane and Weziwe Mabusela, whose sacrifices and encouragement have been the guiding lights throughout this academic journey; to my sister, Iviwe Mabusela, whose companionship and shared experiences have enriched my life; to my late grandmother, **Nomziwokuthula (Gumbi) Mabusela**, whose wisdom and love continue to inspire me, even in her absence; and to my children, Aluve Nyongwana and Akuminanye Phahla, who have been the joy and motivation behind my pursuit of knowledge.

RESEARCH OUTPUTS

Published articles

I. **Mabusela, B. P**., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, Mathabe, P. M. K., & Caleb, O. J. (2021). Trends in ethylene management strategies: towards mitigating postharvest losses along the South African value chain of fresh produce – a review. *South African Journal of Plant and Soil*, *38*(5), 347–360. https://doi.org/10.1080/02571862.2021.1938260.

II. **Mabusela, B. P**., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, & Caleb, O. J. (2022). Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of Fruit and Vegetables Along the Value Chains: a Review. *Food and Bioprocess Technology*, *15*(1), 28–46. https://doi.org/10.1007/s11947-021-02703-1.

III. **Mabusela, B. P**., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023). Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics and removal in mixed-fruit storage, and direct exposure to 'Fuji' apples during storage. *Journal of Food Science and Technology*. https://doi.org/10.1007/s13197-023-05775-3.

IV. **Mabusela, B**., Belay, Z., Godongwana, B., & Caleb, O. (2023). Application of VUV photolysis reactor and loss of firmness prediction for stored 'Fuji' apples. Acta Hortic. 1382, 9-16. DOI: 10.17660/ActaHortic.2023.1382.2

V. **Mabusela, B. P.**, Godongwana, B., Belay, Z. A., & Caleb, O. J. (2024). Ethylene degradation via vacuum ultraviolet photolysis: nth-order kinetic model, energy consumption assessment, and a case study for "Fuji" apples under retail conditions. Food and Bioproducts Processing, 147, 230–238. https://doi.org/10.1016/j.fbp.2024.07.006

Articles under review

VI. **Mabusela, B. P.**, Godongwana, B., Belay, Z. A., Mathabe, P.M.K & Caleb, O. J. (2024). Ethylene degradation via ultraviolet photolysis: Up-scaling reactor design and optimizing operating parameters. Submitted to **Food and Bioproducts Processing**.

VII. **Mabusela, B**., Belay, Z., Husselmann, L.H.H., Godongwana, B., & Caleb, O Proteomic Changes Associated with Ethylene Removal by Vacuum Ultraviolet (VUV) Photolysis for Apple Fruit During Cold Storage. **Under Review.**

PREFACE

This research was carried out at the Department of Chemical Engineering, Cape Peninsula University of Technology (CPUT), in collaboration with the Agricultural Research Council (ARC) - Infruitec Nietvoorbij, Stellenbosch. This dissertation comprises a collection of manuscripts, with each chapter standing as an individual entity. As a result, some degree of repetition between chapters was unavoidable. Chapters 1 and 8 are written according to the CPUT thesis guidelines, while Chapters 2 through 7 follow the writing and reference styles of the specific journals in which they were published or submitted.

Chapter One: This chapter provides an overview of the background and motivation behind the study. It outlines the problem statement, research questions, aim, objectives, and hypotheses.

Chapter Two: This chapter focuses on the literature review of ethylene biosynthesis and its effect on fruits and vegetables. The different conventional techniques for ethylene removal with their drawbacks are also discussed here.

Chapter Three: This chapter gives a comprehensive overview of VUV photolysis. It focuses on the mechanisms of VUV photolysis and the operating variables influencing its efficiency. Furthermore, it introduces the proposed mechanism for microbial inactivation.

Chapter Four: This chapter focused on the application of VUV photolysis for short-term storage of mixed fruits. The evaluation includes the assessment of VUV photolysis efficiency in degrading ethylene at various initial concentrations. A predictive model for estimating shelf life is also given.

Chapter Five: This chapter explores the prospect of utilizing VUV photolysis to suppress proteins and enzymes associated with early ripening. The approach involves a detailed proteomic analysis comparing treated and untreated apples, providing valuable insights into the efficacy of VUV photolysis in inhibiting ripening-related biological processes.

Chapter Six: This chapter focused on developing a kinetic model for ethylene degradation through VUV photolysis. The study takes a unique approach by adopting an nth-order kinetic model to capture the varied reaction mechanisms under different conditions. Additionally, the economic feasibility of the proposed reactor is assessed using the electrical energy per order (EEO) figure of merit, providing valuable insights into the energy efficiency and viability of the VUV photolysis system.

Chapter Seven: This chapter focused on developing a mathematical model for the reactor, which was used to simulate temperature and ethylene concentration profiles.

Additionally, the model was employed for sensitivity analysis to optimize the reactor's performance.

Chapter Eight: In this conclusive chapter, a concise summary of the study's key findings is presented. Additionally, the chapter offers insights into potential avenues for future research, outlining areas where further exploration and refinement of the VUV photolysis application in postharvest management could yield valuable contributions to the field.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER ONE:

INTRODUCTION

1 INTRODUCTION

1.1 Background

Ethylene is a naturally occurring plant hormone that has numerous effects on many fruits and vegetables at part-per-million (µL/L) and part-per-billion (ppb) concentrations. It is a colourless and odourless gas that is naturally produced as a by-product of plant metabolism and is also generated during the burning of hydrocarbons. Ethylene, even at very low concentrations (0.001 µL/ L), is responsible for the regulation of many aspects of growth and development of fruits and vegetables (Golden et al., 2014). The responses of harvested fruit and vegetables to endogenously produced and exogenously applied ethylene are numerous and they can be beneficial or detrimental (Saltveit, 1999). Generally, ethylene can influence the postharvest life of climacteric and non-climacteric fruits by inducing various physiological processes including undesirable ripening of fruits (Aprilliani et al., 2018). Fruit ripening involves a series of changes in colour, flavour, texture, aroma, and nutritional content, which affect quality, post-harvest life, and value (Tucker et al., 2017). The concentration of ethylene in the air of 0.1 µL/L is often cited as the threshold for physiological activity (Kader, 1985), however, the accumulated ethylene concentration in storage containers could be beyond 200 µL/L (Eschbach et al., 2000). Hence, reducing ethylene concentration during postharvest is crucial and can result in the extension of shelf-life, and a reduction of deleterious effects associated with accelerated ripening. According to Wills et al. (1999), the shelf-life of fruit and vegetables can be increased by up to 60% by reducing ethylene concentrations from 0.1 µL/L to > 0.005 µL/L. It is estimated that 10-30% of fruit and vegetables is lost after harvest because of undesired ethylene exposure (Warton et al., 2000a). Therefore, the development of new techniques and improvement of conventional techniques for the removal of ethylene during storage and transportation of fruit and vegetables is of fundamental importance to maintaining quality and increasing shelf-life of fruit and vegetables.

The removal of ethylene from storage systems is one of the major postharvest challenges in the horticultural industry. The conventional methods for ethylene removal include air ventilation, low-temperature storage, and controlled atmosphere (CA) (Watkins, 2006). However, excessive ventilation results in higher weight loss (Wills, 2015), CA is often expensive and sometimes problematic to accurately maintain low concentrations of ethylene. Other techniques include the use of different adsorbers/absorbers, the use of potassium permanganate ($KMnO_4$) (Aprilliani et al., 2018), oxidation with ozone, and catalytic oxidation (El Blidi et al., 1993, Smilanick, 2003). The use of adsorbing/absorbing materials (such as zeolites and activated carbon) and oxidizers such as $KMnO_4$ is not suitable for long-term storage and distant transportation because these materials may get rapidly saturated and require frequent replenishment. Also, $KMnO_4$ oxidation results in toxic residues thereby causing disposal problems, while catalytic oxidation requires high temperatures rendering the technique energy-intensive (Pathak and Mahajan, 2017). Although the application of ozone could be effective in CA storage, high ozone concentrations can be detrimental for stored fruits and to human health (Smilanick, 2003).

The limitations highlighted in the conventional techniques have necessitated the need to search for a more cost-effective and sustainable technique for the efficient management of ethylene. A review by Pathak and Mahajan (2017) highlighted the potential application of advanced oxidation techniques (AOPs) (photocatalytic oxidation (PCO), vacuum ultraviolet (VUV) photolysis and non-thermal plasma discharge) as promising emerging techniques for ethylene removal. As such, a substantial amount of research has been devoted to developing PCO systems for the reduction of ethylene (Sun, 2007, Chiara et al., 2015, Pathak et al., 2017a, Basso et al., 2018). Although the potential of PCO has extensively been studied, its application is still limited due to the associated drawbacks which include, the recombination of hole and electron, which results in the reduction of oxidized species (Malayeri et al., 2019), and the deactivation of the catalyst (Pathak et al., 2017a). These shortcomings have necessitated researchers to investigate the potential of other AOPs, such as VUV photolysis, as alternatives. Pathak et al. (2017b) investigated the effects of process variables on ethylene removal by VUV photolysis and later compared the efficiency of VUV photolysis and PCO for ethylene removal. The removal efficiency of 84.8% and 14.9% by VUV photolysis and PCO were achieved respectively. Another interesting observation was that VUV photolysis showed higher ethylene removal at high relative humidity (RH) while PCO was hindered. This positive observation makes the VUV process more advantageous for fruit storage as RH is often essential for the storage of fruits to reduce transpiration losses (Pathak, 2019). However, this technique is still at a fundamental stage, especially in postharvest treatment, and the degradation mechanisms are still not known.

Thus, for VUV photolysis to better compete with other novel techniques, a comprehensive fundamental study is warranted to gain insight into the governing mechanisms. Also, for VUV photolysis to find industrial application in the horticultural industry, the development of mathematical models that can improve the understanding of reactor performance and the evaluation of the intrinsic kinetic parameters that enable the scale-up or re-design of the VUV reactor is of utmost importance. Therefore, the aim of this study is to develop an integrated mathematical model that will enable VUV photolysis optimization and the better design of reactor systems for efficient ethylene removal, and hence enhance the shelf-life of fruit and vegetables.

1.2 Problem statement

Storage and transportation of fruit and vegetables after postharvest is a challenging task due to their fast ripening in the presence of ethylene gas which leads to deterioration. This could lead to rapid senescence due to discolouration and tissue softening effects on fruit and vegetables. Ethylene is not only released by neighboring crops and plants but also continuously produced from environmental emissions. The presence of ethylene in the storage environment, even in extremely low concentrations can trigger the fast senescence process that may increase post-harvest losses, which could reduce shelf-life and impact the quality of fruit and vegetables. This will result in a critical loss in profits for farmers, pack-houses, and retailers.

Approximately one-third of global fresh fruits and vegetables are thrown away because their quality has dropped below an acceptable limit (Gustavsson et al., 2011). Estimates suggest that about 10 million tons of food go to waste in South Africa every year. This accounts for a third of the 31 million tons of food produced annually. Of this loss, fruit and vegetables comprise 44% making them the largest contributor to food waste (Wwf-Sa, 2017). The need to feed an ever-increasing world population makes it obligatory to reduce the millions of tons of waste resulting from perishable fruits and vegetables. A considerable share of these losses is caused by the lack of proper ethylene management strategies during postharvest. In order to achieve the sustainable development goal of reducing waste by 50% by 2030 (Wwf-Sa, 2017), the South African fruit industry has identified the management of ethylene during postharvest as a research priority.

1.3 Rationale and motivation of study

The most widely used, cost-effective techniques for ethylene management—air ventilation and temperature control—are limited in their effectiveness for long-term storage. Although VUV photolysis is proposed as a promising alternative for efficient ethylene removal, it remains in the developmental stages, particularly within the horticultural industry. Recent comparisons of VUV photolysis to photocatalytic oxidation have shown favorable results (Pathak et al., 2019).

However, the underlying reaction mechanisms and intrinsic kinetics are not yet well understood, and the production of residual ozone has been identified as a significant limitation. Therefore, to design an efficient VUV reactor, it is crucial to gain a deeper understanding of these degradation mechanisms and to develop mathematical models that can be used to optimize reactor performance.

1.4 Research questions and hypotheses

The derived questions for this study are as follows:

- What is the effectiveness of VUV photolysis in the removal of ethylene and what is the subsequent impact on the quality of stored fruit?
- What is the impact of VUV photolysis on the proteins responsible for ethylene biosynthesis and proteins responsible for rapid ripening?
- Can an n-order kinetic model be employed to investigate the kinetics of ethylene removal?

The following hypotheses were formulated based on the research questions:

- The primary degradation pathway of ethylene is initiated through both direct and indirect photolysis.
- The VUV photolysis reactor is effective in removing ethylene and preserving the quality of apples.
- The humidity and ethylene concentration affect the efficiency of photolysis for ethylene removal.
- The kinetics of ethylene removal using a VUV photolysis reactor vary with operating conditions due to differences in the production of reactive species.

1.5 Aim and objectives

The aim of this study was to develop a mathematical model that could be used to optimize a VUV photolysis reactor for effective ethylene removal during the postharvest management of apples. The specific objectives of the study were:

- To investigate the effectiveness of the VUV photolysis reactor in removing ethylene during the storage of apples.
- To examine the impact of the VUV photolysis reactor on the physiological changes that occur during the storage of apples

- To investigate the ability of the VUV photolysis reactor to suppress enzymes and proteins responsible for early ripening.
- To formulate a mathematical model to describe the process of ethylene degradation facilitated by a VUV photolysis reactor.

1.6 Delineation of study

Photolysis is an emerging technology that shows promising potential to surpass conventional ethylene management techniques. Despite being a promising alternative, VUV photolysis is still in the fundamental stage of development, indicating the need for further work before it can find widespread industrial application. One crucial research area that demands special attention, before any industrial implementation, is understanding the reaction mechanisms and addressing the production of residual ozone. While these aspects require urgent attention, the study delineates from actively investigating the reaction mechanisms and addressing the issue of residual ozone.

CHAPTER TWO:

LITERATURE REVIEW (ETHYLENE MANAGEMENT TECHNOLOGIES)

Published as: **Mabusela, B.P**., Belay, Z.A., Godongwana, B., Pathak, N., Mahajan, P.V., Mathabe, P.M.K., & Caleb, O.J. (2020) Ethylene management technologies: Mitigating losses along the postharvest value chain of fresh produce - A review. *South African Journal of Plant and Soil*

2. ETHYLENE MANAGEMENT TECHNOLOGIES

Abstract

The management of ethylene during postharvest storage is of critical importance to fresh produce wholesalers and retailers. The management of ethylene is an important determinant of the quality and shelf life of fresh fruit and vehetable. Ethylene-blockinge blocking action and ethylene removal via potassium permanganate, photocatalytic oxidation and ozonation have been extensively researched and applied on a commercial scale to manage the impacts of ethylene postharvest. However, these techniques have certain inherent limitations that make them ineffective for long-term postharvest applications. This review therefore focuses on ethylene removal strategies during postharvest handling, and characterisation of the merits and demerits of such strategies. In addition, it provides an overview of emerging techniques such as photolysis, photocatalytic oxidation and ozone-assisted catalytic oxidation, as alternatives for ethylene management along the postharvest value chains. The intent of this review was to guide the development of more effective ethylene management technologies for long-term application in the South African fruit industry.

Keywords: Ozone-assisted catalytic oxidation, photolysis, storage, vacuum ultraviolet

2.1 Introduction

In South Africa, 44% of fruit and vegetables are wasted or lost before they reach the retail market shelves (WWF 2017). This magnitude of losses severely influences livelihoods, resulting in chronic malnutrition, micronutrient deficiencies, and growth disorders. However, fruits and vegetables are also a relatively cost-effective way to prevent micronutrient deficiencies and protect against deadly chronic diseases. Ethylene can be either beneficial or detrimental to fresh produce, depending on its functional role, initial concentration and the extent of exposure. If ethylene exposure to fresh produce is not well managed it could induce various physiological processes including senescence, leading to discoloration and softening, and increased susceptibility to decay (Saltveit 1999; Pathak et al. 2017a). According to Wills et al. (1999), reducing ethylene concentration from 0.1 $\mu L\ L^{-1}$ to > 0.005 $\mu L\ L^{-1}$ can increase the shelf life of FV by up to 60%. Hence, reducing ethylene concentration during postharvest can have a beneficial impact via the reduction in the deleterious effects associated with accelerated ripening. Nsumpi et al. (2019) conducted a routine mapping of ethylene hotspots within selected South African fruit packhouses and a questionnaire survey on ethylene management practices. The authors demonstrated from their survey that none of the pack-houses has any effective ethylene management strategy. Similarly, numerous ethylene hotspots were identified within the pack-houses without any removal strategy besides ventilation. Furthermore, Nsumpi et al. (2020) established that mixed-fruit loading without effective ethylene management can have a negative impact on fruit quality and storage life.

Table 2.1 summarizes the scope of existing review articles on ethylene management strategies published over the last two decades. None of these reviews offered an integrated postharvest ethylene management approach for South Africa’s horticultural industry, pack-houses or retail outlets. Thus, the aim of this review is to provide a critical evaluation of the current technologies used for ethylene removal, taking into consideration their merits and limitations to guide emerging researchers. Furthermore, the potential of integrating emerging techniques such as vacuum ultraviolet light (VUV) photolysis and photocatalytic oxidation (PCO) for ethylene management along the South African postharvest value chains was highlighted.

Table 2.1: List of review articles on ethylene management published within the last two decades

Review focus/scope	Horticultural Commodity	Technology limitations for long-term storage	Reference
Adsorbers combined with catalyst	Fruit and vegetable	Rapid saturation on frequent replenishment	Martinez-Romero et al. (2007)
Photocatalysis (PCO)	Fresh produce	Catalyst surface saturates over time	Keller et al. (2013)
Ozone	Fruit and vegetable	Harmful to human	Miller et al. (2013)
1-methylcyclopropene (1-MCP)	Climacteric fruit	Not effective against exogenous ethylene	Zhang et al. (2017)
Absorbent	Fruit and vegetables	Rapid saturation on frequent replenishment	Álvarez-Hernández et al. (2017)
Potassium permanganate ($KMnO_4$)	Blueberries	Produces waste residues and toxic by-products	Álvarez-Hernández et al. (2019a)
Phtotocatalysis and photochemical oxidation	Fresh produce	Electron-hole recombination and ozone production	Pathak (2019)
Absorbent	Fresh produce	Suffer from adsorption capacity and requires frequent replenishment	Gaikwad et al. (2019)
1-MCP, PCO, $KMnO_4$	Fresh produce	Not effective against exogenous ethylene Electron-hole recombination Produces waste residues	Sadeghi et al. (2019)

2.2 Role of ethylene during ripening of fruit and vegetables

Ethylene is responsible for many aspects of plants life cycle including growth, development and storage life. Even at very low concentrations (0.001 µL L^{-1}), ethylene is responsible for the regulation of many aspects of growth and development of fruit and vegetables (Golden et al., 2014). Therefore, to understand the role of ethylene, knowledge of how and when the hormone is produced and regulated is crucial. Fruit are classified into two categories based on their respiration and ethylene production behaviour during maturation and ripening. Ripening is the process by which fruit attain their desirable flavour, quality, colour, palatable nature and other textural properties. Fruit that produces a burst of ethylene when they ripen and show an increase in respiration rate are described as. Generally, during ripening, climacteric fruit undergo changes in colour, flavour, texture, aroma, and nutrient content, which in turn affect the quality and postharvest life (Tucker et al., 2017). All these changes could be induced by endogenous or exogenous ethylene production.

In contrast, non-climacteric fruit are those for which ripening does not occur after harvest. For non-climacteric fruit, there is no significant respiration burst during postharvest and ethylene production is minimal. As such, fruits and vegetables are classified according to their ethylene production rate. Fruit such as tables grapes, strawberry, pomegranate and cherry produce very low (< 0.1 µL Kg^{-1} h^{-1}) amounts of ethylene while banana, tomato and mango produce moderate amounts of ethylene between the ranges of 0.1 – 1 (µL Kg^{-1} h^{-1}). Although the exposure of most fruit and vegetables to ethylene accelerates their senescence, there is no consistent relationship between the ethylene production capacity of a given commodity and its perishability (Kader, 2002). As such, the perishability of a commodity depends on various variables such as duration of exposure, temperature, concentration of ethylene, sensitivity to ethylene, atmospheric composition and type of commodity.

The responses of harvested fruit and vegetables to endogenously produced and exogenously applied ethylene are numerous and varied (Palou et al., 2003). Exposure to ethylene can be via endogenous (i.e. biological) or exogenous (i.e. non-biological and biological) sources. The impact of ethylene on fruit and vegetables may be considered beneficial or detrimental depending on the extent of exposure fruit and the type of product. Generally, ethylene can influence the postharvest life of both climacteric and non-climacteric fruit by affecting their quality attributes and the development of physiological disorders and postharvest diseases. Some of the detrimental effects of ethylene include acceleration of physiological disorders, excessive softening, over ripening and colour change.

The quality attributes of pears stored at -1 and 2 °C with 0, 1, 5 and 10 µL L^{-1} ethylene were studied by Bower et al. (2003). It was found that all concentrations of ethylene increased the incidence of physiological disorders. In another investigation by Nguyen et al. (2000), ethylene concentrations of 0, 10, 100 and 1000 µL L^{-1} were applied to green mature mangoes to evaluate the extent of colour change at 15, 20 and 25 °C. The authors confirmed that colour change increased with increasing ethylene concentration. On the other hand, Abe and Watada (1991) observed undesirable effects of ethylene on the quality of kiwifruits, bananas, broccoli and spinach leaves. Bananas and kiwifruits kept at 20 °C and treated with 2 or 20 µL L^{-1} ethylene showed accelerated softening. However, the rate of softening was reduced with the use of charcoal with palladium chloride, which acted as an ethylene absorbent. The effect of ethylene gas on the ripening and quality of tomatoes during cold storage was studied by Dhall and Singh (2013). Green tomatoes were exposed to ethylene gas (100 µL L^{-1}) for 24 hours at 20 °C and 90-95% RH. Treatment with ethylene gas resulted in adequate ripening of tomatoes with uniform red colour, desirable firmness, minimum rotting and acceptable quality. Also, 'Kensington pride' mango exposed to 0.1 µL L^{-1} ethylene for 12 days at 20 °C and 100% RH demonstrated adequate firmness and reduced RR (Pristijono et al., 2018). Generally, it could be deduced that the effect of ethylene on fruit and vegetables is dependent on the type of produce, ethylene concentration and storage conditions.

2.3 Trends in ethylene management strategies during postharvest

Table 2.2 summarises studies done during the last ten years on assessing the beneficial impacts of removing ethylene during storage on fruit and vegetables. Commercial strategies and best postharvest practices for the handling of fruit and vegetables are based on various principles. These include; (i) inhibiting ethylene biosynthesis or production and minimising or eliminating ethylene action during fruit ripening and harvest; (ii) avoiding exposure of the fresh product to ethylene (control); and, (iii) active removal or scrubbing of ethylene during storage and distribution (Watkins 2002; Pathak et al. 2017b,c). There are various technologies linked to these principles as summarised in Table 2.3. However, most are not suitable for long-term storage, where it is necessary to continuously remove ethylene, during transportation over long distances or in closed storage facilities. Therefore, the development of new technologies that will ensure continuous ethylene removal is imperative.

Table 2.2: Benefits of removing ethylene on the quality of fruit and vegetables.

Commodity	Beneficial impact	Reference
Strawberry	Maintained fruit quality for 15 d	Abdollahi et al. (2013)
Apple	Delayed ripening	Deyman et al. (2014)
Tomato	Decreased firmness	Li et al. (2014a)
Papaya	Suppressed respiration, reduced mass loss and delayed changes in peel colour	Li et al. (2014b)
Banana	Delayed ripening process	Zhu et al. (2015)
Mango	Delayed softening, decreased citric acid level and total sugars	Razzaq et al. (2016)
Green leafy vegetable	Delayed senescence	Al Ubeed et al. (2017)
Mango	Reduced mass loss and delayed ripening	Elzubeir et al. (2017)
Nectarine	Delayed ripening, reduced respiration and retained higher firmness	Bal (2018)
Kiwifruit	Reduced softening and development of skin darkening	Gabioud et al. (2018)
Broccoli	Reduced loss of chlorophyll and maintained texture and chemical composition	He and Xiao (2018)
Strawberry	Improved shelf life	Matar et al. (2018)
Mangoes	Delayed skin degreening and suppressed respiration	Pristijono et al. (2018)
Pineapple	Reduced peduncle mould	Sabater-Vilar et al. (2018)

Table 2.3: Ethylene management strategies applied along the post-harvest value chain of horticultural commodities within the last two decades.

Principle	Strategies	Type of produce	Major outcomes	References
Inhibition	*H_2S fumigation*	Mulberry fruit (*Morus indica* L. cv. Dianmian-1)	• H_2S fumigation was able to slow down decreases in soluble protein, titratable acidity and ascorbate contents.	Hu et al. (2014a)
		Fresh-cut pears (*Pyrus pyrifolia* cv. Dangshan)	• Extended the shelf life of fresh-cut pears (dose-dependent), maintained higher levels of reducing sugar and soluble protein and minimised the accumulation of hydrogen peroxide (H_2O_2).	Hu et al. (2014b)
		Broccoli florets (*Brassica oleracea* var. *italica*)	Maintained higher levels of carotenoids, anthocyanin, and ascorbate, reduces the accumulation of MDA, H_2O_2, and superoxide anion, down-regulated chlorophyll degradation-related genes.	Li et al. (2014b)
		Strawberry (*Fragaria ananassa* L. cv. Fengxiang)	• Inhibited respiration rate and maintained crust colour and minimised fruit decay.	Zhang et al. (2014)
		Fresh-cut apples (*Malus ×pumila cv.* Fuji)	• Maintained higher levels of ascorbic acid, flavonoids, total phenolics, reducing sugars, soluble proteins and down-regulated genes associated with senescence.	Zheng et al. (2016)

Principle	Strategies	Type of produce	Major outcomes	References
		Kiwifruit (*Actinidia deliciosa* cv. Qinmei)	• Effectively alleviated ethylene-induced fruit softening and oxidative stress, attenuated the activity of polygalacturonase (PG), lipoxygenase (LOX), polyphenol oxidase (PPO) and amylase.	Li et al. (2017c)
	Nitric oxide (NO)	Pak choy plants (*B. rapa subsp. Chinensi* cv. Shanghai), Italian basil (*Ocimum basilicum*), and green curly kale (*B. oleracea* var. sabellica)	• Inhibited ethylene production, respiration, mass and chlorophyll loss, reduced various antioxidant factors, total phenols and ion leakage and increased market life of green leafy vegetables.	Al Ubeed et al. (2017)
		Strawberry (*F.* × *ananassa* Duch. cv. Sweet Charlie)	• Maintained higher fruit firmness and titratable acidit, inhibited the loss in extractable juice via the modification of water mobility.	Zhi et al. (2018)
		Oranges (*Citrus sinensis* cvs. Valencia and Navel)	• The treatment reduced the incidence of calyx drop, calyx browning and fungal decay.	Alhassan et al. (2020)
		Strawberry (*F.* × *ananassa* Duch. cv. Selva)	• Maintained fruit quality for 15 days and delayed postharvest decay.	Abdollahi et al. (2013)

		Litchi (*Litchi chinensis* Sonn cv. China)	• Significantly reduce the pericarp browning, mass loss, MDA content and delayed loss of total soluble solids, titratable acidity, and ascorbic acid.	Barman et al. (2014)
		Papaya (*Carica papayas* cv. Sui you 2)	• Suppressed ethylene production and respiration, reduced mass loss, maintained firmness and delayed changes in peel colour.	Li et a. (2014c)

Principle	Strategies	Type of produce	Major outcomes	References
	Nitric oxide (NO)	Banana (*Musa* spp., AAA group cv. Brazil)	• The nitric oxide treatment increased chilling tolerance of banana fruit due to improved antioxidant enzyme, induced expression of antioxidant related genes and decreased the accumulation of reactive oxygen species (ROS).	Wu et al. (2014)
		Mango (cv. Tainong)	• Nitric oxide treatment suppressed the respiration rate, enhanced firmness, and decrease rot index and mass loss of mango fruit. • The treatment enhanced the antioxidant activities and reduced accumulation of MDA, superoxide anion radical and H_2O_2	Ren et al. (2017)
		Oranges (*C. sinensis* cv. Navel)	• Nitric acid treatment induced the activity of several antioxidant enzymes, reduced the incidence of chilling injury in orange fruit	Ghorbani et al. (2018)

			• The treatment also reduced the lipid peroxidation levels and H_2O_2 contents of the peel and pulp during storage.	
		Oranges (*C. sinensis* cvs. Midknight Valencia and Lane Late sweet)	• Nitric acid treatment reduced the concentrations of glucose, fructose, sucrose and total sugars in "Midknight Valencia" only, where as, the treatment was effective to reduce the mass loss of both cultivars compared to the control.	Rehman et al. (2019)
	1-MCP	Pears (*Pyrus communis* L. cvs. Bartlett and d′Anjou)	• 1-MCP treatment was effective to suppressed respiration and substantially to decreased superficial scald during storage.	Bai et al. (2006)

Principle	**Strategies**	**Type of produce**	**Major outcomes**	**References**
	1-MCP	Pears (*P. communis* L. cvs. Bartlett)	• The treatment decreased the rate of respiration and ethylene production, softening, and yellow colour development on pear fruit.	Villalobos-Acuna et al. (2011)
		Broccoli (*Brassica oleracea* var. *Italica* cv. Cicco)	• 1-MCP treatment selectively inhibited some of the genes encoding enzymes related chlorophyll catabolism, induced a higher expression of *BoCLH2,* thus resulted delayed degreening and chlorophyll degradation.	Gómez-Lobato et al. (2012)

		Jujube fruit (*Zizyphus jujuba* cv. Huping)	• 1-MCP treatment significantly induced the activities of phenylalanine ammonia-lyase (PAL), PPO, catalase (CAT) and superoxide dismutase (SOD). • The treatment was also effective to reduced the growth of blue mould rot and incidence of natural decay.	Zhang et al. (2012)
		Apple (*Malus domestica* Borkh. cv. Empire)	• 1-MCP treatment delayed ethylene mediated ripening of apple during control atmosphere storage. Furthermore, the treatment resulted lowering the level of total putrescine, total spermine, inhibit 4-aminobutryrate (GABA), whereas, stimulated the glutamate decarboxylase activity.	Deyman et al. (2014)
		Tomato (*Solanum lycopersicum* cv. Ailsa Craig)	• The treatment delayed ethylene production and strongly inhibited the polygalacturonase activity.	Li et al. (2014a)

Principle	Strategies	Type of produce	Major outcomes	References
		Banana (*Musa* spp. cv. Brazil)	• Effectively delayed and decreased respiration rate and ethylene production. • The treatment also inhibited the activity of pectin lyase (PL), pectin methylesterase (PME), cellulase (CX) and polygalacturonase (PG), and delayed the peak activity of ACC synthase (ACS) and ACC oxidase (ACO).	Zhu et al. (2015)

		Nectarines (*Prunus persica* cv. Maria Aurelia)	• 1-MCP treatment reduced the ethylene production and respiration rate of nectarine during cold storage (0 °C) and shelf life (20 °C). • Reduced the incidence of chilling injury, significantly reduced enzyme activities, colour and the activities of PPO, PG, and PEM.	Özkaya et al. (2016)
		Mango (*Mangifera indica* L. cv. Kenington Pride)	• Activities of softening enzymes significantly inhibited and ripening delayed by the 1-MCP treatment. The treatment further effectively decreased citric acid, malic acid, succinic acid and total organic acids level and total sugars.	Razzaq et al. (2016)
		Plum (*Prunus salicina* Lindl. cv. Songold)	• The treatment reduced firmness loss, colour changes, impact of chilling injury, where as maintained fruit acidity.	Velardo-Micharet et al. (2017)

Principle	**Strategies**	**Type of produce**	**Major outcomes**	**References**
Minimizing exposure	*Cold temperature*	Plum (*P. salicina* Lindl. cv. Younai)	• 1-MCP treatment lowered the activities of cell wall degradation enzyme and content of water soluble pectin, whereas, maintained higher contents of cell wall polysaccharides, thus retarded softening development.	Lin et al. (2018)

Principle	Strategies	Type of produce	Major outcomes	References
		Green vegetables (pak choi, broccoli, mint, and green bean)	• Chilling injury for green bean, increased as the storage temperature increased even with decline in ethylene concentration	Li et al. (2017c)
		Banana (*Musa acuminata colla* cv. Raja Sere)	• Cold storage (13 °C) increased the shelf life of banana by 12 d compared to 6 d for the banana stored at room temperature (28 °C)	Crismas et al. (2018)
	MAP	Broccoli (*B. oleracea* var. *italica*)	• MAP treatment reduced loss of green colour and maintained texture and chemical composition. • The treatment maintained the acceptable sensory score for 25 d, compared with only ~ 15 d for control samples.	He and Xiao (2018)
		Strawberry (*F.* × *ananassa* Duch. cv. Charlotte)	• Extended shelf life	Matar et al. (2018)
	MA/CA storage	Mangoes (*M. indica* L. cvs. Haden and Tommy Atkins)	• Low O_2 enviroment slightly reduce ethylene production • ‘Haden’ fruit also showed a residual inhibitory effect on ethylene production after 2 or 3 kPa O_2 storage • ‘Tommy Atkins’ fruit stored in 2 kPa O_2 produced a burst of ethylene upon transfer to air at 20 °C	Bender et al. (2000)
		Mango (*M. indica* L. cv. Delta R2E2)	• CA storage (6% CO_2 and 3% O_2) allowed the fruit to ripen normally with a yellow skin colour, good taste, high TSS, TSS/acid ratio, and a high total sugars content, resulted extended shelf-life of mango fruit for 38 d.	Lalel et al. (2005)

		Bananas plantain (*Musa paradisiacal* L. cv. French)	• MA or CA ? Reduce ethylene production and enhanced the shelf life of the plantain.	Agoreyo et al. (2007)
		Pear (*Pyrus bretschneideri* Rehd. cv. Zaosuli)	• Reduce ethylene production • Thirteen volatile compounds were found to differentiate CA treatment from control	Goliáš et al. (2016)
		Avocado (*Persea americana* Mill. cv. Hass) and Strawberry (*F. x ananassa* Duch. cv. Sonata)	• Irrespective of timing, respiration and ethylene production of avocados stored at 20 °C was reduced under CA storage while regular atmosphere had higher ethylene production. CA storage maintained the avocado skin colour and internal discolouration. • Strawberry were firmer and maintained a more vibrant colour despite bursts of increased respiration rate	Alamar et al. (2017)
		Apple (*M. domestica* cv. Jonagold) and Pear (*P. bretschneideri* Rehd. cv.	• CA condition of 0.5 kPa O_2 + 6.0 kPa CO_2 was most effective in suppressing ethylene production, respiration rate and resulted higher respiratory quotient	Saquet and Streif (2017)

Principle	**Strategies**	**Type of produce**	**Major outcomes**	**References**
	Bio-filter	Bananas (*Musa acuminata colla*)	• Reduced ethylene production by a factor of two and reduced the autocatalytic process of ethylene.	Moghadam et al. (2015)

Principle	Strategies	Type of produce	Major outcomes	References
Ethylene scrubbers	*Zeolite or $KMNO_2$ or $KMNO_2$- or zeolite-based matrix*	Papaya (*Carica papaya*)	• specify the treatment delayed reduction firmness and significantly extended shelf-life of the fruit	Corrêa (2005)
		Kiwifruit (*A. deliciosa* cv. Hayward)	• same here and below Delayed degreening and maintained firmness	Ramin et al. (2010)
		Apple (*M. domestica* cv. Golden Delicious)	• Delayed mass loss, slowed firmness loss and retarded the ripening process.	Sardabi et al. (2014)
		Tomato (*S. lycopersicum* L. cv. Chonto)	• Delayed ripening, retained higher firmness, and reduced respiration rate	Salamanca et al. (2014)
		Nectarine (*P. persica* cv. Bayramiç Beyazı)	• Delayed fruit softening, and extended shelf life.	Bal (2018)
		Tomato (*S. lycopersicum* L. cv. Valouro)	• Effectively removed ethylene and delayed ripening	Mansourbahmani et al. (2018)
		Tomato (*S. lycopersicum* L. cv. Medano)	• Reduced ethylene production by a factor of two • Reduced the autocatalytic process of ethylene	De Bruijn et al. (2020)
		Fresh-cut celery (*Apium gravelens* L.)	• Reduced respiration rate.	Zhang et al. (2005)
Principle	**Strategies**	**Type of produce**	**Major outcomes**	**References**
		Tomato (*S. lycopersicum* L. cv. Carousel)	• Maintained soluble sugars, increased β-carotene, lutein, and lycopene contents, maintained fruit firmness.	Tzortzakis et al. (2007)

Ozone	Papaya fruit (*Carica papaya* L. cv Sekaki)	• The fruit treated with ozone had lower respiration rate and delayed ripening compared to the control	Ong et al. (2014)
	Mango (*M. indica* L. cv. Nam Dok Mai No. 4)	• Significantly decreased the respiration rate and Initially decreased ethylene production.	Tran et al. (2015)
	Black mulberry (Morus nigra cv. Dashi)	• Ozon treatment resulted higher levels of titratable acidity and total soluble solids of back mulberry. The treatment further assisted in better retention of colour, firmness and Retarded respiratory intensity and decay rate.	Han et al. (2017)
UV-C	Mangoes (*M. indica* L. cv. Kensington Pride)	• UV-C treatment delayed mango skin degreening, reduced endogenous ethylene production, suppressed respiration and lowered chlorophyll content.	Pristijono et al. (2018)
	Tahitian limes (*C. latifolia*)	• The treatment maintained lime peel green colour, low ethylene production and low respiration rates and retained calyx attachment after 28 days storage.	Pristijono et al. (2019a)
	Sweet cherry (*P. avium* L. cvs. Sweetheart and Lapin)	• UV-C treatment significantly lowered the levels of postharvest rot on the sweet cherry and resulted greater firmness retention for 'Lapin' relative to the control.	Pristijono et al. (2019b)

2.4 Ethylene inhibitors

2.4.1 *Hydrogen sulphide (H_2S)*

Hydrogen sulphide (H_2S) has recently been identified as a gaseous plant growth regulator that can also inhibit fruit ripening and senescence programs in numerous fruit (Ubeeda et al., 2017). The application of H_2S has been shown to participate in measures preventing ethylene-induced stomatal closure, however, the signaling pathways of H_2S and interaction with ethylene are still unclear (Jia et al., 2018). Similarly, the effects of fumigation with 250 µL L^{-1} H_2S and 10 µL L^{-1} 1-MCP on a range of factors associated with senescence was compared for the leafy vegetable, pak choy stored at 10 °C and under-ventilated ethylene free-air or air containing 0.1 µL L^{-1} ethylene by Ubeed et al. (2018). The authors showed that both H_2S and 1-MCP were effective in inhibiting the loss of green colour, ion leakage, respiration and endogenous ethylene production for pak choy under ethylene-free air conditions. However, for containers ventilated with ethylene, treatment with 1-MCP was more effective in maintaining pak choy quality and inhibiting ethylene production compared to treatment with H_2S. Effects of fumigation with H_2S on horticultural commodities are summarised in Table 2.3.

The extension in postharvest storage life due to H_2S is attributed to the inhibition of various actions associated with senescence (Fotopoulos et al. 2015). H_2S is believed to be involved in the inhibition of endogenous ethylene production and of the actions of ethylene (Al Ubeed et al. 2018). The possible role and mechanism of H_2S in prolonging storage life and conserving the quality of fruit and vegetables have been recently reviewed by Ziogas et al. (2018) and Ali et al. (2019). However, in-depth research is still needed to standardize the optimal application of H_2S for fresh produce. In addition, the commercial use of H_2S as a fumigant for fresh produce poses logistical and safety issues and it is regulatory approval remains unresolved. An alternative approach would be the use of precursors of H_2S such as cysteine (Ali et al., 2019; Ziogas et al. 2018).

2.4.2 *Nitric oxide (NO)*

Nitric oxide (NO), is a highly reactive free radical gas and acts as a multifunctional signaling molecule in various plant physiological processes, such as fruit ripening and senescence (Aghdam et al. 2019; Wang et al. 2017b; Wendehenne et al. 2004). Optimum NO concentrations have been reported to delay the climacteric phase of many tropical fruits and prolong the postharvest storage life by impeding ripening and senescence, as well as suppressing the biosynthesis of ethylene (Table 2.3). The successful application of NO is well documented in the literature for horticultural commodities (Manjunatha et al. 2012; Singh et al. 2013; Wang et al. 2016).

Zaharah and Sing (2011) investigated the effect of NO at a concentration varying from 0 – 40 µL L^{-1} for mango cv. "Kensington" stored for 4 weeks at 5 °C. The results of this study indicated that NO treatments significantly alleviated chilling injury, ethylene production and respiration during storage. Selecting the optimum concentration of NO for a particular fresh produce should be based on factors such as their ethylene sensitivity, which can have a significant impact on quality and shelf life**.** In addition, the application of NO during postharvest is limited due to the need for ultralow O_2 concentration during the application of NO treatment to minimize its oxidation.

2.4.3 *1-methylcyclopropene (1-MCP)*

1-methylcyclopropene is an ethylene action inhibitor. It acts directly on the endogenous capacity of ripening by fixing the ethylene receptor and thus prevents its coupling (Velardo-Micharet et al. 2017). It is used to delay the ripening process and to extend the shelf life of climacteric fruit (Luo et al. 2008; Watkins 2006). Han et al. (2014) demonstrated that the application of 1-MCP treatment inhibited ethylene production and maintained ascorbic acid, soluble protein content, and antioxidant enzyme activities of bitter melon cv. "Duobaol" stored at 20 °C and 85-90% RH. Sun et al. (2012) reported that 1-MCP treatment effectively extended the shelf life of Chinese kale cv. "Bailey" by delaying the mass loss, chlorophyll degradation and colour change, as well as minimising the rate of softening.

Various studies demonstrated a positive impact of postharvest 1-MCP treatment on fresh produce (Table 2.3). However, its effectiveness varies depending on factors such as cultivar, ripening stage, fruit dry matter content, time and temperature of application, and harvesting season (Pan et al. 2016; Villalobos-Acuna et al. 2011). For instance, Bower et al. (2003) reported accelerated rot development in 1-MCP-treated strawberry fruit. Similarly, Jiang et al. (2001) demonstrated the onset of disease in fruit treated with 1.0 µL L^{-1} 1-MCP and stored at 5 °C. These results suggest that the effect of 1-MCP treatment to block ethylene could have a negative influence on fruit disease resistance, hence, further studies are needed.

2.5 Minimizing exposure to ethylene

2.5.1 Storage temperature

Storage of fruit at a low temperature is probably the most simple and effective means of controlling ethylene production and reducing the overall metabolisms (Watkins, 2002) and consequently delaying the parameters associated with fruit ripening and quality degradation. The RR of fruits is regarded as the main parameter defining the metabolic activity (Wills et al., 2007b). Storage at a low temperature is associated with delaying the onset of ripening by reducing the rate of deterioration, ethylene production rate and RR (Wills et al., 2007a). It is therefore important that fruit and vegetables be stored at low temperatures to decrease all metabolic activities and biochemical reactions during postharvest handling to maintain thier quality.

Four non-climacteric green vegetables (pak choi, broccoli, mint, and green bean) were stored at 0, 5, 10 and 20 °C in an atmosphere containing 0.001, 0.01, 0.1, and 1.0 μL/L ethylene as reported by Li et al. (2017). The results showed that the postharvest life as determined by consumer acceptance criteria of yellowing for pak choi and broccoli, leaf abscission for mint, and pod softening and chilling injury for green bean, increased as the temperature and ethylene concentration decreased. Álvarez-Hernández et al. (2019b) studied the effect of KMO_4 scrubber on the main quality attributes of 'Duke' blueberry fruit during storage at 2 and 10 °C for 46 days. The shelf-life of fruit stored at 2 °C was extended by 25 days while at 10 °C the shelf-life was extended by 14 days. Crismas et al. (2018) investigated the effect of cold storage on the quality of bananas stored at 13 °C for 0, 3, 6, 9 and 12 days. The ripening process was initiated by injecting 100 ppm of ethylene gas at 25 °C for 24 hours. The shelf-life of banana stored at 13 °C was increased by 12 days compared to 6 days for the banana stored at room temperature (28 °C). The effect of low-temperature storage at 0 and 20 °C for 30 days with and without a passive modified atmosphere packaging (MAP) and the effect of a freezing storage at -20, -40 and -80 °C for 10 months followed by 1 week at 5 °C on overall quality of 'Deglet Nour' dates was studied by Jemni et al. (2019). The use of MAP did not have any effect at 0 °C storage while it showed favorable effects at 20 °C. It was also found that storage at 0 °C -20, -40 and -80 °C all reserved the overall quality of dates better and -20 °C was considered the most adequate temperature for a long-term freezing storage period. Although storage at low temperature could extend the shelf-life of most fruits, storage at extremely low temperatures (>2 °C) might induce physiological disorders and chilling injuries to some fruits.

A study by Jiang et al. (2004) was conducted to compare ethylene binding during storage of banana at chilling (3 and 8 °C) versus optimum (13 °C) temperatures. It was found that the skin of banana fruit stored at 3 and 8 °C gradually darkened as storage duration was increased while banana fruit stored at 13 °C for 8 days showed no chilling injury. The main reason for the different observations in the study is attributed to the fact that low temperatures result into chilling injury of most fruits due to their sensitivity to low temperatures, thus bananas stored at optimum temperature (13 °C) showed no chilling injury. Therefore, appropriate temperature management is crucial to avoid chilling injuries and to improve fruit quality. Although temperature storage is well practiced and very common, its efficiency in maintaining the shelf life of produce is depended on the type of produce and other storage conditions such as RH, therefore strict measures and tools need to be considered, depending on the produce to be stored, before opting for low temperature storage.

2.5.2 Controlled/Modified atmosphere systems

Controlled atmosphere (CA) storage involves adjusting and maintaining an atmospheric composition different from that of air. This is achieved by decreasing O_2 and increasing CO_2 levels. Generally, O_2 below 8% and CO_2 above 1% are used, but these values depend on the type of commodity (Kader, 2004). Goliáš et al. (2016) studied the effect of CA storage on the production of ethylene from pears. The pears were stored at 1-1.5 °C under two different experimental atmospheres. The CA had low oxygen (2.0%) and high CO_2 (7%), while the regular atmosphere (RA) had 20.9% O_2 and 0.1% CO_2. The results showed that ethylene production was lower in the CA experiment. Similar results were observed for the storage of plantain under CA conditions compared to fruit held at RA (Agoreyo et al., 2007). Pigment changes in parsley leaves during storage in a controlled atmosphere (10% O_2 and 10% CO_2) or ethylene-containing atmosphere (air + 10 ppm ethylene) were studied by Yamauchi and Watada (1993). Although chlorophylls a and b decreased sharply in leaves held in air + 10 ppm ethylene, the decrease was much less in leaves held in 10% O_2 and 10% CO_2. The suppression of ethylene production in CA storage is due to the decreased levels of O_2, which is responsible for retarding the activation of ACC oxidase, which hinders ethylene biosynthesis. Although CA storage has been used in many studies, extremely low O_2 and high CO_2 levels may result in unexpected physiological disorders due to the occurrence of anaerobic respiration (Abdalnoor, 2015). It is important to mention that CA storage needs a special infrastructure, which is often capital intensive to set up in the South African context, whereas, MA can be easily used in standard storage room.

2.6 Active ethylene removal

2.6.1 Bio-filtration

Bio-filtration is another technique of ethylene removal that requires low energy consumption. It utilizes a biologically active filter material such as layers of compost, peat or soil that contains ethylene-degrading microorganisms (Kim, 2003). The contaminant flows through a packed bed where the pollutants are transferred into a thin biofilm at the surface of the packing material. The pollutants are then consumed by microorganisms and transformed into odourless compounds such as carbon dioxide, water and organic biomass (Devinny et al., 1999). The use of biological catalysts for the removal of ethylene in horticulture has been proposed since the early 80s (Sherman, 1985) but very few papers have been published on its potential for ethylene removal and its application in real storage and transport conditions is scarce (Keller et al., 2013a).

The use of a biofilter for the removal of ethylene was explored by Elsgaard (1998). Isolated ethylene-oxidizing bacteria were immobilized on peat soil in a biofilter and subjected to atmospheric gas flow (73.3 mL/min) with 2 or 117 ppm of ethylene. The biofilter was successful in eliminating ethylene to levels of 0.017 ppm after operation with 2.05 ppm of ethylene for 16 days. The effect of low temperature on the efficiency of a biofilter for ethylene removal was also investigated by Elsgaard (2000). The resulting removal efficiencies achieved at 20, 10 and 5 °C respectively were 99.0, 98.8 and 98.4%. The removal efficiency dropped to 83% when the temperature was lowered to 2 °C. This could be due to the slow activity of the bacteria at such low temperatures. A bench-scale biofilter for ethylene removal from artificially contaminated air by a natural zeolite as a filter, for potential use in horticultural facilities, was evaluated by Fu et al. (2011). The biofilter was successful in removing 100% of ethylene at loading rates of 0.26 – 3.76 g/m^3h when operated with inoculum containing enriched ethylene-degrading bacteria. The potential of biofilters with different packing materials to remove ethylene in order to increase the storage life of bananas was studied by Moghadam et al. (2015). The results showed that the column packed with active sludge, peat wood chips and humus with organic soil had higher ethylene removal rates. Most of the above studies were conducted to test the potential of the technology for ethylene removal as such, application of the technique on real storage conditions is scarce.

Ethylene removal by biofilters is economically and environmentally more advantageous than chemical and physical methods. However, biological systems are slow processes and may have problems of pressure drop and also require a larger area, which may limit their commercialization. Another major drawback of bio-filtration is finding a readily accessible and cheap substrate. These shortcomings of bio-filters may limit their commercialization. Thus, further research about the efficacy of biofilters in reducing ethylene from fruit and vegetable, which is continuously produced and accumulates over time, is still needed.

2.6.2 Ethylene scrubbers

Potassium permanganate ($KMnO_4$) is an active compound that can be used as an oxidizing agent against ethylene. Potassium permanganate is generally considered a low-cost technology, easy to apply, relatively eco-friendly, and powerful agent that oxidizes ethylene to CO_2 and H_2O (Dash et al., 2009). The use of effective oxidation agents to manage ethylene removal during postharvest handling of fruit and vegetables has been extensively reported.

$$3C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (2.1)$$

The use of $KMnO_4$ to reduce ethylene concentration in the atmosphere around horticultural produce was first demonstrated by Forsyth et al. (1967). Potassium permanganate is well suited for ethylene removal for short storage durations. However, with longer storage durations with high ethylene-producing commodities, $KMnO_4$ may be rapidly saturated, thereby necessitating frequent replacement. Additionally, the oxidation reaction leads to the formation of by-products that need further disposal. In a complete reaction, $KMnO_4$ oxidizes ethylene into CO_2 and water, while $KMnO_4$ itself is converted into MnO_2 and KOH. An incomplete oxidation reaction produces intermediates, such as potassium acetate, which may remain bound to the residue (Keller et al., 2013b). The stoichiometric oxidation reaction pathway can be rationalized as follows, based on partially oxidized CH_3CHO and CH_3COOH intermediates (Keller et al., 2013):

$$3CH_2CH_2 + 2KMnO + H_2O \rightarrow 2MnO_2 + 3CH_3CHO + 2KOH \qquad (2.2)$$

$$3CH_3CHO + 2KMnO_4 + H_2O \rightarrow 3CH_3COOH + 2MnO_2 + 2KOH \qquad (2.3)$$

$$3CH_3COOH + 8KMnO_4 \rightarrow 6CO_2 + 8MnO_2 + 8KOH + 2H_2O \qquad (2.4)$$

Overall, the stoichiometric oxidation reaction is based on the combination of eqn. (2.1−2.4) will result in:

$$3CH_2CH + 12KMnO_4 \rightarrow 12MnO_2 + 12KOH + 6CO_2 \qquad (2.5)$$

When the oxidation is not complete (eqn. 2.5), many of the intermediate by-products formed are irreversibly bound and can act as a reactant. For example, KOH will react with the acetic acid formed in eqn. 2.3 to produce potassium acetate:

$$CH_3COOH + KOH \rightarrow KCOOCH_3 + H_2O \quad (2.6)$$

Integrating eqns. 2.2, 2.3, and 2.6, will result:

$$3CH_2CH_2 + 4KMnO_4 \rightarrow 3KCOOCH_3 + 4MnO_2 + KOH + H_2O \quad (2.7)$$

However, since ethylene is a gas and natural convection and diffusion are the only driving forces involved, hence, $KMnO_4$ is not recommended for direct use application without support material (Aprilliani et al., 2018). For this reason, $KMnO_4$ is usually supported onto a porous inert solid material with a large surface area to facilitate and improve the oxidation process. The most commonly used support materials are vermiculite, activated alumina, zeolite, silica gel, activated carbon and clays. These materials are described as adsorbent scrubbers. The major groups of adsorbents used as support are zeolites and carbon-based adsorbents (Keller et al., 2013). The postharvest application of $KMnO_4$ and support materials was extensively reviewed by Álvarez-Hernández et al. (2018). Although vermiculite and activated alumina are the most commonly preferred materials, silica gel and zeolite were suggested to be promising materials for better ethylene management during long-term storage. Most of these support materials used in combination with $KMnO_4$, absorb ethylene creating an adsorption–oxidation system, wherein, the support material adsorbs C_2H_4 and permanganate (MnO_4^-) oxidizes it. The adsorption techniques only transfer the ethylene to the solid adsorbent, rather than destroying it. Therefore, the supporting residue raises a disposal concern. This is the drawback of most ethylene scrubbers. In addition, the application of ethylene scrubbers is unsuitable for typical storage conditions (with high RH and low temperatures) and as such, their efficiency has been shown to decline under such conditions. The use of ethylene scrubbers-based technology remains limited at a commercial scale since there are still lots of doubts about its potential as an effective postharvest tool, as well as in relation to health and environmental safety concerns.

Ozone gas is another efficient ethylene-oxidizing agent. Extensive reviews on the application of ozone were published by Miller et al. (2013) and Karaca and Velioglu (2007). Ozone is formed through high energy input, which splits available oxygen to form an unstable triatomic oxygen (O_3), and oriented at an obtuse angle (Karaca and Velioglu, 2007, Miller et al., 2013). Higher concentrations of ozone have been shown to have a critical influence on respiration and ethylene production rates during postharvest storage. For instance, Toivonen and Stan (2004) demonstrated that ozonation reduced the respiration rate for minimally processed green peppers. It was noted that once the samples were washed in water containing ozone their respiration was found to be lower than the ones that have not been treated. Zhang et al. (2005) reported a similar observation of respiration rate inhibition for fresh-cut celery treated with 0.08 and 0.18 ppm of ozonated water. Crisosto et al. (2000) investigated the capability of an ozone generator to remove ethylene from an empty 60 m^3 refrigerated container. Ethylene and ozone concentrations were measured over 24 hours after introducing an initial concentration of 3.8 ppm of ethylene at 0 °C. The authors found that the ethylene reduction rate was proportional to the ozone production rate. Under the most efficient operational settings, the ozone generator reduced the ethylene concentration in the container to a rate of 145 ppb h^{-1}. However, due to human safety concerns and the irreversible tissue damage caused to horticultural commodities by exposure to ozone. Monitoring and controlling ozone comes at an extremely high cost. These drawbacks limit the introduction of such technologies.

2.7 Advanced oxidation process

2.7.1 Photocatalysis

Photocatalytic oxidation (PCO) is an emerging technology that has been studied for the removal of volatile organic compounds (VOCs). The technique has shown great potential to eliminate gaseous pollutants (Zhong and Haghighat, 2015). The remarkable features of this technology, which include operating at ambient temperature and the environmentally friendly by-products (CO_2 and H_2O) have spiked an interest to evaluate the technology in postharvest for the removal of ethylene to prolong the shelf life of horticultural commodities (Sun, 2007, Chiara et al., 2015, Pathak et al., 2019). The photocatalytic reaction occurs in semiconductor materials, such as TiO_2, that when irradiated at a wavelength able to activate the photocatalyst results in the transfer of electrons from the valence band to the conduction band (Fig. 2). This reaction produces an electron (e-) – hole (h+) pair (Basso et al., 2018). The generated electron-hole pairs at the surface of the catalyst react with surface-adsorbed oxygen and water to produce reactive oxygen species (such as hydroxyl radicals, $OH^{\bullet}$ and superoxide ions, O_2^-) that ultimately oxidise ethylene to carbon dioxide and water (Pathak et al., 2017b). In most cases, TiO_2 is the commonly used photocatalyst because it is chemically inert, highly stable, environmentally friendly, and of low cost (Chiara et al., 2015). Another interesting feature is its low bandgap energy, which makes it a suitable semiconductor.

Numerous studies have been carried out to improve the effectiveness and performance of photocatalysis. The lack of practical tools to design, optimize and scale up photocatalytic reactors is the main reason for the limited commercial application of this technology (Gerven et al., 2007, Khodadadian et al., 2018). Recently, Malayeri et al. (2019) reviewed recent research on the mathematical modeling of photocatalytic reactors used to enhance the understanding of reactor performance and the evaluation of kinetic parameters that enable the scale-up or re-design of more efficient large-scale photocatalytic reactors. The authors found that the combination of the mass transfer model and reaction kinetic model provided a comprehensive model that can be used for a larger-scale PCO reactor. In the same study, the influence of key operating parameters (flow rate, catalyst surface area and porosity and catalyst thickness) on the photocatalytic process was also studied. Of the studied parameters, catalyst surface area and porosity were reported to have a major impact on photocatalytic activity and degradation rate. For this reason, there has been an increase in research interest on catalyst surface modification to increase catalyst surface area and porosity by using different support systems. Even though the potential application of PCO to degrade ethylene for possible use in the postharvest storage of fruit and vegetables has been proposed as promising (Licciulli et al., 2016, Lourenço et al., 2016, Liu et al., 2018), its commercial application for ethylene removal during the storage of fruit and vegetables is very limited. The ability of photocatalytic degradation of ethylene by a novel TiO_2 at 3 °C was investigated by Hussain et al. (2011). Although the study was not done on a selected produce, the ethylene removal efficiency (>80%) achieved was significant. Chiara et al. (2015) investigated the photocatalytic degradation of ethylene using mixed titania/silica (TiO_2/SiO_4) materials under UV light radiation. In their study, mature green tomatoes were exposed to an ethylene-enriched atmosphere treated with 80Ti - 20Si nanocomposite. The results showed that ethylene was photocatalytically destroyed by TiO_2, thereby reducing the ripening trend of mature green tomatoes. In another study, Basso et al. (2018) investigated the effect of operating conditions on the photocatalytic degradation of ethylene in a continuous reactor using TiO_2 applied to tomato ripening. It was found that the photocatalytic reactor was able to maintain ethylene concentration close to zero in the gas phase and decreased RR. Considerable work has been conducted on the effects of process and storage conditions on the removal efficiency of ethylene by PCO such as catalyst thickness (Basso et al., 2018), oxygen, RH, and light intensity (Lin et al., 2014), as well as on initial ethylene flow rate, light wavelength and temperature (Pathak et al., 2018, Pathak et al., 2019). Amongst the studied variables, RH remains the variable with the most significant effect on ethylene removal efficiency, as PCO declines in performance at higher RH. High humidity is essential in the storage of fresh produce to minimise mass loss (Pathak et al., 2017a), and can range from 85% - 98% (Bovi et al., 2016). Hence, the application of PCO in tropical and subtropical regions of Africa requires careful optimization of this parameter.

Although photocatalysis has emerged as a promising technology for the removal of ethylene during postharvest, unfavourable phenomena during the photocatalytic reaction, such as the recombination of hole and electron, which happen on the surface, reduce the performance of PCO due to the reduction of oxidised species (Malayeri et al., 2019). To address this, different modification methods such as surface sensitization, precious metal deposition, non-metal ion loading and semiconductor composites have been suggested by (Song et al., 2018). This, however, has not yielded satisfactory results for TiO_2, thus, the research on developing new photocatalysts should continue. In addition, the deactivation of the catalyst, which is caused by water vapour deposition and the accumulation of intermediates on the surface catalyst, is another major drawback. This can be solved by the use of hydrophobic catalysts (Kuwahara et al., 2009). Furthermore, the dominant degradation mechanism in PCO is adsorption on the catalyst surface and so the disposal of the catalyst will exert an environmental concern since the spent catalyst will be contaminated. This limitation could be addressed by investigating the feasibility of recycling and regenerating the spent catalyst. Therefore, the hindered performance of PCO in such crucial conditions could prevent its commercial application. In order to increase the efficiency of PCO, coupling PCO reactors to other processes could be one possible approach. Another alternative could be to use reactors in series to improve the overall performance.

2.7.2 Vacuum ultraviolet radiation

Photo-degradation employs vacuum ultraviolet (VUV) light sources, such as low-pressure and medium-pressure mercury lamps with approximately 85% output at 254 nm and 15% output at 185 nm (Kang et al. 2018; Xu et al., 2019). Photolysis based on VUV has better potential than PCO for removal performance due to the following characteristics: (i) the high-energy photons generated by 185 nm irradiation can degrade organic compounds; (ii) the generation of oxidising agents such as hydroxyl radicals (•OH) from water molecules; and (iii) in the presence of O_2, the 185 nm irradiation can generate ozone (Yang et al. 2007). VUV photolysis has been used for the removal of organics in the aqueous phase and air pollutants (Cheng et al. 2011; Ollis et al. 1991; Xu et al. 2014).

This performance attracted various researchers to explore its postharvest application (Scott et al. 1971). In the study by Scott et al. (1971), a UV lamp successfully reduced ethylene produced by bananas from 0.3 µg L^{-1} to 0.1 µg L^{-1} and < 0.03 µg L^{-1} in 10 min and 2 h, respectively. Pathak et al. (2017b, c) re-highlighted the potential of VUV photolysis for ethylene removal in fruit storage. Their results showed that flow rate exerted the most significant effect on the amount of ethylene removed, followed by initial ethylene concentration, and lamp power. In another comparative study, Pathaka et al. (2019) compared the removal efficiency of VUV photolysis to PCO technology. The percentage of ethylene removal in the VUV photolysis reactor was 84.8%, whereas in the PCO reactor, it was less than 14.86%. Although VUV photolysis showed better performance, the low removal rates and generation of toxic ozone (O_3) remain a major drawback and could delay the adoption of this technique. To improve the removal rate and reduce residual O_3, VUV photolysis can be combined with downstream processes, such as ozone-assisted catalytic oxidation (OZCO) and/or PCO.

This novel combination (VUV-OZCO or VUV-PCO or VUV-OZCO-PCO) can generate additional reactive radicals for effective oxidation of ethylene, and the catalyst can eliminate the residual O_3. Huang et al. (2011) demonstrated that toluene removal efficiency was increased by 18.2% in the VUV-PCO process. In addition, the outlet concentration of O_3 was reduced from 30 µL L^{-1} to 1.8 µL L^{-1} in the VUV-PCO process compared to the VUV process alone. In another study, the VUV-PCO combination showed enhanced performance in the degradation of ethylene, and a high mineralisation rate compared to VUV photolysis alone (Chang et al. 2013). The viability of combining VUV photolysis with OZCO to eliminate O_3 and improve benzene degradation efficiency was studied by Huang et al. (2016a). The possible combinations of VUV-based processes including VUV combined with ozone-assisted oxidation and VUV-PCO for air purification were reviewed by Huang et al. (2016b). Studies on ethylene removal by VUV-combined systems are still limited. Hence, further research is needed in South Africa on the optimization of VUV photolysis systems.

2.8 Conclusion

Based on the current technologies reviewed, in South Africa, the ethylene inhibition approach using compounds such as 1-MCP and other agents has been well adopted by the fruit industry. However, strict international regulations on minimum chemical residues allowed on fresh horticultural commodities, imply that other alternatives are needed. Technologies linked to cold storage and CA/MA systems are often capital-intensive and far out of the reach of small-medium scale farmers. In addition, this approach does not prevent produce from exogenous ethylene. On the other hand, advanced oxidation technologies such as photocatalytic oxidation, and vacuum ultraviolet light (VUV) photolysis could offer potential applications in ethylene removal under long-term storage and distant distribution. However, these emerging technologies require further improvement or system optimization to be efficient. Overall, to mitigate postharvest losses due to endo- or exogenous ethylene exposure, a concerted effort is required in South Africa with multidisciplinary collaboration between research institutions and the industry to drive this innovation. Commercial upscaling of these technologies in order to ensure South Africa’s food security will require a public-private partnership.

2.9 Summary

This chapter provided a thorough review of existing ethylene management techniques, highlighting their effectiveness and limitations. Additionally, it explores the prospective application of VUV photolysis as an innovative postharvest management technology in South Africa. The foundational theories presented herein are essential for comprehending the discussions in Chapters 3, 4, 5, 6, and 7.

References

Abdalnoor, K. 2015. Effect of 1-Methylcyclopropene (1-MCP) on quality and shelf-life of banana fruits. *University of Khartoum, Sudan*.

Abdollahi, R., Asghari, M., Esmaiili, M. & Abdollahi, A. 2013. Postharvest Nitric Oxide Treatment Effectively Reduced Decays of Selva Strawberry Fruit. *International Journal of Agriculture and Crop Sciences,* **6(6),** 353-355.

Abe, K. & Watada, A. E. 1991. Ethylene Absorbent to Maintain Quality of Lightly Processed Fruits and Vegetables. *Journal of Food Science,* 56**,** 1589-1592.

Al Ubeed, H. M. S., Wills, R. B. H., Bowyer, M. C., Vuong, Q. V. & Golding, J. B. 2017. Interaction of exogenous hydrogen sulphide and ethylene on senescence of green leafy vegetables. *Postharvest Biology and Technology,* 133**,** 81-87.

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Juan Carlos Contreras-Esquivel, J. C., Ventura-Sobrevilla, J. M. & Martínez-Hernández, G. B. 2017. Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food Bioprocess Technology,* 11**,** 511-525.

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C. & Artés-Hernández, F. 2019. Potassium Permanganate-Based Ethylene Scavengers for Fresh Horticultural Produce as an Active Packaging. *Food Engineering Reviews,* https://doi.org/10.1007/s12393-019-09193-0.

Aprilliani, F., Warsiki & Iskandar, A. 2018. Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science,* 141**,** IOP Conference Series: Earth and Environmental Science.

Bailén, G., Guillén, F., Castillo, S., Zapata, P. J., Serrano, M. & Valero, D. 2007. Use of a palladium catalyst to improve the capacity of activated carbon to absorb ethylene, and its effect on tomato ripening. *Spanish Journal of Agricultural Research,* 5(4)**,** 579-586.

Bal, E. 2018. Extension of the Postharvest Life of Nectarine Using Modified Atmosphere Packaging and Potassium Permanganate Treatment. *Turkish Journal of Agriculture - Food Science and Technology,* 6(10)**,** 1362-1369.

Basso, A., Moreira, R. D. F. P. M. & José, H. J. 2018. Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening. *Journal of Photochemistry & Photobiology A: Chemistry* 367**,** 294-301.

Bower, J. H., Biasi, W. V. & Mitcham, E. J. 2003. Effect of ethylene in the storage environment on quality of 'Bartlett pears'. *Postharvest Biology and Technology,* 28**,** 371-379.

Chamara, D., Illeperuma, K., Galappatty, T. & Sarananda, K. 2000. Modified atmosphere packaging of 'Kolikuttu' bananas at low temperature. *J Hortic Sci Biotechnology,* 75.

Chiara, M. L. V. D., Pal, S., Licciulli, A., Amodio, M. L. & Colell, G. 2015. Photocatalytic degradation of ethylene on mesoporous TiO_2/SiO_2 nanocomposites: Effects on the ripening of mature green tomatoes. *Biosystems Engineering,* 132**,** 61-70.

Coloma, A., Rodríguez, F. J., Bruna, J. E., Guarda, A. & Galotto, M. J. 2014. Development of an active film with natural zeolite as ethylene scavenger. *Journal of the Chilean Chemical Society,* 59(2)**,** 2409-2414.

Corrêa, S. 2005. Effect of the potassium permanganate during papaya fruit ripening: ethylene production. *Journal of Physics IV France,* 125**,** 869-871. https://doi.org/10.1051/jp4:2005125201.

Devinny, J. S., Deshusses, M. A. & Webster, T. S. 1999. Biofiltration for Air Pollution Control. *Lewis Publishers*.

Deyman, K. L., Brikis, C. J., Bozzo, G. G. & Shelp, B. J. 2014. Impact of 1-methylcyclopropene and controlled atmosphere storage on polyamine and 4-aminobutyrate levels in "Empire" apple fruit. *Frontiers in Plant Science,* **5(125)**.

Dhineshkumar, V., Ramasamy, D. & Srivastav, P. P. 2015. Modified atmospher packaging of pomegranate arils: review. *Applied Engineering and Technology,* 5(3)**,** 8-24.

Elsgaard, L. 1998. Ethylene Removal by a Biofilter with Immobilized Bacteria. *Applied and Environmental Microbiology,* 64(11)**,** 4168-4173.

Elsgaard, L. 2000. Ethylene Removal at Low Temperatures under Biofilter and Batch Conditions. *Applied and Environmental Microbiology,* **66(9),** 3878-3882.

Elzubeir, M. M., Abu-Goukh, A. A. & Osman, O. 2017. Effect of Polyethylene Film lining and Potassium Permanganate on Quality and Shelf-life of MangoFruits. *Journal of Environmental and Social Sciences,* 4(1)**,** :130.

Fotopoulos, V., Christou, A., Antoniou, C., Manganaris, G.A., 2015. Hydrogen sulphide: a versatile tool for the regulation of growth and defence responses in horticultural crops. J. Hortic. Sci. Biotechnol. 90, 227–234.

Forsyth, F. R., Eaves, C. A. & Lockhard, C. L. 1967. Controlling ethylene levels in the atmosphere of small containers of apples. *Canadian Journal of Plant Science,* 47**,** 717-718.

Fu, Y., Shao, L., Tong, L. & Liu, H. 2011. Ethylene removal efficiency and bacterial community diversity of a natural zeolite biofilter. *Bioresource Technology,* **102,** 576-586.

Gabioud Rebeaud, S., Varone, V., Cotter, P. Y., Ançay, A. & Christen, D. Influence of 1-MCP and modified atmosphere on quality of hardy kiwifruit. 2018. International Society for Horticultural Science (ISHS), Leuven, Belgium, 713-720.

Gaikwad, K. K., Singh, S. & Negi, Y. S. 2019. Ethylene scavengers for active packaging of fresh food produce. *Environmental Chemistry Letters,* https://doi.org/10.1007/s10311-019-00938-1.

Golden, K. D., Williams, O. J. & Dunkley, H. M. 2014. Ethylene in Postharvest Technology: A Review. *Assian Journal of Biological Science,* 7(4)**,** 135-143.

Goodburn, K. E. & Halligan, A. C. 1987. Modified atmosphere packaging - a technology guide. *Publication of the British Food Manufacturing Association, Leatherhead, UK***,** 1-44.

He, Q. & Xiao, K. 2018. Quality of broccoli (Brassica oleracea L. var. italica) in modified atmosphere packaging made by gas barrier-gas promoter blending materials. *Postharvest Biology and Technology,* **144,** 63-69.

Holzer, F., Roland, U. & Kopinke, F. D. 2002. Combination of non-thermal plasma and heterogeneous catalysis for oxidation of volatile organic compounds Part 1. Accessibility of the intra-particle volume. *Applied Catalysis B: Environmental,* 38**,** 163-181.

Huang, H., Leung, D. Y. C., Li, G., Leung, M. K. H. & Fu, X. 2011. Photocatalytic destruction of air pollutants with vacuum ultraviolet (VUV) irradiation. *Catalysis Today,* **175,** 310-315.

Hussain, M., Bensaid, S., Geobaldo, F., Saracco, G. & Russo, N. 2011. Photocatalytic Degradation of Ethylene Emitted by Fruits with TiO_2 Nanoparticles. *Industrial & Engineering Chemistry Research,* **50 (5),** 2536-2543.

K. Graham, T., N. Veenstra, J. & R. Armstrong, P. 1998. Ethylene removal in fruit and vegetable storages using a plasma reactor. *Transactions of the ASAE,* 41**,** 1767-1773.

Kader, A. A. 2002. Postharvest Biology and Technology: An Overview. In Kader AA (Ed) Postharvest Technology of Horticultural Crops. *Pub. 3311, Oakland, CA.***,** 39-47.

Kang, I.-S., Xi, J. & Hu, H.-Y. 2018. Photolysis and photooxidation of typical gaseous VOCs by UV Irradiation: Removal performance and mechanisms. *Frontiers of Environmental Science and Engineering,* 12(3): https://doi.org/10.1007/s11783-018-1032-0.

Karatum, O. & Deshusses, M. A. 2016. A comparative study of dilute VOCs treatment in a non-thermal plasma reactor. *Chemical Engineering Journal,* 294**,** 308-315.

Kays, S. J. & Beaudry, R. M. 1987. Techniques for inducing ethylene effects. *Acta Hort,* 201**,** 77-116.

Keller, N., Ducamp, M.-N., Robert, D. & Keller, V. 2013. Ethylene Removal and Fresh Product Storage: A Challenge at the Frontiers of Chemistry. Toward an Approach by Photocatalytic Oxidation. *Chemical Reviews,* **113(7),** 5029-5070.

Kim, J. O. 2003. Degradation of benzene and ethylene in biofilters. *Process Biochemistry***,** 39(4).

Li, L., Guo, M., Wang, X., Zhang, X. & Liu, T. 2014a. Effects and Mechanism of 1-Methylcyclopropene and Ethephon on Softening in Ailsa Craig Tomato Fruit. *Food Process Preserv,* **41**.

Li, S. P., Hu, K. D., Hu, Y., Li, Y. H., Jiang, A. M., Xiao, F., Han, Y., Liu, Y. S., Zhang, H., 2014. Hydrogen sulfide alleviates postharvest senescence of broccoli by modulating antioxidant defense and senescence-related gene expression. J. Agric. Food Chem. 62, 1119–1129.

Li, X.-P., Wu, B., Guo, Q., Wang, J.-D., Zhang, P. & Chen, W.-X. 2014b. Effects of nitric oxide on postharvest quality and soluble sugar content in papaya fruit during ripening. *Journal of Food Processing and Preservation,* **38,** 591-599.

Ma, T. J. & Lan, W. S. 2015. Ethylene decomposition with a wire-plate dielectric barrier discharge reactor: parameters and kinetic study. *International Journal of Environmental Science and Technology,* 12**,** 3951-3956.

Mahmoudkhani, F., Rezaei, M., Asili, V., Atyabi, M., Vaisman, E., Langford, C. H. & Visscher, A. D. 2016. Benzene degradation in waste gas by photolysis and photolysis-ozonation: experiments and modeling. *Frontiers in Environmental Science,* 10(6)**,** :DOI 10.1007/s11783-016-0876-4.

Malayeri, M., Haghighat, F. & Lee, C.-S. 2019. Modeling of volatile organic compounds degradation by photocatalytic oxidation reactor in indoor air: A review. *Building and Environment,* 154**,** 309-323.

Martinez-Romero, D., Bailen, G., Serrano, M., Guillen, F., Valverde, J. M., Zapata, P., Castillo, S. & Valero, D. 2007. Tools to Maintain Postharvest Fruit and Vegetable Quality through the Inhibition of Ethylene Action: A Review. *Critical Reviews in Food Science and Nutrition,* 47**,** 543-560.

Massolo, J. F., Concellón, A., Chaves, A. R. & Vicente, A. R. 2011. 1-Methylcyclopropene (1-MCP) delays senescence: maintains quality and reduces browning of nonclimacteric eggplant (Solanum melongena L.) fruit. *Postharvest Biology and Technology,* 59**,** 10-15.

Matar, C., Gaucel, S., Gontard, N., Guilbert, S. & Guillard, V. 2018. Predicting shelf life gain of fresh strawberries 'Charlotte cv' in modified atmosphere packaging. *Postharvest Biology and Technology,* **142,** 28-38.

Miller, F. A., Silva, C. L. M. & Brandão, T. R. S. 2013. A Review on Ozone-Based Treatments for Fruit and Vegetables Preservation. *Food Engineering Reviews,* 5**,** 77-106.

Moghadam, H. Z., Kheirkhah, B. & Kariminik, A. 2015. Ethylene Removal by Bio-filters in order to Increase Storage Life of Bananas. *International Journal of Life Science,* **9(5),** 62-65.

Nguyen, H., Mcconchie, R., Hofman, P., Smith, L., Stubbings, B. & Adkins, M. Effect of ethylene and ripening temperatures on the skin colour and flesh characteristics of ripe'Kensington Pride'mango fruit. International Symposium on Tropical and Subtropical Fruits 575, 2000. 635-642.

Nishimura, J., Takahashi, K., Takaki, K., Koide, S., Suga, M., Orikasa, T., Teramoto, Y. & Uchino, T. 2016. Removal of Ethylene and By-products Using Dielectric Barrier Discharge with Ag Nanoparticle-Loaded Zeolite for Keeping Freshness of Fruits and Vegetables. *Transactions of the Materials Research Society of Japan,* 41**,** 41-45.

Palou, L. S., Crisosto, C. H., Garner, D. & Basinal, L. M. 2003. Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes. *Postharvest Biology and Technology* 27**,** 243-254.

Pathak, N. 2019. *Photocatalysis and vacuum ultraviolet light photolysis as ethylene removal techniques for potential application in fruit storage.* PhD, Leibniz Institute for Agricultural Engineering and Bioeconomy.

Pathaka, N., Caleb, O. J., Rauhc, C. & Mahajan, P. V. 2019. Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions. *Posthavest Biology and Technology,* 147**,** 68-77.

Pristijono, P., Golding, J. B. & Bowyer, M. C. 2018. Postharvest UV-C Treatment, Followed by Storage in a Continuous Low-Level Ethylene Atmosphere, Maintains the Quality of ‘Kensington Pride’ Mango Fruit Stored at 20 ^{0}C. *Horticulturae,* 5(1)**,** doi:10.3390.

Ramin, A., Rezaei, A. & Shams, M. 2010. Potassium permanganates and short term hypobaric enhances shelf-life of kiwifruits. *Acta Hortic,* 877**,** 849-852. https://doi.org/10.17660/ActaHortic.2010.877.113.

Razzaq, K., Singh, Z., Khan, A. S., Khan, S. a. K. U. & Ullah, S. 2016. Role of 1-MCP in regulating ‘Kensington Pride’ mango fruit softening and ripening. *Plant Growth Regulation,* **78,** 401-411.

Sabater-Vilar, M., Suñé-Colell, E., Castro-Chinchilla, J. & Sáenz-Murillo, M. V. Reduction of postharvest rotting with an ethylene absorbent: a case study with pineapple. 2018. International Society for Horticultural Science (ISHS), Leuven, Belgium, 721-728.

Sadeghi, K., Lee, Y. & Seo, J. 2019. Ethylene Scavenging Systems in Packaging of Fresh Produce: A Review. *Food Reviews International***,** 1-22.

Salamanca, F., Balaguera-López, H. & Herrera, A. 2014. Effect of potassium permanganate on some postharvest characteristics of tomato ‘Chonto’ fruits (Solanum lycopersicum L.). *Acta Hortic,* 1016.

Saltveit, M. E. 1999. Effect of ethylene on quality of fresh fruits and vegetables. *Postharvest Biology and Technology,* 15**,** 279-292.

Sardabi, F., Mohtadinia, J., Shavakhi, F. & Jafari, A. 2014. The effects of 1-methylcyclopropen (1-MCP) and potassium permanganate coated zeolite nanoparticles on shelf life extension and quality loss of golden delicious apples. *Food Process Preserv,* 38**,** 2176-2182.https://doi.org/10.1111/jfpp.12197

Sherman, M. 1985. Control of ethylene in the postharvest environment. *HortScience,* 20**,** 57-60.

Sisler, E. C., Dupille, E. & Serek, M. 1996. Effect of 1-methylcyclopropene and methylenecyclopropane on ethylene binding and ethylene action on cut carnations. *Plant Growth Regulation,* 18**,** 79-86.

Siti Amirah, M. Z., Nor Afifah, A. R., Husni Hayati, M. R. & Wan Zaliha, W. S. 2017. The effects of charcoal from different agricultural wastes in reducing ethylene production of berangan banana (Musa sp. AAA Berangan). *Proceedings of The International Conference of FoSSA Jember, August 1st - 3rd***,** 201-210.

Tas, C. E., Hendessi, S., Baysal, M., Unal, S., Cebeci, F. C. & Menceloglu, Y. Z. 2017. Halloysite Nanotubes/Polyethylene Nanocomposites for Active Food Packaging Materials with Ethylene Scavenging and Gas Barrier Properties. *Food Bioprocess Technology***,** 1-10.

Tucker, G., Yin, X., Zhang, A., Wang, M., Zhu, Q., Liu, X., Xie, X., Chen, K. & Grierson, D. 2017. Ethylene and Fruit Softening. *Food quality and Safety,* 1(4)**,** 253-267.

Ubeed, H. M. S. A., Wills, R. B. H., Bowyer, M. C. & Golding, J. B. 2018. Comparison of hydrogen sulphide with 1-methylcyclopropene (1-MCP) to inhibit senescence of the leafy vegetable, pak choy. *Postharvest Biology and Technology,* 137**,** 129-133.

Wang, B., Chi, C., Xu, M., Wang, C. & Meng, D. 2017. Plasma-catalytic removal of toluene over CeO2-MnOx catalysts in an atmosphere dielectric barrier discharge. *Chemical Engineering Journal,* 322**,** 679-692.

Wills, R. B. 2015. Low ethylene technology in non-optimal storage temperatures. In R. B. H. Wills & J. Golding (Eds.),. *Advances in postharvest fruit and vegetable technology***,** (pp. 167–190). Boca Raton: CRC Press.

Wills, R. B. H., Ku, V. V. V., Shohet, D. & Kim, G. H. 1999. Importance of low ethylene levels to delay senescence of non-climacteric fruit and vegetables. *Australian Journal of Experimental Agriculture,* 39**,** 221-224.

Wills, R. B. H. & Warton, M. A. 2000. A new rating scale for ethylene action on postharvest fruit and vegetables. In: *Improving Postharvest Technologies of Fruits, Vegetables and*

Ornamentals. 43-47. **,** 43-47. Art´es, F., Gil, M.I., and Conesa, M. A., Eds., Institute International of Refrigeration, Murcia, Spain.

Xu, J., Li, C., Liu, P., He, D., Wang, J. & Zhang, Q. 2014. Photolysis of low concentration H2S under UV/VUV irradiation emitted from high frequency discharge electrodeless lamps. *Chemosphere,* 109**,** 202-207.

Zhang, J., Cheng, D., Wang, B., Khan, I. & Ni, Y. 2017. Ethylene Control Thechnologies in Extending Postharvest Shelf Life of Climacteric Fruit. *Journal of Agricultural and Food Chemistry,* 65**,** 7308-7319.

Zheng, J. L., Hu, L. Y., Hu, K. D., Wu, J., Yang, F., Zhang, H., 2016. Hydrogen sulfide alleviates senescence of fresh-cut apple by regulating antioxidant defense system and senescence-related gene expression. HortScience 51, 152–158.

Zhong, L. & Haghighat, F. 2015. Photocatalytic air cleaners and materials technologies – abilities and limitations. *Building and Environment,* 91**,** 191-203.

Zhu, X., Shen, L., Fu, D., Si, Z., Wu, B., Chen, W. & Li, X. 2015. Effects of the combination treatment of 1-MCP and ethylene on the ripening of harvested banana fruit. *Postharvest Biology and Technology,* 107**,** 23-32.

CHAPTER THREE:

LITERATURE REVIEW (ADVANCES IN VUV PHOTOLYSIS)

Published as: **Mabusela, B.P**., Belay, Z.A., Godongwana, B., Pathak, N., Mahajan, P.V., & Caleb, O.J. (2020) Advances in vacuum ultraviolet photolysis in the postharvest management of fruit and vegetables along the value chains – A review. *Food and Bioprocess Technology*

3. ADVANCES IN VUV PHOTOLYSIS

Abstract

Postharvest losses and quality changes of fruit and vegetables, along the value chain, are a result of microbial activity and negative impacts of ethylene. It has become important to develop technologies that can remove ethylene while simultaneously resisting bacteria to reduce postharvest losses. Various technologies have been successfully developed and applied for the management of ethylene along the postharvest value chain, but there are still some inherent drawbacks that affect their effectiveness, and their ability for antimicrobial activity has been rarely reviewed. Vacuum ultraviolet (VUV) photolysis is an emerging technology with promising characteristics for ethylene and microbial management. This technology relies onthe generation of highly reactive radicals that can oxidise ethylene to carbon dioxide and water while simultaneously inactivating pathogenic microorganisms. This paper presents a critical review of VUV photolysis as an alternative technology in postharvest ethylene management. Mechanisms of VUV photolysis action against ethylene and microbial activity, as well as the factors affecting its efficiency, were discussed. Additionally, the impact of UV irradiation on microbial load and fruit enzymes associated with textural quality and antioxidant protection was highlighted.

Keywords: Ethylene management, Postharvest losses, mechanisms, antimicrobial activity

3.1 Introduction

Ethylene is a naturally occurring plant hormone that even at very low concentrations (0.01 µL/L), is responsible for the regulation of many aspects of growth and development of fruit and vegetables (Golden et al., 2014, Luo et al., 2009). The responses of harvested fruit and vegetables to endogenously produced and exogenously applied ethylene are numerous and can either be beneficial or detrimental (Saltveit, 1999). Generally, ethylene can influence the postharvest life of climacteric and non-climacteric fruit by inducing various physiological processes including undesirable ripening (Aprilliani et al., 2018). Fruit and vegetable ripening involves a series of changes in colour, flavour, texture, aroma, and nutrient content, which affect quality, postharvest life, and economic value (Tucker et al., 2017). The harmful effects of ethylene on fruit and vegetables are estimated to cause a significant loss which can be as high as 10-80% (Keller et al., 2013).

Hence, reducing ethylene concentration during postharvest can have a beneficial impact and subsequently result in a reduction in the deleterious effects associated with accelerated ripening (Luo et al., 2008). The development of effective technologies under real-time storage conditions of fruit and vegetables is of fundamental importance to maintaining quality and increasing the shelf-life of fruit and vegetables. The traditional methods for ethylene removal include refrigerated storage (Ponce-Valadez et al., 2016) and controlled atmosphere (CA). Other strategies include (i) inhibition of ethylene action by 1-methylcyclopropene (1-MCP) (Luo et al., 2007), hydrogen sulphide (H_2S) (Li et al., 2016, Luo et al., 2015, Li et al., 2017) and nitric oxide (NO) (Wang et al., 2017) (ii) avoidance of ethylene exposure by modified atmosphere packaging (MAP) and (iii) active removal by the use of different adsorber/absorber, the use of potassium permanganate ($KMnO_4$), ozonation and photocatalytic oxidation (PCO) (Mabusela et al., 2021).

Removal of ethylene by adsorption involves the use of adsorbents in the form of sachets placed inside the packaging or in the form of active films (Tas et al., 2017). A large number of adsorbents, including activated charcoal, molecular sieves of crystalline aluminosilicates, bentonite, silica gel, aluminum oxide and natural clays such as zeolite, halloysite and ceramics have been developed and reported in the literature (Goodburn and Halligan, 1987, Kays and Beaudry, 1987, Gaikwad et al., 2019). The performance efficiency of some adsorbents is reviewed by Gaikwad et al. (2019). Although the removal of ethylene by adsorption is a simple technique, there are still major challenges that limit its application. In adsorption removal, the pollutant is only transferred from the gaseous phase to the surface of the absorbent rather than destroying it and thus will pose additional disposal costs for the absorbent material. In addition, they are not applicable for long-term storage because they rapidly saturate thereby necessitating frequent replenishment. Moreover, adsorption technologies suffer from limited adsorption capacity.

Oxidation by potassium permanganate ($KMnO_4$) is the most used technology to remove ethylene and has been used for the past 50 years. $KMnO_4$-based scrubbers are considered a low-cost technology with easy application, eco-friendly and powerful agents that oxidise ethylene to CO_2 and H_2O (Dash et al., 2009). The application of $KMnO_4$ has been successfully used to reduce ethylene concentrations, preserve the quality attributes of fruit and delay fruit ripening (Wills & Warton, 2004; Corrêa et al., 2005; Salamanca et al., 2014; Sardabi et al., 2014; Emadpour et al., 2015; Elzubeir et al., 2017; Bal, 2018). Several reviews on ethylene removal by potassium permanganate have been published. Álvarez-Hernández et al. (2018) provided an outline of the most common materials used as potassium permanganate supports on postharvest treatment and their respective effects on quality aspects of various fresh produce during postharvest life. Most recently, they provided an updated overview of the current knowledge regarding the use of $KMnO_4$ for ethylene removal and provided a concise appraisal of $KMnO_4$-based ethylene removal application (Álvarez-Hernández et al., 2019). However, the use of $KMnO_4$ remains limited on a commercial scale because, in high ethylene-producing commodities, $KMnO_4$ may get rapidly saturated thereby necessitating frequent replacement (Wills, 2015). In addition, there are still lots of doubts about its application as an effective postharvest tool, as well as concerning health, environmental and safety concerns. Ozone is also an alternative oxidant that has been used for the extension of the shelf-life of broccoli, to improve the firmness of cucumber (Skog and Chu, 2001), to suppress ethylene production (Minas et al., 2014), to reduce fungal population and to maintain fruit quality (Yaseen et al., 2015). However, O_3 is very unstable and decomposes into O_2 in a very short time (Hussain et al., 2011). Also, exposure to high concentrations of O_3 can cause deleterious effects on both the workers and the treated produce (Horvitz and Cantalejo, 2014).

Photocatalytic oxidation (PCO) of ethylene has received a great deal of attention because it can completely oxidise ethylene to CO_2 and H_2O. Several authors have reported the application of photocatalytic oxidation for ethylene removal (Park et al., 1999; Hussain et al., 2011; Chiara et al., 2015; Liu et al., 2018; Pathak et al., 2018; Song et al., 2018; Pathak et al., 2019), and few reviews on this technology have been published. Keller et al. (2013) and Pathak et al.

(2017a) respectively reviewed the factors affecting photocatalytic oxidation and discussed the advantages and disadvantages associated with the technology. Although photocatalytic oxidation of ethylene has shown good prospects in laboratory studies, there are still unfavourable phenomena associated with this technology that might prevent its adoption for commercial use. The major drawback in photocatalytic techniques is the recombination of electron-hole which reduces the photocatalytic performance due to the reduction of oxidized species. To address this, different modification methods such as surface sensitization, precious metal deposition, non-metal ion loading and semiconductor composites have been suggested (Malayeri et al., 2019). In addition, the deactivation of the catalyst, which is caused by water deposition and the accumulation of intermediates on the catalyst surface, is another major drawback. Also, the dominant removal mechanism in PCO is adsorption, rendering the spent catalyst contaminated, thus the final destination of the spent catalyst is questionable as it poses an environmental threat. Moreover, the reduced efficiency of photocatalysis at high relative humidity is a major concern (Pathak et al., 2019) that could prevent commercial application for this technique. Table 3.1 , summarises recent reviews of various technologies that have been applied for ethylene management.

Furthermore, available reviews on vacuum ultraviolet (VUV) photolysis mainly focus on environmental applications for air pollution control and water treatment (Zoschke et al., 2014, Huang et al., 2016). To the best of our knowledge, no reviews are available that describe the postharvest application of VUV photolysis in the management of ethylene and its role in the inactivation of foodborne pathogens. Postharvest losses and quality changes of fruit and vegetables along the value chains are not only caused by the detrimental effects of ethylene but also by pathogenic microorganisms (Siripatrawan and Kaewklin, 2018). Therefore, this review critically discusses the potential of VUV photolysis for ethylene management and microbial inactivation in postharvest management along the value chain of fruit and vegetables. The factors affecting the performance of VUV photolysis, and the impact on fruit and vegetables are discussed. The review is intended to provide insights to all the role players along the fresh produce value chain on the advances of VUV photolysis and the potential technic to manage both ethylene and spoilage/foodborne pathogen activities.

Table 3.1: Selected reviews on ethylene removal technologies.

Reference	Technology	Scope of review
Martinez-Romero et al. (2007)	Ethylene inhibitors photocatalysis and biofilters	Reviewed application of ethylene inhibitors as well as different tools for ethylene removal
Keller et al. (2013)	Photocatalysis (PCO)	Review focused on the potential of photocatalysis as a promising technology for ethylene removal
Zhang et al. (2017)	1-methylcyclopropene (1-MCP)	Reviewed the potential of 1-MCP for ethylene removal and provided encapsulation technique to improve its stability
Álvarez-Hernández et al. (2018)	Potassium permanganate ($KMnO_4$)	Provided an outline of the common materials used as potassium permanganate supports for improved removal of ethylene
Zhu et al. (2018)	TiO_2 photocatalysis	Summarized recent research developments of TiO_2 photocatalysis for antibacterial applications in liquid, gas and solid systems in the food industry
Hu et al. (2019)	$KMnO_4$, 1-MCP and PCO	Summarized technologies for ethylene removal and inhibition
Pathak (2019)	PCO and photochemical oxidation	Discussed the potential of PCO and VUV photolysis for ethylene management
Gaikwad et al. (2019)	Absorbents	Discussed the application and benefits of ethylene scavengers
Sadeghi et al. (2019)	1-MCP, PCO, $KMnO_4$	Reviewed application of the three technologies for ethylene removal
Wei et al. (2021)	Absorbents and inhibitors	Summarized the various ethylene scavengers/inhibitors and emerging technologies recently developed for the effective removal of ethylene

3.2 Ethylene biosynthesis pathway and associated enzymes

The biochemical pathway of ethylene synthesis is well-established and described by Yang and Hoffman (1984) and Alexander and Grierson (2002). Ethylene formation starts from the amino acid methionine (Met)_via the enzyme S-adenosylmethionine synthase to produce S-adenosyl-l-methionine (S-AdoMet), an intermediate compound (Fig. 3.1). This intermediate is then converted to cyclic non-protein amino acid 1-aminocyclopropane-1-carboxylic acid (ACC) from AdoMet by the action of ACC synthase (ACCS), and ACC is converted to ethylene by ACC oxidase (ACCO) (Wang et al., 2002). In the ethylene biosynthesis pathway, the conversion of S-AdoMet to ACC by the enzyme ACC-S is the rate-limiting step of carbon dioxide to activate ACC oxidase (Kumar et al., 2019; Wang et al., 2002).

In addition, to ACC, ACCS produces 5-methylthioadenosine, which is utilized for the synthesis of new methionine via a methionine or Yang cycle (Fig. 3.1). This salvage pathway ensures the continuous supply of methionine by methionine recycling (Alexander & Grierson, 2002; Kumar et al., 2019). Furthermore, the methionine cycle assists in the preservation of the methylthio group through the cycle via an energy-intense process and at the cost of one molecule of ATP. Thus, high ethylene production rates can be maintained even when the level of available methionine is low. The relationship between ethylene production/respiration rate and fruit ripening responses allows for the grouping of fruits into two categories: non-climacteric and climacteric. For non-climacteric fruit, ethylene production declines with fruit ripening and senescence, while in climacteric fruit, ethylene biosynthesis increases and induces an increase of autocatalytic ethylene production with peaks corresponding to respiration pattern (Fig. 3.1B).

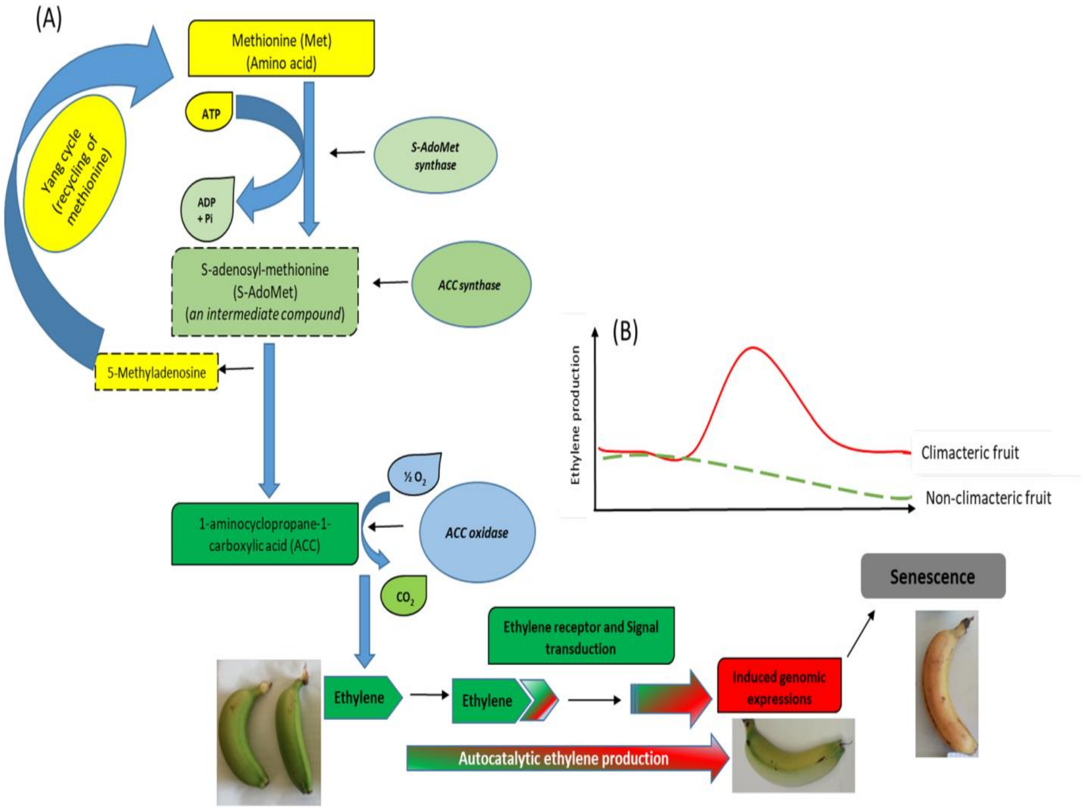


Figure 3.1: Schematic and simplified ethylene biosynthesis during fruit ripening and senescence (A), and classification of fruit based on ethylene production during postharvest (B).

An extensive review of enzymes associated with cell wall softening of fruit during postharvest was published by Brummell and Harpster (2001), and a comprehensive review of enzymes associated with various ethylene regulations has recently been published (Alexander & Grierson, 2002; Iqbal et al., 2017). Therefore, this review will not cover this subject extensively; however, enzymes linked to ethylene actions during ripening and senescence can be clustered into four major groups: (a) pectinase (pectin methyl esterases (PME), polygalacturonase (PG), β-galactosidases, and pectate lyase (PL)), (b) cellulase (cellulase), (c) hemicellulase (xyloglucan transglucosylase/hydrolases) and (d) non-enzymatic protein such as expansins (Alexander and Grierson, 2002; Iqbal et al., 2017; Kumar et al., 2019).

Various metabolic and physiological changes occur in fruit systems in response to ethylene burst (in climacteric fruit). This includes depolymerization of cell wall pectin, changes in colour involving chlorophyll degradation, accumulation of polyphenols, organic sugars and evolution of volatile organic compounds (Iqbal et al., 2017). As fruit ripening progresses, the depolymerization of the cell wall is majorly associated with textural changes and softening. The cell wall becomes increasingly porous and hydrated as the middle lamella rich in pectin is gradually hydrolysed. This phenomenon occurs early in soft fruit such as tomato and late in crisp or hard flesh fruit samples (Alexander & Grierson, 2002). The synthesis of PG has been shown to start at the onset of fruit ripening and correlated with ethylene production in tomatoes (Sitrit & Bennett, 1998), and PG is a major polyuronide-degrading enzyme (Alexander & Grierson, 2002).

Furthermore, the enzyme PME is activated before the onset of ripening, and it is responsible for the de-esterification of the highly methyl-esterified polygalacturonase (methyl group C-6 of galacturonic acid) in the cell wall. The de-esterified pectin becomes a suitable substrate for both polygalacturonase (PGs) (Iqbal et al., 2017; Kumar et al., 2019). Previous studies have shown that esterification differs between immature and mature fruit (Alexander & Grierson, 2002). In addition, PME plays an important role during cell wall degradation and fruit senescence, and the enzyme is stimulated by ethylene (Iqbal et al., 2017; Kumar et al., 2019). Early in the fruit ripening phase, polymeric galactose in the form of β-(1,4)-galactans integrated within the pericarp cell wall is broken down into free galactose by β-galactosidase (Eda et al., 2016). Studies have shown that exogenous application of ethylene increased the activity of β-galactosidase in watermelon, and the higher activities of these enzymes were observed in immature fruit (Karakurt & Huber, 2002).

Pectate lyases are major pectin-degrading enzymes; they are alkaline pectinases, referred to as pectate transelimi-nases. This group of enzymes performs eliminative cleavage of β (1–4) linkages generating oligosaccharides with 4-deoxy-α-d-mann-4-enuronosyl (Uluisik & Seymour, 2020; Wang et al., 2018). In fruit plant immunocytochemistry studies, Yang et al. (2017) also demonstrated that on transgenic tomato PL lines, there was reduced susceptibility to grey mold. Similarly, Pombo et al. (2011) demonstrated that UV–C treatment prevented strawberry rot, and this response was attributed to the activation of defense genes encoding β-1,3-glucanases, chitinases, peroxidases and phenylalanine ammonia-lyase. PLs have been shown to macerate and disassemble the plant cell wall by targeting de-esterified pectins that are located in the tricellular junction zones between cells and the middle lamella regions (Uluisik et al., 2016). Hence, PL can play major roles in both ripening and pathogen resistance in the infection process.

Expansins are cell wall localized non-enzymatic proteins that directly induce cell wall extension (McQueen-Mason et al., 1992; Rose et al., 1997). They are believed to be important regulators causing cell wall loosening by reversibly disrupting the hydrogen bonds between cellulose microfibrils and matrix polysaccharides (glycans) (Cosgrove et al., 2002; Whitney et al., 2000).

Loosening of the hemicellulose-cellulose network by expansion is crucial for normal fruit softening. The disruption allows enzymes resident in the cell wall space access to substrates that were normally unavailable (Kumar et al., 2019). Although the impact of expansion regulations on fruit softening is evident, the biochemical function of this protein in cell wall breakdown remains obscure. For instance, Brummell et al. (1999) demonstrated that transgenic fruit trees with up expansion soften more rapidly compared to wild-type plants. The authors also acknowledged that softening was reduced in antisense plants with reduced expansin expression. Rose et al. (1997) reported that expansion was abundantly expressed during tomato fruit softening. Similarly, the molecular basis for the action and function of expansins in fruit ripening remains unresolved. This short overview demonstrates that further research is required to understand the roles of several enzymes and proteins regulated by ethylene during ripening.

The responses of harvested fruit and vegetables to endogenously produced and exogenously applied ethylene are numerous and varied (Palou et al., 2003). Some of the detrimental effects of ethylene include acceleration of physiological disorders, excessive softening, over ripening and colour change. The quality attributes of pears stored at − 1 and 2 °C with 0, 1, 5 and 10 µL/L ethylene were studied by Bower et al. (2003). It was found that all concentrations of ethylene increased the incidence of physiological disorders. In another investigation by Nguyen et al. (2000), ethylene concentrations of 0, 10, 100 and 1000 µL/L were applied on green mature mangoes to investigate the extent of colour change at 15, 20 and 25 °C. It was found that the amount of green colour increased with increasing ethylene concentration. Most recently, Nsumpi et al. (2020) evaluated the detrimental impact of fruit quality due to varying ethylene sensitivities. The study evaluated the effects of mixed-fruit loading on the physicochemical and physiological changes of bananas during storage. It was found that bananas stored in mixed-fruit load-ing showed accelerated quality degradation and decreased shelf life due to the high amount of ethylene that accumulated in the storage. Overall, these cell wall–degrading enzymes are inhibited by ethylene inhibitors such as 1-methylcyclopropene (1-MCP) (Özkaya et al., 2016; Srivastava et al., 2012). Similarly, their activities can also be retarded by other postharvest treatments/applications: UV–C irradiation and calcium chloride treatment (Mansourbahmani et al., 2017), modified atmosphere storage/packaging (Kaur et al., 2014; Phakdee & Chaiprasart, 2020), hot water treatment (Zhang et al., 2012; Mirshekari et al., 2015) and edible coatings (Conforti & Zinck, 2002; Zhou et al., 2011). Hence, for better postharvest management of fruit and vegetables, it is of crucial importance to develop strategies to regulate ethylene concentrations.

3.3 Mechanism of VUV photolysis

The overall efficiency of VUV photolysis and the degradation mechanisms are strongly influenced by the types and amounts of reactive species (Cheng et al., 2011b). Generally, the photodegradation mechanism (Fig. 3.2) occurs in three decomposition modes: (i) the direct photolysis where the ethylene is decomposed by VUV as described in Equation 3.1 (Chang et al., 2013); (ii) the indirect oxidation by active radicals such $^{\bullet}OH$, $^{\bullet}OH_2$, $O(^3P)$, $O(^1P)$, H_2O_2 and O_3 in Equations 3.2-3.6 (Pathak et al. (2017a) which are produced from photolysis of small molecules of H_2O and O_2, (iii) and the chain reaction by some atoms (Chen et al., 2002).

$$C_2H_4 + hv\ (185\ nm) \longrightarrow \text{oxidation products} \tag{3.1}$$

$$O_2 + hv\ (185\ nm) \longrightarrow O(^1D) + O(^3P) \tag{3.2}$$

$$O\ (^1D) + M \longrightarrow O(^3P) + M\ (M = O_2 \text{ or } N_2) \tag{3.3}$$

$$O\ (^3P) + O_2 + M \longrightarrow O_3 + M \tag{3.4}$$

$$O_3 + hv\ (<310\ nm) \longrightarrow O(^1D) + O \tag{3.5}$$

$$O\ (^1D) + H \longrightarrow 2^{\bullet}OH \tag{3.6}$$

$$H_2O + hv\ (185\ nm) \longrightarrow {}^{\bullet}OH + H^{\bullet} \tag{3.7}$$

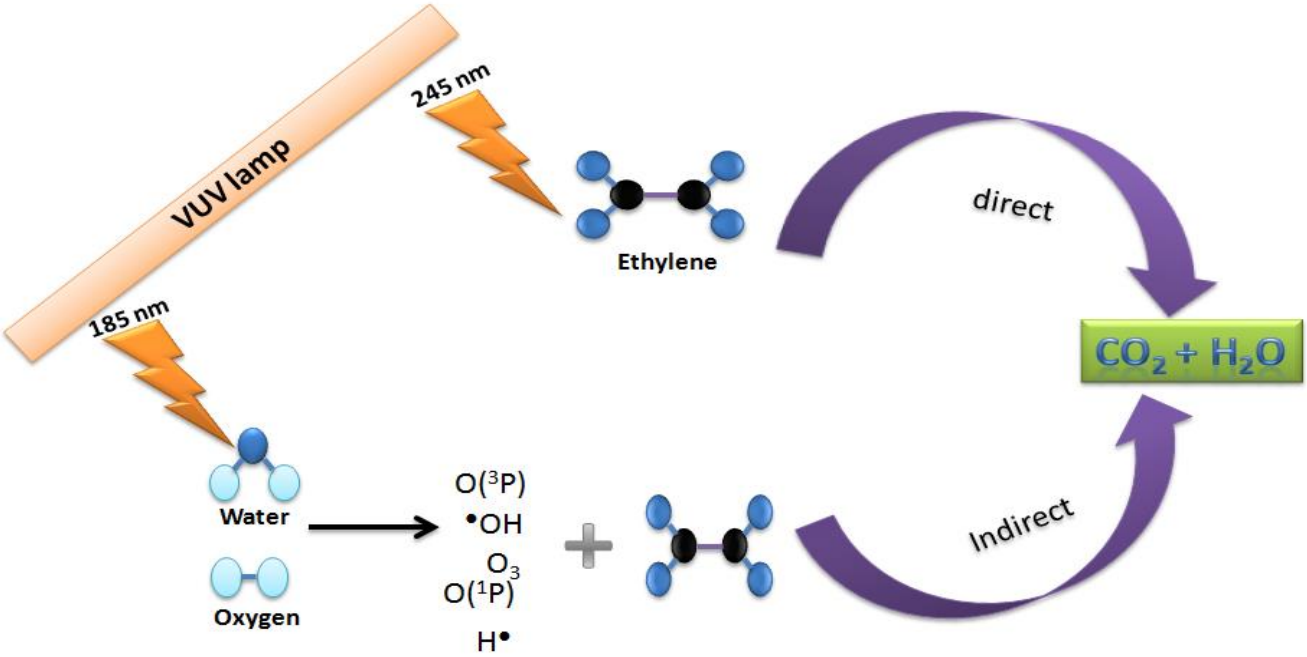


Figure 3.2: Schematic diagram showing the different pathways of photodegradation

Normally, both the indirect and direct modes are responsible for the photodegradation but the specific pathways that contribute most during photodegradation of ethylene have not been comprehensively studied while the results from the few studies available are inconclusive. The first studies proposed oxidation induced by O_3 to be the dominant degradation pathway (Scott et al., 1971). It was also reported by Zagory (1995) that ozone produced from the interaction of atomic oxygen and ultraviolet light was responsible for the degradation of ethylene. Recent studies, however, reported that ozone is produced as a byproduct and is not responsible for major ethylene degradation (Keller et al., 2013a). In other studies, direct photolysis is hypothesized (Shorter and Scott, 1985), while some studies proposed atomic oxygen to be the primary reactant responsible for ethylene decomposition (Jozwiak et al., 2003). Recently, hydroxyl radicals have been suggested to be the dominant oxidizing species in VUV photolysis (Pathak et al., 2019). It is evident that the dominant mechanism that contributes largely to the degradation pathway of ethylene is still unclear. This discrepancy exists because there is no proper understanding of the quantification and roles of the reactive species during ethylene degradation.

The degradation pathways of some VOCs by VUV photolysis are reported to be through the combination of direct photolysis, O_3 oxidation and $^{\bullet}OH$ oxidation (Cheng et al., 2011b; Yu et al., 2012). In the context of postharvest management, VUV photolysis will be applied in humid environments and, since the production of ozone is suppressed at high relative humidity (Ye et al., 2013b), the mechanisms are believed to be via the combination of direct photolysis and •OH photooxidation, with •OH photooxidation contributing the most. This is in accordance with the recent findings of Pathak et al. (2019) who reported that hydroxyl radicals were the dominant oxidizing species in VUV photolysis of ethylene. However, more studies that focus on identifying the intermediates are still warranted to confirm this hypothesis. Thus, efforts to understand the roles of the respective reactive species in the degradation mechanisms and the identification of byproducts are vital. This knowledge is important as it will help with the engineering design of efficient reactor systems and with the development of mathematical tools that could be used for process optimization.

3.4 Factors affecting VUV photolysis

3.4.1 Initial gas concentration

Ethylene concentration in supermarkets can vary from 0.017-0.035 µL/L and can be greater than 0.06 µL/L in wholesale markets and distribution centers and higher than 0.2 µL/L in the presence of climacteric fruits (Warton et al., 2000b). Pathak et al. (2017b) studied the effects of initial ethylene concentration on ethylene oxidation in a VUV photolysis reactor, and they found that increasing the ethylene inlet concentration increased the quantity of ethylene removed, while the percentage of ethylene removal decreased.

Similar observations were reported in the photolysis of H_2S by Xu et al. (2014) in which the authors observed a slight decrease in H_2S percentage from 100% to 93% as inlet concentration increased from 3.1 to 29.6 mg/m^3. Also, Wang and Ray (2000) observed a considerable decrease in the rate constants with the increasing initial concentration of both toluene and benzene. An opposite observation was also reported by the authors which indicated that the rate constant of *cis*-1,2-dichloroethylene increased with increasing *cis*-1,2-dichloroethylene initial ethylene concentration. The authors attributed this difference in observation to the difference in the chemical structures of the compounds. Increasing the initial concentration of ethylene, while keeping the number and energy of photons constant, results in more molecules of ethylene receiving less energy and thus results in lower ethylene removal.

3.4.2 Effects of residence time

Residence time is an important parameter for chemical reaction and design of VUV reactor and is determined by the flow rate. Pathak et al. (2017b) investigated the combined effects of three process variables; residence time, initial ethylene concentration and ultraviolet radiation on the efficiency of VUV photolysis, and they found that residence time exerted the most significant effect on the removal efficiency of ethylene. In their study ethylene removal was significantly enhanced to >60% with increasing residence time. Similar results were reported by Cheng et al. (2011a) for the conversion of α-pinene degraded by VUV light where the authors observed an increase in removal efficiency upon increasing residence time. Increasing residence time increases the probability of collisions between ethylene molecules and hydroxyl radicals and photons, hence increasing removal efficiency. However, care needs to be taken into consideration when increasing residence time since the lifetime of radicals, which are responsible for degradation in VUV systems, is nanoseconds. For example, increasing residence time by 8-fold resulted in a slight removal increase from 95% to 99% for VUV photolysis of H_2S (Xu et al., 2014). Although increasing residence time would have a positive effect on the removal efficiency, it will result in a large reactor volume and thereby increase design costs. Therefore, optimization of residence time is important when designing a cost-effective VUV reactor system.

3.4.3 Light intensity

Light is regarded as the essential element in VUV photolysis as in the absence of light no reactive species are generated and hence there is no ethylene removal. Also, light not only initiates ethylene removal but also dominates the energy consumption and cost of VUV systems. As stated above, ethylene can be degraded through two different pathways; direct photolysis and indirect photolysis, and both pathways require the presence of UV light. Pathak et al. (2017b) found that increasing light intensity from 3W to 9W resulted in increased ethylene removal from 1.62% to 41.8%. Similar results were observed by Wang and Ray (2000) where the authors reported a higher rate constant of oxidation of VOCs with increasing light intensity. Increasing light intensity is associated with increasing the number of photons and consequently increases the number of generated reactive species which results in higher ethylene removal. Likewise, more photons are absorbed by ethylene molecules to promote direct photolysis.

3.4.4 Relative humidity

Generally, fruits and vegetables produce water during respiration, which may alter RH concentration in the storage chamber (Ayomide et al., 2019); therefore, the influence of RH on any ethylene removal technology is crucial. As shown in reaction 7, OH radicals initiate photooxidation and water vapour is the main source of OH radicals (Asili and Vissche, 2014). In a study by Pathak et al. (2019), increasing RH from 10.7% to 84.9% increased the oxidation rate of ethylene under VUV by reducing the half-time from 1.95 to 0.63. Chang et al. (2013) also reported positive results in which the removal of ethylene increased to 95.7% upon increasing RH from <1% to >80%. Also, increasing RH has been associated with high removal for VOCs. Xu et al. (2014) investigated the photolysis of H_2S and they found that increasing RH from <5% to 43% resulted in a 58% removal increase. Although increasing RH has positive effects, it might have negative effects on the removal of some pollutants as increasing RH is associated with inhibiting ozone generation (Ye et al., 2013a). For example in the study by Cheng et al. (2011a), the degradation of α-pinene decreased with increased RH because of the reduced contact of α-pinene with light and O_3 due to the abundant water molecules and reduced ozone production. The effect of RH on ethylene removal by VUV photolysis still needs to be comprehensively investigated to understand the interaction of hydroxyl radicals on ethylene removal and O_3 inhibition.

3.5.5 Oxygen concentration

Oxygen is an important precursor of active substances such as •O and O_3, hence its content has a significant role in ethylene removal. Oxygen absorbs the 185 nm light to form ozone through reactions (Eqs. (2)-(4)). Increasing O_2 concentration from 2% to 6% resulted in increased ozone production (Ye et al., 2013a). Jozwiak et al. (2003) studied the effects of different O_2 concentrations (1%, 2% and 3%) on the removal of ethylene by UV lamp in a CA. The authors observed that increasing the O_2 concentration resulted in a slight increase in ethylene removal. Pathak et al. (2019) also investigated the effect of O_2 concentration on the half-time of ethylene at an RH of 84.9%. They found that increasing the concentration of O_2 from 0.67% to 20.8% greatly reduced the half-time from 0.9 min to 0.63 min resulting in higher removal for ethylene. Although there are few studies on the effect of O_2 concentration on ethylene removal by VUV photolysis, similar results for the purification of air by VUV photolysis have been reported. For instance, Wang and Ray (2000) investigated the influence of O_2

concentration on oxidation of toluene and found that the oxidation of toluene in pure O_2 was considerably faster than that in nitrogen. Also, Xu et al. (2014) observed higher removal rates of H_2S under air and oxygen environments compared to argon environments. Although the presence of O_2 has a positive effect on the removal of ethylene, it is important to properly manage the concentration of O_2 to prevent the accumulation of O_3 which could be detrimental to the stored produce and harmful to human health. Furthermore, higher production of O_3 will require a filtering system which would increase the capital cost for the process.

3.5 Mechanism of microbial inactivation

Fresh produce is frequently associated with outbreaks of food-borne diseases thus there is a need to develop effective intervention technologies and antimicrobial treatments to improve the microbial safety of fresh produce. Based on VUV photolysis capability to degrade organic and inorganic compounds, it has been used for the destruction of microorganisms. The main emission of the low-pressure mercury vapor lamp at 254 nm causes the inactivation of microorganisms. The degree of photo-deactivation of microorganisms depends on various treatment parameters and the nature of microorganisms. Gram-positive bacteria were found to be more resistant to photocatalytic inactivation than Gram-negative bacteria.

According to Wang et al. (2010), the disinfection efficacy of VUV photolysis relies on the action of the generated reactive oxygen species, which induce surface oxidation on the cell wall and cell membrane molecules. In addition, generated hydroxyl radicals could diffuse into the cell to damage intracellular organelles, inactivate enzymes and hinder protein synthesis (Mamane et al., 207). This is followed by increased damage to the cell wall and leads to the leakage of ions and small molecules from the bacterial cells leading to cell death or complete mineralization of the cell. A schematic diagram of the mechanisms of microbial inactivation via photolysis is shown in Figure 3.3.

Furthermore, the UV processing wavelength ranges from 100 to 400 nm. This range could be subdivided into UV-A (315-400 nm), normally responsible for changes in human skin referred as tanning; UV-B (280-315 nm), which can cause skin burn and skin cancer; UV-C (200–280 nm), which is referred to as the germicidal range, with capability to inactivate microorganisms; and the vacuum UV range (100-200 nm), with the ability to absorb organic and inorganic substances (Oppenlaender, 2003; Koutchma et al., 2009). The most commonly used ultraviolet radiation in postharvest management are the UV-A, UV-B and UV-C, and their application in postharvest storage of fruit and vegetables is well established and has recently been reviewed. Low doses of short-wave ultra-violet light irradiation (0.25-8.0 kJ/m^2) can affect the DNA of microbes (Terry and Joyce, 2004). In addition, it has been demonstrated that low doses of UV can create a hermetic effect in plant tissue (stimulating a beneficial response) leading to induced resistance agents and food pathogens (Alothman et al., 2009; Terry and Joyce, 2004). Therefore, bacterial inactivation by photolysis depends on the amount of generated reactive oxygen species and the resistant ability of the cell wall structure. More work is needed to understand the mechanisms of VUV inactivation.

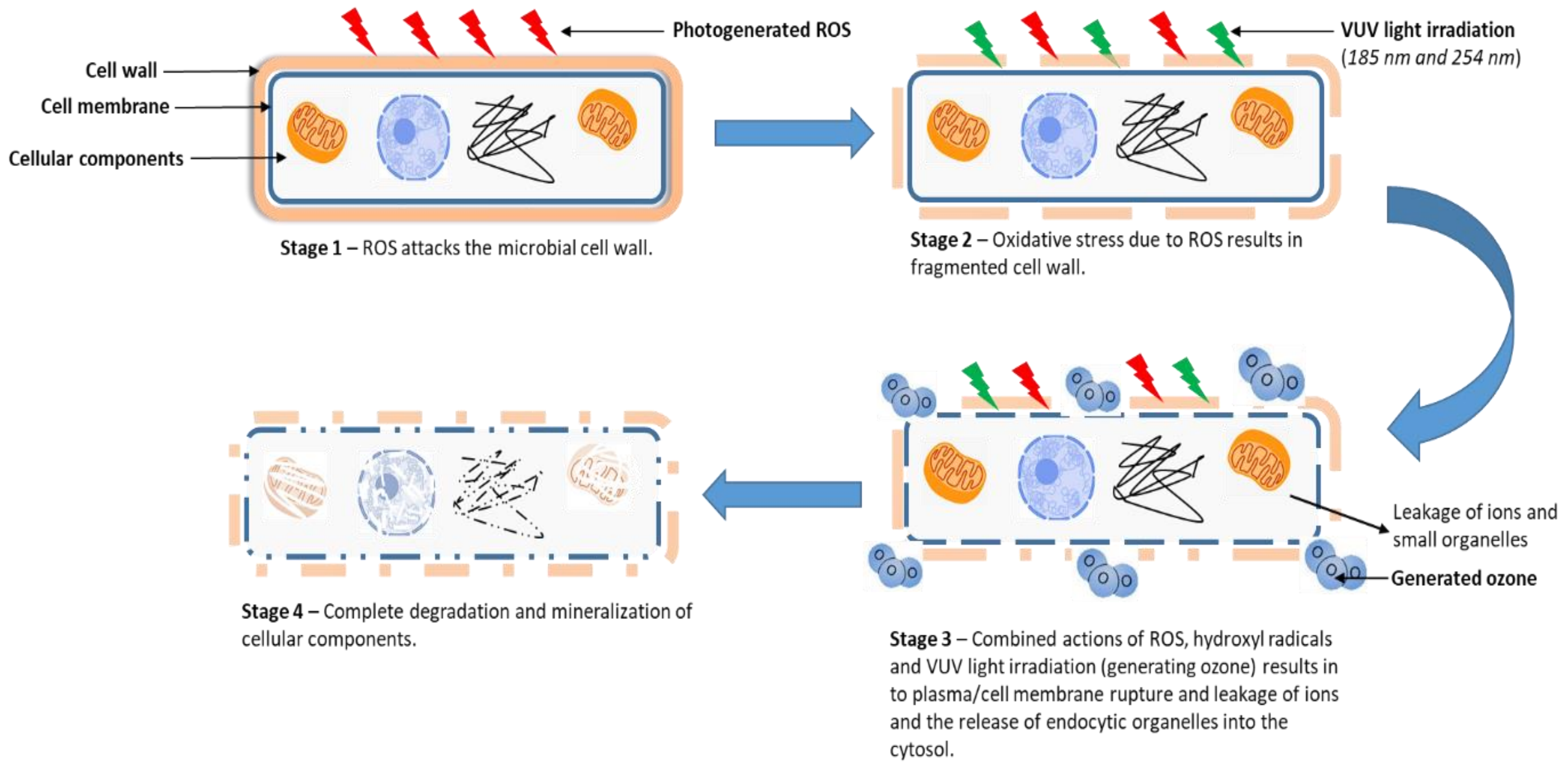


Figure 3.3: Schematic diagram of the mechanisms of microbial inactivation via VUV photolysis

3.6 Application of VUV photolysis for microbial inactivation

Current strategies such as washing with chemical sanitizers (especially chlorine) are designed to minimize the risk of contamination during postharvest operations. However, these compounds are potentially harmful to humans and the environment. According to a recent review by Fan and Song (2020), advanced oxidation processes offer a better potential for antimicrobial activity because of the production of highly reactive species. While VUV radiation has received much attention for the inactivation of microorganisms in wastewater (Zoschke et al., 2014), the exploitation of VUV photolysis for microbial inactivation in postharvest management has been less researched attention. Most of the published research on the delivery of low UV doses to fresh horticultural commodities has focused on a relatively small quantity of treated fruit at a laboratory experimental scale. Hence, future consideration should be given to upscaling from laboratory to pilot and large scale under industrial conditions.

Table 3.2 lists studies on the effects of UV radiation on the inactivation of microorganisms during postharvest on fruit and vegetables within the last decade. Other articles have extensively reported on catalyse-assisted photolysis (photocatalysis) as a nonthermal alternative tool for microbial inactivation (Ramesh et al., 2016; Zhu et al., 2018). For instance, Choi et al. (2020) recently investigated the efficiencies of various treatments for UVC photolysis, VUV photolysis, UVC-assisted titanium dioxide photocatalysis (UVC-TiO_2), and VUV-assisted titanium dioxide photocatalysis (VUV- TiO_2) for the degradation of pesticides and inactivation of microorganisms in aqueous solution and on the surface of fresh-cut carrots. It was reported that the degradation efficiencies of VUV photolysis were higher than for UVC photolysis on pesticides in aqueous solutions. The results also showed that VUV photolysis had the highest inactivation effect, almost 2 log CFU/mL, compared to all other treatments for the first 30s. VUV photolysis has attractive characteristics that make it a promising potential technology in the postharvest value chain. Hence, this review is solely focused on the use of photolysis.

Fonseca and Rushing (2006) compared the effects of UV-C light (254 nm) treatments with that of common sanitizing solutions such as chlorine and ozone for fresh-cut watermelon on the quality and microbial load. The authors found UV-C treatments to be better than ozone and chlorine in reducing microbial populations and maintaining quality. They achieved good results with 1.4 kJ/m^2. Similarly, Erkan et al. (2008), demonstrated that treating strawberry fruit with

UV-C illumination for different durations and dosages (1, 5 and 10 min and 0.43, 2.15 and 4.30 kJ/m^2) significantly reduced the severity of decay during storage at 10 °C. With 5 and 10 min illumination it performed the best. Pinheiro et al. (2015) reported that low doses of UV treatment of 0.97 kJ/m^2 were effective in a 2.1 log CFU/g reduction in mesophilic load and delayed red colour development of tomatoes. Similarly, Bialka and Demirci (2008) showed that strawberries and raspberries treated with UVC at varying doses and times: resulted in a reduction of *E. coli* O157:H7 and *Salmonella* of 3.9 and 3.4 log CFU/g achieved, respectively, on raspberries and 2.1 and 2.8 log CFU/g, respectively, on the surface of strawberries. Overall, the performance of UV irradiation is dependent not only on the UV dosage and exposure time. The variations in results could be attributed to the initial microbial load/contamination level. However, more research is still required for a complete understanding of the interaction of hydroxyl radicals under VUV photolysis with spoilage and pathogenic microorganisms.

Table 3.2: Studies on the effects of ultraviolet radiation on the inactivation of microorganisms during postharvest on fruit and vegetables within the last decade

*F&V	Microorganisms	UV-Treatments condition	Microbial Log reduction (log CFU/g)	Reference
*FC-apples	*E. coli, L. innocua, Saccharomyces cerevisiae*	Blanching + 1.1 to 11.2 kJ/m^2 for 2, 8, 14 or 20 min 5.6 to 14.1 kJ/m^2 for 10, 15 or 25 min	• Reduction ranges varied between 1.0 and 1.9	Gomez et al. (2010)
Mushroom	*Bacillus cereus*	Sanitizers + UV (6 to 504 Ws/cm^3)	• Reductions were between 0.21- 1.74 depending on the UV irradiation dose • Synergistic effects of combined ethanol/UV, H_2O_2/UV and NaClO/UV treatments were 0.14-1.59, 0.05-0.88, and 0.09-0.81, respectively.	Ha et al. (2011)
Apple Juice	*E. coli* K12, *L. innocua*	2.66 J/cm^2 for 15s; 5.31 J/cm^2 for 30s	• Reduction below the detection level (<1 log) for both *E. coli* and *L. innocua* in apple juice	Caminiti et al. (2012)
	*E. coli O*157:H7	0.45-3.15 Kj/m^2	• Treatment resulted in 0.7 to 1.1 reduction	Guan et al. (2012)

*F&V	Microorganisms	UV-Treatments condition	Microbial Log reduction (log CFU/g)	Reference
Blueberries	*E. coli O*157:H7	20 mW/cm^2 at a distance of 0.9 cm for 1, 5 and 10 min Ozone + 7.95 mW/cm^2 for 2 min	• UV treatment for 1 and 5 min significantly reduced the population (5.53 log CFU/g) on the skin of blueberries to 2.42 and 1.83 log, respectively. • UV treatment for 10 min decreased *E. coli* O157:H7 counts by ≥4.05 log. • Combined ozone and UV and vice versa reduced the populations (6.38 log CFU/g) on the calyx of blueberries to 3.33 and 4.02 log.	Kim and Hung (2012)
Apricot	*E. coli O*157:H7, *Salmonella* spp.	74 and 442 mJ/cm^2	• Populations on UV-C treated fruit were 1-2 log lower	Yun et al. (2013)
	*E. coli O*157:H7	1.0-2.54 kJ/m^2	• UV- treatment resulted to 0.5 to 1.8 reduction	Yan et al. (2014)

*F&V	Microorganisms	UV-Treatments condition	Microbial Log reduction (log CFU/g)	Reference
Apples and pears	*E. coli O*157:H7, *L. monocytogenes*	0.92-5 KJ/m^2 for 60-300 s	• *E.coli* O157:H7 on apples and pears by 2.9 and 2.1, respectively • 1.6 and 1.7 for *L. monocytogenes* on apples and pears	Adhikari et al. (2015)
	*E. coli O*157:H7, *S. Enterica*	7.9 mW/cm^2 for 2 to 10 min – dry treatment 4.6 mW/cm^2 - wet treatment	• Dry UV treatment for 2, 5, and 10 min reduced *E. coli* O157:H7 spot-inoculated by 2.0, 3.7, and 4.0 log, respectively. • Average differences between the wet and dry UV treatments were 0.9 log and 1.9 log for the skinand calyx inoculation, respectively.	Liu et al. (2015)
	Botrytis cinerea	12.36 J/m^2 for 0, 30, and 60s, 2, 3, 4, 5, 10, 20, 30, 40, 50, and 60 min + 4 h in dark	• Controlled gray mould in tunnel produced strawberries	Janisiewicz et al. (2016)

*F&V	Microorganisms	UV-Treatments condition	Microbial Log reduction (log CFU/g)	Reference
Raspberries	*E. coli* O157:H7, *Salmonella, L. monocytogenes*	7.8 × 102 Mj/cm^2	• A 1.5 log reduction of *L. monocytogenes* population	Liao et al. (2017)
Berries (straw-, rasp- & blueberries)	*L. monocytogenes, Salmonella and E. coli O157:H7, HAV*, MNV* S99*	212 to 4000 mJ/cm^2 for 20s to 9 min	• For MNV, a >1 log reduction was obtained only on fresh blueberries treated for 120 s. • For HAV, all treatments of frozen berries resulted in at least 1 log reduction • No treatment inactivated above 1 log of pathogenic bacteria cocktail	Butot et al. (2018)
*FC-Mango	*E. coli, Cronobacter sakazakii*	2.5, 5, 7.5 and 10 kJ/m^2 at different temperatures (4, 8, 12 and 20 °C)	• Highest reductions 2.4 to 2.7 in *C. sakazakii* were achieved with various doses • Lowest bacterial decrease of 2.1 was achieved at UV-C dose of 2.5 Kj/m^2.	Santo et al. (2018)
Grape tomato	**Four strains of Salmonella enterica*	0, 7, 10, and 30 mW/cm^2 for 2, 5, and 10 min	• 30 mW/cm^2 UV for 10 min, resulted in >4 reductions of *Salmonella* dip- or spot-inoculated grape tomato	Yao and Chen (2021)

*F&V	Microorganisms	UV-Treatments condition	Microbial Log reduction (log CFU/g)	Reference
*FC-Lettuce	*L. monocytogenes*, *S. enterica*	0.1–0.5 kJ/m2 , 60–300 s, PA + MAP	• 1.2-2.1, and 1.8-2.5 reduction for *L. monocytogenes*, and *S. enterica,* respectively	Collazo et al. (2019)
Baby spinach	*Salmonella*	2 Mw/cm^2 water assisted UV with dose of 17400 Mj/cm^2	• Significant reduction *Salmonella* compared to tap water.	Guo et al. (2019)
Blueberries	*Salmonella*	2 mW/cm^2 water assisted UV with dose 17400 mJ/cm^2	• reduced populations of spot-inoculated *Salmonella* by 5.45	
	Salmonella	2 Mw/cm^2 water assisted UV with dose of 17400 Mj/cm^2	• Significant reduction *Salmonella* compared to tap water.	
Peaches	*E. coli O*157:H7	Fuzz + 0, 221, and 442 Mj/cm^2	At 442 Mj/cm^2 *E. coli* was reduced by 1.2 to 1.4 with fuzz, and 0.9 to 1.1 without fuzz	Yan et al. (2020)

*F&V = Fruit and vegetables; Strains of *Salmonella (S. Montevideo 51, S. Newport H1073, S. Heidelberg 45955, S. Typhimurium 14028),* FC = Fresh cut, HAV = hepatitis A virus, MNV = murine norovirus

3.7 VUV or UV Irradiation and fruit quality associated enzymes

Even though the effects of VUV on quality of fresh produce is very limited, Pathak et al. (2017a; 2017b; 2019) conducted a significant amount of research trying to understand the impact of VUV photolysis on the quality attributes of produce. Their results showed that tissue softening on Kiwifruit was delayed, with a slight reduction in respiration rate and a significant reduction in ethylene was observed (Pathak et al., 2017a, Pathak et al., 2017b). The direct effects of VUV photolysis on the quality attributes of fresh produce remain unknown, however, VUV photolysis has been demonstrated as an effective removal system for ethylene (Pathak et al., 2019). Ethylene management has been well correlated with the overall maintenance of fresh produce quality attributes. Research interest in investigating the direct impact of VUV photolysis on produce quality remains a priority. It is crucial to understand if the VUV photolysis process (generation of ozone and other intermediates) has any detrimental effects, whatsoever, on the sensory and nutritional quality of fruit and vegetables. This section of the review focused on enzymatic changes during UV treatments (a similar approach but a different wavelength to VUV), with emphasis on enzymes associated with ethylene regulation and cell wall degradation.

UV treatments such as UV–C and UV–A have been successful in maintaining the quality of fruit and vegetables and maintaining lower enzymatic changes during processing (Lante et al., 2016; Teoh et al., 2016; Zhang & Jiang, 2019). For example, Barka et al. (2000) found that a dose of UV–C at 254 nm decreased the activity of enzymes involved in tomato cell wall degradation (PG, PME, cellulase, xylanase, β-d-galactosidase and protease) and delayed the fruit softening compared to control samples. As indicated earlier under the ethylene biosynthesis section, PME and PG are considered the primary hydrolase enzymes involved in the fruit tissue softening process (Alexander & Grierson, 2002; Iqbal et al., 2017). Barka et al. (2000) suggested that the UV–C treatment induced a significant reduction of cell wall degradation enzyme activities by inducing proteolysis of the enzymes or reducing their de novo synthesis.

In another study, UV–C treatment was found to be successful in enhancing the activities of antioxidant enzymes including glutathione peroxidase, glutathione reductase, superoxide dismutase, ascorbate peroxidase, guaiacol peroxidase, monodehydroascorbate reductase, and dehydroascorbate reductase and significantly retarded the development of decay in the storage of strawberry fruit (Erkan et al., 2008). The increase of glutathione peroxidase in the strawberry fruit during storage was associated with glutathione, which plays a crucial role in the stabilization of numerous enzymes and serves as a substrate for dehydroascorbate reductase. It also reacts with free radicals such as hydroxyl radicals directly to prevent the inactivation of enzymes by oxidation of the essential thiol group (Foyer & Noctor, 2011; Ziegler, 1985). Similarly, UV–C treatment of strawberries led to higher activities of guaiacol peroxidase and ascorbate peroxidase. These enzymes are beneficial for antioxidant protection in the fruit against lipid peroxidation and DNA hydroperoxides (Chaudiere & Ferrari-Iliou, 1999).

Yang et al. (2014) investigated the impact of 3.0 kJ/m UV–C treatment on respiratory and mitochondrial membrane activity associated with fruit senescence in 'Yulu' peach fruit stored at 20 °C for 8 days. The authors confirmed that the UV–C treatment delayed senescence development and inhibited fruit respiratory activity. This response was attributed to the decline in the activities of important respiratory enzymes; succinic dehydrogenase and cytochrome C oxidase both located on the inner mitochondrial membrane in plant cells. Furthermore, UV–C treatment was shown to enhance and increase the activities of antioxidant enzymes such as catalase, ascorbate peroxidase and superoxide dismutase (Yang et al., 2014). On the other hand, Maharaj et al (2014) showed that UV–C irradiation of tomato with UV–C 24.4 kJ/m dose did not induce the accumulation of any specific phytochemicals besides the accumulation of non-specific phytochemicals such as phenols. In addition, the UV–C treatment did not stimulate superoxide dismutase activity, except in the exocarp of UV–C-treated tomatoes wherein the maximum activity was delayed for a short duration in comparison to the control samples. The differences observed in various fruit responses to UV-C treatment could suggest that it is possible that in the tissues of these fruits, the mechanisms involved in antioxidant protection and capacity to overcome oxidative stress differ.

Furthermore, UV-C treatment was shown to have delayed softening and ripening 'aroma' strawberries (Pombo et al., 2009). The authors reported that strawberries harvested at 50% red ripening stage and irradiated with a non-lethal UV–C dose (kJ/m) showed higher firmness than controls even 96 h after irradiation. Based on genomic expression, the irradiation treatment was confirmed to have lowered the expression of the genes encoding cell wall–degrading enzymes and proteins. However, at given sampling times, the activities of PME, PG and endoglucanase remained either relatively unchanged or lower level than in non-irradiated strawberry fruit (Pombo et al., 2009). Tran and Farid (2004) showed no reduction in the activity of PME in orange juice treated with UV light with the exposure at 73.8 mJ/cm. However, the authors noted that the residual activity of this enzyme declined significantly (30%) when samples were treated with mild heat at 70 °C for 2 s. Similarly, Sew et al. (2014) demonstrated that for freshly made pineapple juice, the activities of PME and proteolytic were not significantly affected by UV dosage but by mild heat treatment. Overall, these studies and their diverse report on the impact of UV light treatment demonstrate that further research is required to elucidate the impact of UV and VUV application on fresh fruit and vegetables. Additionally, the roles of several enzymes and proteins underpinning ethylene biosynthesis and oxidative stress response during fruit ripening or postharvest storage remain obscured, and further work is required.

The UV doses in the reported enzyme studies varied in a broad range from 1.5 to 108 kJ/L. The highest enzyme inactivation occurred with MPM lamps in clear apple, grape and pear juices as well as in buffered solutions. Complete inactivation of enzymes was only reported with the use of an MPM lamp, which was an identical Phillips 400 W unit, emitting UV light between 250 and 740 nm with the highest intensity at 415 nm.

3.8 Conclusions

VUV photolysis is an emerging alternative technology with great potential to compete with conventional postharvest management technologies. In VUV photolysis, ethylene is oxidised to CO_2 and H_2O. The process is very fast with no limitations as the degradation occurs in the gaseous phase. The most attractive trait that makes VUV photolysis a promising alternative technology is the improved removal rates at higher RH. The major challenges for the practical application of VUV photolysis for ethylene removal include improving the low ethylene removal rates at low initial ethylene concentrations and the removal of the generated ozone as a by-product. These can be overcome by the use of VUV reactors in series to increase removal rates or coupling the VUV photolysis reactor with other systems that can utilise the ozone for further ethylene degradation. Therefore, understanding the degradation mechanisms and removal kinetics for ethylene should be the focus area for current research. This understanding can be used in the development of mathematical models that could serve as engineering tools in translating lab work for commercial adoption. In addition, VUV systems are considered to be cheap and the only factor affecting the running cost is the energy input. Thus, feasibility studies focusing on assessing energy utilization are needed. There are still a few technical issues to be resolved before the realization of practical application. Furthermore, the generated reactive species and free radicals in VUV photolysis systems could have a dual purpose: microbial inactivation and ethylene removal. However, there is still a critical need to study the characteristics of these reactive species and their interaction with microorganisms and plant tissues at the biochemical and molecular level. Lastly, the effects of VUV treatments on the enzyme activities of fruits and vegetables are currently lacking, while those reported on the impact of UV remain obscured based on conflicting outcomes. Therefore, further research is needed to investigate existing disparities among studies and generate new knowledge to guide future postharvest applications. A multi-omics research approach would be a valuable tool to better guide our understanding of these changes.

3.9 Summary

This chapter has delivered a comprehensive overview of the VUV photolysis reactor's role in ethylene degradation and its impact on antimicrobial activity. It unravels the mechanisms governing ethylene degradation and its correlation with antimicrobial activity. The insights and knowledge garnered from this chapter provide a robust foundation for the ensuing discussions and investigations in Chapters 4, 5, and 6.

References

Adhikari, A., Syamaladevi, R. M., Killinger, K., & Sablani, S. S. (2015). Ultraviolet-C light inactivation of *Escherichia coli* O157:H7 and *Listeria monocytogenes* on organic fruit surfaces. *International Journal of Food Microbiology, 210*, 136–142.

Alexander, L., & Grierson, D. (2002). Ethylene biosynthesis and action in tomato: A model for climacteric fruit ripening. *Journal of Experimental Botany, 53*, 2039–2055.

Alothman, M., Bhat, R., & Karim, A. A. (2009). Effects of radiation processing on phytochemicals and antioxidants in plant produce. *Trends in Food Science & Technology, 20*, 201–212.

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., Ventura -Sobrevilla, J. M., & Martínez-Hernández, G. B. (2018). Current scenario of adsorbent materials used in ethylene scav-enging systems to extend fruit and vegetable postharvest life. *Food Bioprocess Technology, 11*, 511–525.

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Bel-montes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, C., & Artés-Hernández, F. (2019). Potassium permanganate-based ethylene scavengers for fresh horticultural produce as an active packaging. *Food Engineering Reviews*. https://doi.org/10. 1007/s12393-019-09193-0

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science, 141*, 012003.

Asili, V., & Vissche, A. D. (2014) . Mechanistic model for ultraviolet degradation of $H\text{-}_2S$ and NOx in waste gas. *Chemical Engineering Journal, 244*, 597–603.

Ayomide, O. B., Ajayi, O. O., & Ajayi, A. A. (2019). Advances in the development of a tomato postharvest storage system: towards eradicating postharvest losses. *Journal of Physics: Conference Series, 1378*, 022064.

Bal, E. (2018). Extension of the postharvest life of nectarine using modified atmosphere packaging and potassium permanganate treatment. *Turkish Journal of Agriculture—Food Science and Technology, 6*(10), 1362–1369.

Barka, E. A., Kalantari, S., Makhlouf, J., & Arul, J. (2000). Impact of UV–C irradiation on the cell wall-degrading enzymes during ripening of tomato (*Lycopersicon esculentum* L.) fruit. *Journal of Agricultural and Food Chemistry, 48*, 667–671.

Bermudez-Aguirre, D., Barbosa-Canovas, G. V. (2013). Disinfection of selected vegetables under non-thermal treatments: Chlorine, acid citric, ultraviolet light and ozone. Food Control, 29, 82–90.

Birmpa, A., Sfika, V., Vantarakis, A. (2013). Ultraviolet light and ultra-sound as non-thermal treatments for the inactivation of micro-organisms in fresh ready-to-eat foods. International Journal of Food Microbiology, 167, 96–102.

Birmpa, A., Bellou, M., Kokkinos, P., & Vantarakis, A. (2016). Effect of nonthermal, conventional, and combined disinfection technologies on the stability of human adenoviruses as fecal contaminants on surfaces of fresh ready to eat products. Journal of Food Protection, 79, 454–462.

Bialka, K. L. & Demirci, A. (2008). Efficacy of Pulsed UV-Light for the Decontamination of Escherichia coli O157:H7 and Salmo-nella spp. on Raspberries and Strawberries. Journal of Food Science, 73, M201-M207.

Bower, J. H., Biasi, W. V., & Mitcham, E. J. (2003). Effect of ethylene in the storage environment on quality of 'Bartlett pears.' *Post-harvest Biology and Technology, 28*, 371–379.

Brummell, D. A., & Harpster, M. H. (2001). Cell wall metabolism in fruit softening and quality and its manipulation in transgenic plants. *Plant Molecular Biology, 47*, 311–340.

Brummell, D. A., Harpster, M. H., Civello, P. M., Palys, J. M., Bennett, A. B., & Dunsmuir, P. (1999). Modification of expansin protein abundance in tomato fruit alters softening and cell wall polymer metabolism during ripening. *The Plant Cell, 11*, 2203–2216.

Butot, S., Cantergiani, F., Moser, M., Jean, J., Lima, A., Michot, L., Putallaz, T., Stroheker, T., & Zuber, S. (2018). UV-C inactivation of foodborne bacterial and viral pathogens and surrogates on fresh and frozen berries. International Journal of Food Microbiology, 275, 8 16

Caminiti, I. M., Palgan, I., Muñoz, A., Noci, F., Whyte, P., Morgan, D. J., Cronin, D. A., & Lyng, J. G. (2012). The effect of ultraviolet light on microbial inactivation and quality attributes of apple juice. Food and Bioprocess Technology, 5, 680-686.

Chang, K.-L., Sekiguchi, K., Wang, Q., & Zhao, F. (2013). Removal of ethylene and secondary organic aerosols using UV–C254 + 185 nm with TiO_2 catalyst. *Aerosol and Air Quality Research, 13*, 618–626.

Chaudiere, J., & Ferrari-Iliou, R. (1999). Intracellular antioxidants: from chemical to biochemical mechanisms. *Food and Chemical Toxicology, 37*, 949–962.

Chen, F. Y., Pehkonen, S. O., & Ray, M. B. (2002). Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. *Water Research, 36*, 4203–4214.

Cheng, Z.-W., Jiang, Y.-F., Zhang, L.-L., Chen, J.-M., & Wei, Y.-Y. (2011). Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. *Separation and Purification Technology, 77*, 26–32. https://doi.org/10.1016/j.seppur.2010.11.014

Chiara, M. L. V. D., Pal, S., Licciulli, A., Amodio, M. L., & Colell, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO_2/SiO_2 nanocomposites: effects on the ripening of mature green tomatoes. *Biosystems Engineering, 132*, 61–70.

Choi, S. W., Shahbaz, H. M., Kim, J. U., Kim, D.-H., Yoon, S., Jeong, H., Park, J., & Lee, D.-U. (2020). Photolysis and -TiO_2 photocatalytic treatment under uvc/vuv irradiation for simultaneous degradation of pesticides and microorganisms. *Applied Sciences, 10*, 4493.

Collazo, C., Noguera, V., Aguilo-Aguayo, I., Abadias, M., Colas-Meda, P., Nicolau, I., & Vinas, I. (2019) . Assessing water-assisted UV-C light and its combination with peroxyacetic acid and Pseu-domonas graminis CPA-7 for the inactivation and inhibition of Listeria monocytogenes and Salmonella enterica in fresh-cut 'Iceberg' lettuce and babyspinach leaves. International Journal of Food Microbiology, 297, 11–20.

Conforti, F. D., & Zinck, J. B. (2002). Hydrocolloid-lipid coating affect on weight loss, pectin content, and textural quality of green bell peppers. *Journal of Food Science, 67*(4), 1360–1363.

Corrêa, S., Filho, M. B., Silva, M. G. D., Oliveira, J. G., Aroucha, E. M. M., Silva, R. F., Pereira, M. G., & Vargas, H. (2005). Effect of the potassium permanganate during papaya fruit ripening: ethylene production. *Journal of Physics IV France, 125*, 869–871.

Cosgrove, D. J., Li, L. C., Cho, H. T., Hoffmann- Benning, S., Moore, R. C., & Blecker, D. (2002). The growing world of expansins. *Plant Cell Physiology, 43*, 1436–1444.

Cote, S., Rodoni, L., Miceli, E., Concellon, A., Civello, P. M., & Vincente, A. R. (2013). Effect of radiation intensity on the outcome of postharvest UV-C treatments. Postharvest Biology and Technology, 83, 83–89.

Dash, S., Patel, S., & Mishra, B. (2009). Oxidation by permanganate: synthetic and mechanistic aspects. *Tetrahedron, 65*(4), 707–739.

Eda, M., Matsumoto, T., Ishimaru, M., & Tada, T. (2016) . Structural and functional analysis of tomato β-galactosidase 4: insight into the substrate specificity of the fruit softening-related enzyme. *Plant Journal, 86*, 300–307.

Elzubeir, M. M., Abu-Goukh, A. A., & Osman, O. (2017). Effect of polyethylene film lining and potassium permanganate on quality and shelf-life of mangofruits. *Journal of Environmental and Social Sciences, 4*(1), 130.

Emadpour, M., Ghareyazie, B., Kalaj, Y. R., Entesari, M., & Bouzari, N. (2015). Effect of the potassium permanganate coated zeolite nanoparticles on the quality characteristic and shelf life of peach and nectarine. *Journal of Agricultural Technology, 11*(5), 1263–1273.

Erkan, M., Wang, S., & Wang, C. (2008). Effect of UV treatment on antioxidant capacity, antioxidant enzyme activity and decay in strawberry fruit. *Postharvest Biology and Technology, 48*, 163–171.

Fan, X., & Song, Y. (2020). Advanced oxidation process as a post-harvest decontamination technology to improve microbial safety of fresh produce. *Journal of Agricultural and Food Chemistry*. https://doi.org/10.1021/acs.jafc.0c01381

Fernández-Suárez, R., Ramírez-Villatoro, G., Díaz-Ruiz, G., Eslava, C., Calderón, M., Navarro-Ocaña, A., Trejo-Márquez, A., Wacher, C. (2013). Effect of postharvest UV-C treatment on the bacterial diversity of Ataulfo mangoes by PCR- DGGE, survival of E. coli and antimicrobial activity. Frontier in Microbiology, 4, 134.

Fonseca, J., & Rushing, J. (2006). Effect of ultraviolet -C light on the qual-ity of fresh-cut watermelon. *Postharvest Biology and Technology, 40*, 256–261.

Foyer, C. H., & Noctor, G. (2011). Ascorbate and glutathione: the heart of the redox hub-[1]. *Plant Physiology, 155*, 2–18.

Gaikwad, K. K., Singh, S., & Negi, Y. S. (2019). Ethylene scavengers for active packaging of fresh food produce. *Environmental Chemistry Letters*. https://doi.org/10.1007/s10311-019-00938-1

Graça, A., Salazar, M., Quintas, C., & Nunesaday, C. (2013). Low dose UV-C illumination as an eco-innovative disinfection system on minimally processed apples. Postharvest Biology and Technology, 85, 1-7.

Golden, K. D., Williams, O. J., & Dunkley, H. M. (2014). Ethylene in postharvest technology: a review. *Assian Journal of Biological Science, 7*(4), 135–143.

Goodburn, K. E., & Halligan, A. C. (1987). *Modified atmosphere packaging—a technology guide* (pp. 1–44). Publication of the British Food Manufacturing Association.

Gómez, P. L., Alzamora, S. M., Castadhikariro, M. A., & Salvatori, D. M. (2010). Effect of ultraviolet- C light dose on quality of cut-apple: Microorganism, color and compression behavior. Journal of Food Engineering, 98, 60–70.

Guan, W., Fan, X. & Yan, R. (2012) . Effects of UV-C treatment on inactivation of Escherichia coli O157:H7, microbial loads, and quality of button mushrooms. Postharvest Biology and Technology, 64, 119-125.

Guo S., Huang, R., Chen, H. (2019). Evaluating a combined method of UV and washing for sanitizing blueberries, tomatoes, strawberries, baby spinach, and lettuce. Journal of Food Protection, 82(11), 1879–1889.

Ha, J.-H., Lee, D.-U., Auh, J.-H., & Ha, S.-D. (2011). Synergistic effects of combined disinfecting treatments using sanitizers and uv to reduce levels of Bacillus cereus in oyster mushroom. Journal of the Korean Society for Applied Biological Chemistry, 54, 269–274.

Horvitz, S., & Cantalejo, M. J. (2014). Application of ozone for the postharvest treatment of fruits and vegetables. *Critical Reviews in Food Science and Nutrition, 54*, 312–339.

Hu, B., Sun, D.-W., Pu, H. & Wei, Q. (2019). Recent advances in detecting and regulating ethylene concentrations for shelf-life extension and maturity control of fruit: A review. Trends in Food Science & Technology, 91, 66-82

Huang, H., Ge, Z., Limwachiranon, J., Li, L., Li, W., & Luo, Z. (2017). UV–C treatment affects browning and starch metabolism of minimally processed lily bulb. *Postharvest Biology and Technology, 128*, 105–111.

Huang, H., Lu, H., Huang, H., Wang, L., Jieni, Z., & Leung, D. Y.C (2016). Recent development of VUV-based processes for air pollutant degradation. *Frontiers in Environmental Science, 4*, 17.

Hussain, M., Bensaid, S., Geobaldo, F., Saracco, G., & Russo, N. (2011). Photocatalytic degradation of ethylene emitted by fruits with TiO_2 nanoparticles. *Industrial & Engineering Chemistry Research, 50*(5), 2536–2543.

Iqbal, N., Khan, N. A., Ferrante, A., Trivellini, A., Francini, A., & Khan, M. I. R. (2017). Ethylene role in plant growth, development and senescence: Interaction with other phytohormones. *Frontiers in Plant Science, 8*, 475.

Janisiewicz, W. J., Takeda, F., Glenn, D. M., Camp, M. J., & Jurick II, W.M. (2016). Dark period following UV-C treatment enhances killing of Botrytis cinerea conidia and control gray mould of strawberries. Phytopathology, 106(4), 386-394.

Jozwiak, Z. B., Bartsch, J. A., & Aneshansley, D. J. (2003). Experimental verification of a model describing uv initiated decomposition of ethylene in CA storage of apples. *Acta Horticulturae, 600*, 707.

Karakurt, Y., & Huber, D. J. (2002). Cell wall-degrading enzymes and pectin solubility and depolymerization in immature and ripe watermelon (*Citrullus lanatus*) fruit in response to exogenous ethylene. *Physiology Plant, 116*, 398–405.

Kaur, K., Dhillon, W. S., & Mahajan, B. V. (2014). Changes in pectin methyl esterase activity with different packaging materials and stages of fruit harvesting during cold storage of pear cv. Pun-jab beauty. *Journal of Food Science and Technology, 51*(10), 2867–2871.

Kays, S. J., & Beaudry, R. M. (1987). Techniques for inducing ethylene effects. *Acta Horticulturae, 201*, 77–116.

Keller, N., Ducamp, M.- N., Robert, D., & Keller, V. (2013). Ethylene removal and fresh product storage: a challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation. *Chemical Reviews, 113*(7), 5029–5070.

Kim, C. & Hung, Y. -C. (2012). Inactivation of E. coli O157:H7 on blueberries by electrolyzed water, ultraviolet light, and ozone. Journal of Food Science, 77, M206-M211.

Kim, Y.-H., Jeong, S.-G., Back, K. - H., Park, K.-H., Chung, M.-S., & Kang, D.-H. (2013). Effect of various conditions on inactivation of Escherichia coli O157:H7, Salmonella Typhimurium, and Listeria monocytogenes in fresh-cut lettuce using ultraviolet radiation. International Journal of Food Microbiology, 166, 349-355.

Koutchma, T. N., Forney, L. J. & Moraru, C. I. (2009). Ultraviolet light in food technology. Principles and Applications. CRC Press, Taylor & Francis Group. Boca Raton, FL.

Kumar, S., Kumar, R., Pal, A., & Chopra, D. S. (2019). Enzymes. In E. M. Yahia (Ed.), *Postharvest physiology and biochemistry of fruits and vegetables* (pp. 335–358). Woodhead Publishing.

Lante, A., Tinello, F., & Nicoletto, M. (2016). UV–A light treatment for controlling enzymatic browning of fresh-cut fruits. *Innovative Food Science & Emerging Technologies, 34*, 141.

Li, D., Li, L., Ge, Z., Limwachiranon, J., Ban, Z., Yang, D., & Luo, Z. (2017). Effects of hydrogen sulfide on yellowing and energy metabolism in broccoli. *Postharvest Biology and Technology, 129*, 136–142.

Li, D., Limwachiranon, J., Li, L., Du, R., & Luo, Z. (2016). Involvement of energy metabolism to chilling tolerance induced by hydrogen sulfide in cold-stored banana fruit. *Food Chemistry, 208*, 272–278.

Li, D., Luo, Z., Mou, W., Wang, Y., Ying, T., & Mao, L. (2014). ABA and UV–C effects on quality, antioxidant capacity and anthocyanin contents of strawberry fruit (*Fragaria ananassa* Duch.). *Postharvest Biology and Technology, 90*, 56–62.

Liao, Y. -T., Syamaladevi, R. M., Zhang, H., Killinger, K., & Sablani, S. (2017). Inactivation of Listeria monocytogenes on frozen red raspberries by using UV-C light. Journal of Food Protection, 80(4), 545–550.

Liu, H., Wang, Z., Li, H., Zhang, X., Qin, X., Dai, Y., Wang, P., Liu, Y.,& Huang, B. (2018). Photocatalytic degradation of ethylene by Ga_2O_3 polymorphs. *Royal Society of Chemistry, 8*, 14328–14334. https://doi.org/10.1039/c8ra02212g

Liu, C., Huang, Y., Chen, H. (2015). Inactivation of Escherichia coli O157:H7 and Salmonella enterica on blueberries in water using ultraviolet light. Journal of Food Science, 80(7), M1532-M1537.

Luo, Z., Li, D., Du, R., & Mou, W. (2015). Hydrogen sulfide alleviates chilling injury of banana fruit by enhanced antioxidant system and proline content. *Scientia Horticulturae, 183*, 144–151.

Luo, Z., Xie, J., Xu, T., & Zhang, L. (2009). Delay ripening of ‘Qing-nai’ plum (*Prunus salicina* Lindl.) with 1-methylcyclopropene. *Plant Science, 177*, 705–709.

Luo, Z., Xu, X., Cai, Z., & Yan, B. (2007). Effects of ethylene and 1-methylcyclopropene (1-MCP) on lignification of postharvest bamboo shoot. *Food Chemistry, 105*, 521–527.

Luo, Z., Xu, X., & Yan, B. (2008). Use of 1-methylcyclopropene for alleviating chilling injury and lignification of bamboo shoot (*Phyllostachys praecox* f. prevernalis) during cold storage. *Journal of the Science of Food and Agriculture, 88*, 151–157.

Mabusela, B., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V., Mathabe, P. M. K. & Caleb, O. J. (2021). Trends in ethylene management strategies: towards mitigating postharvest losses along the South African value chain of fresh produce—a review. Manuscript submitted for publication.

Maharaj, R., Arul, J., & Nadeau, P. (2014). UV–C irradiation effects on levels of enzymic and non-enzymic phytochemicals in tomato. *Innovative Food Science & Emerging Technologies, 21*, 99–106.

Malayeri, M., Haghighat, F., & Lee, C.-S. (2019). Modeling of volatile organic compounds degradation by photocatalytic oxidation reactor in indoor air: a review. *Building and Environment, 154*, 309–323.

Maness, P. C., Smolinski, S., Blake, D. M., Huang, Z., Wolfrum, E. J., & Jacoby, W. A. (1999). Bactericidal activity of photo-catalytic TiO(2) reaction: Toward an understanding of its killing mechanism. *Applied and Environmental Microbiology, 65*, 4094–4098.

Mansourbahmani, S., Ghareyazie, B., Kalatejar, S., Mohammadi, R. S., & Zarinnia, . (2017). Effect of post-harvest UV–C irradiation and calcium chloride on enzymatic activity and decay of tomato (*Lycopersicon esculentum* L.) fruit during storage. *Journal of Integrative Agriculture, 16*(9), 2093–2100.

Martínez-Hernandez, G. B., Huertas, J.-P., Navarro-Rico, J., Gomez,A., Artes, F., Palop, A., & Artes-Hernandez, F. (2015). Inactivation kinetics of foodborne pathogens by UV–C radiation and its subsequent growth in fresh-cut kailan-hybrid broccoli. *Food Microbiology, 46*, 263–271.

Martinez-Romero, D., Bailen, G., Serrano, M., Guillen, F., Valverde, J. M., Zapata, P., Castillo, S. & Valero, D. (2007). Tools to Maintain Postharvest Fruit and Vegetable Quality through the Inhibition of Ethylene Action: A Review. Critical Reviews in Food Science and Nutrition, 47, 543-560.

McQueen- Mason, S. J., Durachko, D. M., & Cosgrove, D. J. (1992). Two endogenous proteins that induce cell-wall extension in plants. *The Plant Cell, 4*, 1425–1433.

Minas, I. S., Vicente, A. R., Dhanapal, A. P., Manganaris, G. A., Goulas, V., Vasilakakis, M., Crisosto, C. H., & Molassiotis, A. (2014). Ozone-induced kiwifruit ripening delay is mediated by ethylene biosynthesis inhibition and cell wall dismantling regulation. *Plant Science, 229*, 76–85.

Mirshkari, A., Ding, Ph., & Ghazali, H. M. (2015). Enzymatic activity and microstructural changes of hot water treated banana during ripening. *Journal of Agricultural Science and Technology, 17*, 949–962.

Mukhopadhyay, S., Ukuku, D., Fan, X. & Juneja, V. K. (2013). Efficacy of integrated treatment of UV light and low dose gamma irradiation on inactivation of Escherichia coli O157:H7 and Salmonella enterica on grape tomatoes. Journal of Food Science, 78, M1049-56.

Nguyen, H., Mcconchie, R., Hofman, P., Smith, L., Stubbings, B., & Adkins, M. (2000) . Effect of ethylene and ripening temperatures on the skin colour and flesh characteristics of ripe 'Kensington Pride'mango fruit. *International Symposium on Tropical and Subtropical Fruits, 575*, 635–642.

Nsumpi, A. N., Belay, Z. A., & Caleb, O. J. (2020). Good intentions, bad outcomes: Impact of mixed-fruit loading on banana fruit protein expression, physiological responses and quality. *Food Packaging and Shelf Life, 26*, 100594.

Özkaya, O., Yildirim, D., Dündar, Ö., & Tükel, S. S. (2016). Effects of 1-methylcyclopropene (1-MCP) and modified atmosphere packaging on postharvest storage quality of nectarine fruit. *Scientia Horticulturae, 198*, 454–461.

Oppenlaender, T. (2003). Photochemical purification of water and air. Advanced Oxidation Processes (AOPs): principles, reaction mechanisms and reactor concepts, Germany, Wiley-VCH, Wein-heim (Germany).

Palou, L. S., Crisosto, C. H., Garner, D., & Basinal, L. M. (2003). Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes. *Postharvest Biology and Technology, 27*, 243–254.

Pala, Ç. U. & Toklucu, A. K. (2013). Microbial, physicochemical and sensory properties of UV-C processed orange juice and its microbial stability during refrigerated storage. LWT - Food Science and Technology, 50, 426-431.

Park, D.-R., Zhang, J., Ikeue, K., Yamashita, H., & Anpo, M. (1999). *Photocatalytic oxidation of ethylene to CO2 and H2O on ultrafine powdered TiO2 photocatalysts in the presence of O2 and H2O* (pp. 114–119). Academia Press.

Pathak, N., Caleb, O. J., Geyer, M., Herppich, W. B., Rauh, C., & Mahajan, P. V. (2017a). Photocatalytic and photochemical oxidation of ethylene: Potential for storage of fresh produce—A review. *Food Bioprocess Technology, 10*, 982–1001.

Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2017b). Effect of process variables on ethylene removal by vacuum ultraviolet radiation: application in fresh produce storage. *Biosystems Engineering, 159*, 33–45.

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

Pathak, N., Rux, G., Geyer, M., Herppich, W., Rauh, C., & Mahajan, P. (2018). Effect of light wavelength and TiO-$_2$ on photocatalytic removal of ethylene under low oxygen and high humidity storage conditions. *VIII International Postharvest Symposium, 10*, 17660.

Pinheiro, J., Alegria, C., Abreu, M., Goncalves, E. M., & Silva, C. L.(2015). Use of UV-C postharvest treatment for extending fresh whole tomato (Solanum lycopersicum, cv. Zinac) shelf-life. Journal Food Science and Technology, 52, 5066-5074.

Phakdee, N., & Chaiprasart, P. (2020). Modified atmosphere storage extends the shelf life of 'Nam Dok Mai Sri Tong' mango fruit. *International Journal of Fruit Science, 20*(3), 495–505.

Pombo, M. A., Dotto, M. C., Martínez, G. A., & Civello, P. M. (2009). UV–C irradiation delays strawberry fruit softening and modifies the expression of genes involved in cell wall degradation. *Post-harvest Biology and Technology, 51*(2), 141–148.

Pombo, M. A., Rosli, H. G., Martínez, G. A., & Civello, M. (2011). UV–C treatment affects the expression and activity of defense genes in strawberry fruit (*Fragaria* × *ananassa* Duch.). *Postharvest Biology Technology, 59*, 94–102.

Ponce-Valadez, M., Escalona-Buendía, H. B., Villa -Hernández, J. M., De León-Sánchez, F. D., Rivera -Cabrera, F., Alia-Tejacal, I., & Pérez-Flores, L. J. (2016). Effect of refrigerated storage (12.5 °C) on tomato (*Solanum lycopersicum*) fruit flavor: a biochemical and sensory analysis. *Postharvest Biology and Technology, 111*, 6–14.

Ramesh, T., Nayak, B., Amirbahman, A., Tripp, C. P., & Mukhopadhyay, S. (2016). Application of ultraviolet light assisted titanium dioxide photocatalysis for food safety: a review. *Innovative Food Science & Emerging Technologies, 38*, 105–115.

Rose, J. K., Lee, H. H., & Bennett, A. B. (1997). Expression of a divergent expansin gene is fruit-specific and ripening-regulated. *Proceedings of the National Academy of Sciences of the United States of America, 94*(11), 5955–5960.

Sadeghi, K., Lee, Y. & Seo, J. (2021) . Ethylene Scavenging Systems in Packaging of Fresh Produce: A Review. Food Reviews International, 37, 155-176.

Salamanca, F., Balaguera-López, H., & Herrera, A. (2014). Effect of potassium permanganate on some postharvest characteristics of tomato 'Chonto' fruits (*Solanum lycopersicum* L.). *Acta Horti-culture, 1016*, 171–176.

Saltveit, M. E. (1999). Effect of ethylene on quality of fresh fruits and vegetables. *Postharvest Biology and Technology, 15*, 279–292.

Sardabi, F., Mohtadinia, J., Shavakhi, F., & Jafari, A. (2014). The effects of 1-methylcyclopropen (1-MCP) and potassium permanganate coated zeolite nanoparticles on shelf life extension and quality loss of golden delicious apples. *Food Process Preserv, 38*, 2176–2182.

Santo, D., Graça, A., Nunes, C., & Quintas, C. (2018). Escherichia coli and Cronobacter sakazakii in 'Tommy Atkins' minimally processed mangos: Survival, growth and effect of UV-C and electrolyzed water. Food Microbiology, 70, https://doi.org/10.1007/ s11947-021-02703-149-54

Scott, K. J., Wills, R. B. H., & Patterson, B. D. (1971). Removal by the ultra-violet lamp of ethylene and other hydrocarbons produced by bananas. *Science Food and Agriculture, 22*, 496.

Sew, C. C., Mohd Ghazali, H., Martín-Belloso, O., & Noranizan, M. A. (2014). Effects of combining ultraviolet and mild heat treatments on enzymatic activities and total phenolic contents in pineapple juice. *Innovation in Food Science and Emerging Technology, 26*, 511–516.

Shorter, A. J., & Scott, K. J. (1985). Ethylene removal. In: Proceedings Postharvest Horticulture Workshop, Melbourne. pp. 220–225.

Siripatrawan, U., & Kaewklin, P. (2018). Fabrication and characterization of chitosan -titanium dioxide nanocomposite film as ethylene scavenging and antimicrobial active food packaging. *Food Hydrocolloids, 84*, 125–134.

Sitrit, Y., & Bennett, A. B. (1998). Regulation of tomato fruit polygalacturonase mRNA accumulation by ethylene: a re-examination. *Plant Physiology, 116*, 1145–1150.

Skog, L. J., & Chu, C. L. (2001). Effect of ozone on qualities of fruits and vegetables in cold storage. *Canadian Journal of Plant Science, 81*, 773–778.

Song, X., Wang, H., Li, Y., Ye, S., & Dionysiou, D. D. (2018). Solvothermal synthesis of P25/Bi_2WO_6 nanocomposite photocatalyst and photocatalytic degradation of ethylene under visible light. *Applied Surface Science, 439*, 815–822.

Srivastava, S., Gupta, S. M., Sane, A. P., & Nath, P. (2012). Isolation and characterization of ripening-related pectin methylesterase inhibitor gene from banana fruit. *Physiology and Molecular Biology of Plants, 18*(2), 191–195.

Syamaladevi, R. M., Lu, X., Sablani, S. S., Insan, S. K. Adhikari, A., Killinger, K., Rasco, B., Dhingra, A., Bandyopadhyay, A., Annapure, U. (2013). Inactivation of Escherichia coli population on fruit surfaces using ultraviolet-C light: influence of fruit surface characteristics. Food and Bioprocess Technology, 6, 2959-2973.

Tas, C. E., Hendessi, S., Baysal, M., Unal, S., Cebeci, F. C., & Menceloglu, Y. Z. (2017). Halloysite nanotubes/polyethylene nanocomposites for active food packaging materials with ethylene scavenging and gas barrier properties. *Food Bioprocess Technology, 10*, 789–798.

Teoh, L. S., Lasekan, O., Adzahan, N. M., & Hashim, N. (2016). The effect of ultraviolet treatment on enzymatic activity and total phenolic content of minimally processed potato slices. *Journal of Food Science and Technology, 53*, 3035–3042.

Terry, L. A., & Joyce, D. C. (2004). Elicitors of induced disease resistance in postharvest horticultural crops: a brief review. *Postharvest Biology and Technology, 32*, 1–13.

Tran, M. T. T., & Farid, M. (2004). Ultraviolet treatment of orange juice. *Innovation in Food Science and Emerging Technology, 5*(4), 495–502.

Tucker, G., Yin, X., Zhang, A., Wang, M., Zhu, Q., Liu, X., Xie, X., Chen, K., & Grierson, D. (2017). Ethylene and fruit softening. *Food Quality and Safety, 1*(4), 253–267.

Uluisik, S., Chapman, N. H., Smith, R., Poole, M., Gary, A., Gillis, R. B., et al. (2016). Genetic improvement of tomato by targeted control of fruit softening. *Nature Biotechnology, 34*, 950–952.

Uluisik, S., & Seymour, G. B. (2020). Pectate lyases: their role in plants and importance in fruit ripening. *Food Chemistry, 309*, 125559.

Vurma, M. (2009). *Development of ozone-based processes for decontamination of fresh produce to enhance safety and extend shelflife PhD*. The Ohio State University.

Wang, D., Li, L., Xu, Y., Limwachiranon, J., Li, D., Ban, Z., & Luo, Z. (2017). Effect of exogenous nitro oxide on chilling tolerance, polyamine, proline, and γ-aminobutyric acid in Bamboo shoots (*Phyllostachys praecox* f. prevernalis). *Journal of Agricultural and Food Chemistry, 65*, 5607–5613.

Wang, D., Oppenländer, T., El-Din, M. G., & Bolton, J. R. (2010). Comparison of the disinfection effects of vacuum -UV (VUV) and UV light on *Bacillus subtilis* spores in aqueous suspensions at 172, 222 and 254 nm. *Photochemistry and Photobiology, 86*, 176–181.

Wang, D., Yeats, T. H., Uluisik, S., Rose, J. K. C., & Seymour, G. B. (2018). Fruit softening: revisiting the role of pectin. *Trends in Plant Science, 23*(4), 302–310.

Wang, J. H., & Ray, M. B. (2000). Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. *Separation and Purification Technology, 19*, 11–20.

Wang, K. L., Li, H., & Ecker, J. R. (2002). Ethylene biosynthesis and signaling networks. *The Plant Cell, 14*, 131–151.

Warton, M. A., Wills, R. B. H., & Ku, V. V. V. (2000). Ethylene levels associated with fruit and vegetables during marketing. *Australian Journal of Experimental Agriculture, 40*, 465–470.

Wei, H., Seidi, F., Zhang, T., Jin, Y. & Xiao, H. (2021). Ethylene scavengers for the preservation of fruits and vegetables: A review. Food Chemistry, 337, 127750.

Whitney, S. E. C., Gidley, M. J., & McQueen-Mason, S. J. (2000). Probing expansin action using cellulose/hemicellulose composites. *The Plant Journal, 22*, 327–334.

Wills, R. B. (2015). Low ethylene technology in non-optimal storage temperatures. In R. B. H. Wills & J. Golding (Eds.), *Advances in postharvest fruit and vegetable technology* (pp. 167–190). CRC Press.

Wills, R. B. H., & Warton, M. A. (2004). Efficacy of potassium per-manganate impregnated into alumina beads to reduce atmospheric ethylene. *Journal of the American Society for Horticultural Science, 129*(3), 433–438.

Xu, J., Li, C., Liu, P., He, D., Wang, J., & Zhang, Q. (2014). Photolysis of low concentration H2S under UV/VUV irradiation emitted from high-frequency discharge electrodeless lamps. *Chemos-phere, 109*, 202–207.

Xu, Y., & Charles, M. T. (2019). Ultraviolet-C priming of strawberry leaves against subsequent *Mycosphaerella fragaria* e infection involves the action of reactive oxygen species, plant hormones, and terpenes. *Plant Cell & Environment, 42*, 815–831.

Xu, Y., Charles, M. T., Luo, Z., Mimee, B., Veronneau, P. Y., Rolland, D., & Roussel, D. (2017). Preharvest ultraviolet C irradiation increased the level of polyphenol accumulation and flavonoid pathway gene expression in strawberry fruit. *Journal of Agricultural and Food Chemistry, 65*(46), 9970–9979.

Yan, R., Mattheis, J., Gurtler, J., Sites, J., & Fan, X. (2014) . UV-C inactivation of Escherichia coli and dose uniformity on apricot fruit in a commercial setting. Postharvest Biology and Technology, 95, 46-49.

Yan, R., Yun, J., Gurtler, J., & Fan, X. (2017). Radiochromic film dosimetry for UV-C treatments of apple fruit. Postharvest Biology and Technology,127, 14–20.

Yan, R., Gurtler, J. B, Mattheis, J. P., & Fan, X. (2020). Effect of trichome removal and UV-C on populations of E. coli O157:H7 and quality of peach fruit. HortScience, 55(10), 1626-1631.

Yang, L., Huang, W., Xiong, F., Xian, Z., Su, D., Ren, M., & Zheng-guo, L. (2017). Silencing of SlPL, which encodes a pectate lyase in tomato, confers enhanced fruit firmness, prolonged shelf-life and reduced susceptibility to grey mould. *Plant Biotechnology Journal, 15*(12), 1544–1555.

Yang, S. F., & Hoffman, N. E. (1984). Ethylene biosynthesis and its regulation in higher plants. *Annual Review of Plant Physiology, 35*, 155–189.

Yang, Z., Cao, S., Su, X., & Jiang, Y. (2014) . Respiratory activity and mitochondrial membrane associated with fruit senescence in postharvest peaches in response to UV–C treatment. *Food Chemistry, 161*, 16–21.

Yaseen, T., Ricelli, A., Turan, B., Albanese, P., & D'onghia, A. M. (2015). Ozone for post-harvest treatment of apple fruits. *Phyto-pathologia Mediterranea, 54*(1), 94–103.

Yao, S. and Chen, H. (2021). Development and evaluation of a point-of-use UV appliance for fresh produce decontamination. International Journal of Food Microbiology, 339, 109024.

Ye, J., Shang, J., Song, H., Li, Q., & Zhu, T. (2013). Generation of reactive oxygen species in simulated flue gas under vacuum ultraviolet radiation. *Chemical Engineering Journal, 232*, 26–33.

Yu, J., Cai, W., Chen, J., Feng, L., Jiang, Y., & Cheng, Z. (2012). Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. *Environmental Siences, 24*(10), 1777–1784.

Yun, J., Yan, R., Fan, X., Gurtler, J., Phillips, J. (2013). Fate of E. coli O157:H7, Salmonella spp. and potential surrogate bacteria on apricot fruit, following exposure to UV-C light. International Journal of Food Microbiology, 166, 356–363.

Zagory, D. (1995). Ethylene-removing packaging. In M. L. Rooney (Ed.), *Active food packaging.* Springer.

Zhang, W., & Jiang, W. (2019). UV treatment improved the quality of postharvest fruits and vegetables by inducing resistance. *Trends in Food Science & Technology, 92*, 71–80.

Zhang, Z., Gao, Z., Li, M., Hu, M., Gao, H., Yang, D., & Yang, B. (2012). Hot water treatment maintains normal ripening and cell wall metabolism in mango (*Mangifera indica* L.) fruit. *HortSci-ence, 47*(10), 1466–1471.

Zhang, J., Cheng, D., Wang, B., Khan, I. & Ni, Y. (2017). Ethylene Control Thechnologies in Extending Postharvest Shelf Life of Climacteric Fruit. Journal of Agricultural and Food Chemistry, 65, 7308-7319.

Zhou, R., Li, Y., Yan, L., & Xie, J. (2011). Effect of edible coatings on enzymes, cell-membrane integrity, and cell-wall constituents in relation to brittleness and firmness of Huanghua pears (*Pyrus pyrifolia* Nakai, cv. Huanghua) during storage. *Food Chemistry, 124*, 569–575.

Zhu, Z., Cai, H., & Sun, D.-W. (2018). Titanium dioxide (TiO_{-2}) photo-catalysis technology for nonthermal inactivation of microorganisms in foods. *Trends in Food Science & Technology, 75*, 23–35.

Ziegler, D. M. (1985). Role of reversible oxidation-reduction of enzyme thiolsdisulfides in metabolic regulation. *Annual Review in Biochemistry, 54*, 305–329.

Zoschke, K., Börnick, H., & Worch, E. (2014). Vacuum- UV radiation at 185 nm in water treatment–a review. *Water Research, 52*, 131–145.

CHAPTER FOUR:

DEGRADATION KINETICS AND APPLICATION OF VUV PHOTOLYSIS REACTOR AND DIRECT VUV EXPOSURE FOR ETHYLENE DEGRADATION TO CONTROL APPLE RIPENING

Published as: **Mabusela, B.P.,** Belay, Z.A., Godongwana, B., Pathak, N., Mahajan, P.V., & Caleb, O.J. (2020) Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics, mixed-fruit storage, and direct exposure to ‘Fuji’ apples during storage. *Journal of Food Science and Technology*. **https://doi.org/10.1007/s13197-023-05775-3**

Published as: **Mabusela, B.P.,** Belay, Z.A., Godongwana, B. and Caleb, O.J., (2023). Application of vacuum ultraviolet photolysis reactor and loss of firmness prediction for stored Fuji apples. In *VII International Symposium on Applications of Modelling as an Innovative Technology in the Horticultural Supply Chain- 1382* (pp. 9-16).

4. DEGRADATION KINETICS AND APPLICATION OF VUV PHOTOLYSIS REACTOR AND DIRECT VUV EXPOSURE FOR ETHYLENE DEGRADATION TO CONTROL APPLE RIPENING

Abstract

Accumulated ethylene in fruit storage/transportation causes rapid senescence resulting in reduced shelf-life and postharvest losses. The aim of this study was to investigate the application of a vacuum ultraviolet (VUV) photolysis modular reactor for fruit storage. The first experiment compared the effectiveness of VUV photolysis reactor with the standard fruit industry adsorbent (potassium permanganate, $KMnO_4$) on the removal of ethylene from mixed-fruit loading of apples, banana, and pears stored at ambient temperature (16 °C) for 6 days. The second study evaluated the impact of direct VUV radiation on the quality attributes of apples stored at 10 °C for 21 days. Results showed that ethylene produced in mixed-fruit loading storage significantly ($p < 0.05$) reduced by 86.9% in the storage chamber connected to VUV modular reactor compared to 25.4% for storage under potassium permanganate. Direct exposure of apples to VUV radiation successfully reduced both ethylene and respiration rate but damaged the skin of the apples. Hue angle and lightness (L*) for apples exposed to VUV radiation declined significantly ($p < 0.05$) from 60.7 ± 1.09 to 33.5 ± 9.51 and 58.1 ± 3.60 to 50.4 ± 1.13, respectively. This study showed the potential of VUV photolysis as an innovative technique for removing ethylene from storage facilities.

Keywords: Fresh fruit, respiration rate, shelf-life extension, degradation kinetics

4.1 Introduction

The response of harvested fruit to endogenously produced and exogenously applied ethylene is numerous and varied (Palou et al., 2003). The impact of ethylene on fresh fruit could be considered beneficial or detrimental depending on the extent of exposure and the type of product. The presence of ethylene even at low concentrations (1 ppm) induces precocious fruit ripening. Some of the detrimental impacts of ethylene include acceleration of physiological disorders, excessive softening, over-ripening and colour change leading to a reduction in postharvest life. Thus, the removal of ethylene from storage systems is of paramount importance in the horticultural industry. Improving conventional techniques and developing new techniques for the control of ethylene during the transport and storage period has proven to be challenging (Pathak et al. 2017).

Conventional ethylene removal postharvest strategies include air ventilation, low-temperature storage and controlled atmosphere (CA) storage (Mabusela et al. 2021). Other techniques include the use of different adsorbers/absorbers, the use of potassium permanganate ($KMnO_4$) (Aprilliani et al. 2018a), ozone and catalytic oxidation (Smilanick, 2003). The use of adsorbing/absorbing materials such as zeolites and activated carbon and oxidizers such as KMnO4 are not suitable for long-term storage and distant transportation because these materials saturate rapidly, thereby necessitating frequent replenishment. Moreover, potassium permanganate oxidation results in toxic residues that require further disposal (Duque et al., 2021; Zhu et al., 2019a). Catalytic oxidation, on the other hand, requires high temperatures rendering the technique energy-intensive (Keller et al., 2013). Meanwhile, some studies have shown the efficiency of photocatalytic oxidation (PCO) for ethylene oxidation to carbon dioxide and water. While PCO has found great application in postharvest management, there are still inherent drawbacks that limit its commercialization such as the recombination of hole and electron which results in the reduction of oxidized species, and its declined removal efficiency at high relative humidity caused by the competing water and ethylene molecules for active sites (Pathak et al. 2017).

Vacuum ultraviolet photolysis (VUV) is an emerging technique for ethylene postharvest management. Photolysis generally employs UV light sources, such as low-pressure and medium-pressure mercury lamps with approximately 85% output UV light at 254 nm and 15% output at 185 nm. The high energy photons generated at 185 nm are self-sufficient in decomposing oxygen and water molecules present in the air to produce highly reactive species such as atomic O_2, hydroxyl radicals, and ozone which are responsible for the oxidation of ethylene to carbon dioxide and water (Mabusela et al., 2022). The application of VUV photolysis has been commonly used for the removal of organics in the aqueous phase and air pollutants (Huang et al., 2016; Kang et al., 2018; Mahmoudkhani et al., 2016). This technique has demonstrated promising ethylene removal capabilities and was successful in prolonging the shelf-life of apples and kiwifruit (Pathak et al. 2017). However, its application for postharvest ethylene management is still very limited. The efficiency of this technique is dependent on the generated hydroxyl radicals that are responsible for the oxidation of ethylene to carbon dioxide and water (Mabusela et al. 2022). However, the impact of the radicals on the surface and/or quality of treated fruit is still not known. Additionally, the direct application of VUV radiation on the postharvest quality of fruit has never been investigated. Thus, the aim of this study was to investigate ethylene degradation kinetics and the potential of a VUV photolysis reactor for ethylene degradation in mixed-fruit storage stored at room temperature for 6 days and to evaluate the effect of direct exposure to VUV radiation on physiological parameters of apples at 10 °C for 14 days.

4.2 Materials and methods

4.2.1 Plant material

The fruits were obtained from Blue Jay farm, Stellenbosch, South Africa, and transported to the Agri-Food Systems and Omics Laboratory, Agricultural Research Council (ARC) Infruitec-Nietvoorbij, Stellenbosch. The samples were sorted carefully to ensure uniformness and eliminate damaged or decayed fruit. The fruit surfaces were disinfected using 70% ethanol.

4.2.2 System setup

The photolysis reactions were carried out using an in-house designed batch flow-type reaction system made of stainless steel (diameter = 12 cm, height 11 cm). The reactor has an inlet and outlet ports that are used for flushing gases. An ozone-producing VUV lamp with a power input of 3 W was placed along the central axis of the reactor. A detailed description of the reactor is given by Pathak [11]. The desired concentrations of ethylene were obtained by mixing ethylene from ethylene standard (100 ppm) with synthetic air. The initial ethylene concentrations investigated were 7, 55 and 67 ppm. Ethylene samples were taken at regular intervals from the reactor using an ICA 56-ethylene analyser (Fricaval 89 S.L, Valencia, Spain) which had an in-house pump that returned the gas sample to the reactor to ensure gas volume remained constant. All the experiments were carried out at atmospheric pressure and room temperature. The photolytic efficiency was calculated using the following equation:

$$Ethylene\ removal\ (\%) = \frac{C_0 - C_t}{C_0} \times 100 \quad (4.1)$$

where, C_0 is the initial ethylene concentration (ppm) and C_t is the real-time concentration of ethylene during the photooxidation.

In order to determine the reaction kinetics of the photolysis reaction, a first-order kinetic model (Equation. 4.2) was assumed

$$ln(C) = ln(C_0) + kt \quad (4.2)$$

where t is the reaction time (min), C_0 and C (ppm) is the initial ethylene concentration and ethylene concentration at time t, respectively, and *k* is the first-order reaction rate constant (min^{-1}).

4.2.3 Photolysis degradation of ethylene during fruit storage

To evaluate the photolytic degradation of ethylene produced by mixed fruits, three types of fruit 'Granny Smith' apples, 'Grand Nain' bananas and 'Packham's Truimph' pears were selected. The fruits were separated into three groups in a 13 L storage chamber at room temperature for 6 days. The first group consisted of fruits stored without any ethylene removal material, which served as a control. The second group consisted of fruits stored with 10% (kg/kg) of total fruit) potassium permanganate ($KMnO_4$) deposited on a petri dish hanging in the center of the container to represent the industry practice. The third group consisted of fruits stored in a chamber connected to the VUV photolysis reactor for continuous removal of ethylene (treatment) as shown in Figure 4.1. The ethylene concentration in the gas phase inside the chambers was monitored daily using ICA 56-ethylene analyser (Fricaval 89 S.L, Valencia, Spain).

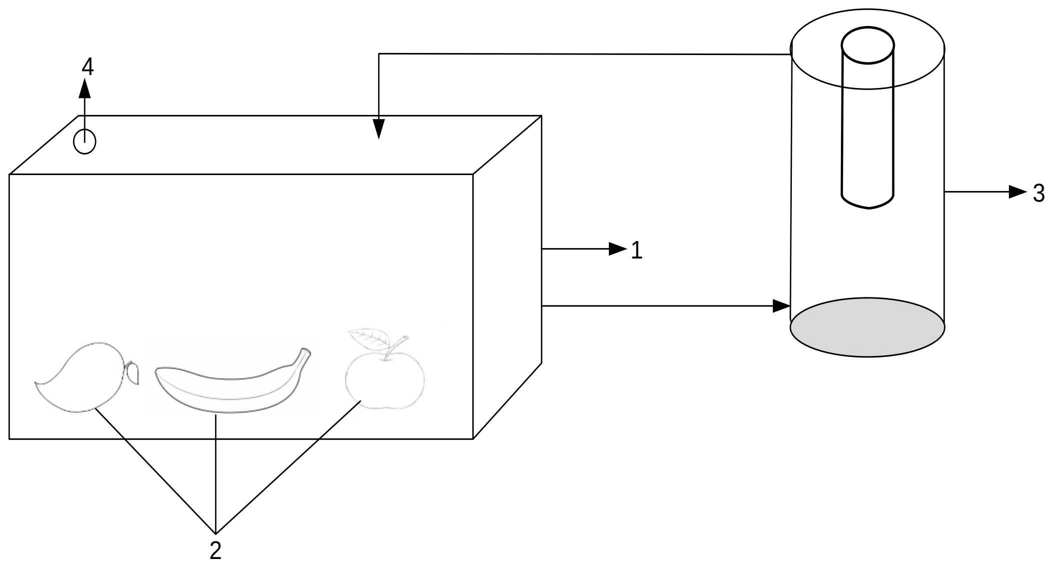


Figure 4.1: Schematic representation of the experimental setup used for the photolytic oxidation of ethylene emitted in the storage of mixed fruits. 1) storage container, 2) fruits (banana, apples and pears), 3) photolytic reactor (same as used in kinetic studies), and 4) sample gas collection.

4.2.4 VUV treatment and storage conditions

The VUV treatment was conducted using a 30 L plastic chamber with three ozone-producing VUV lamps (Dinies, Villingendorf, Germany), with a power input of 3 W each placed in the center of the chamber. A total of 24 apples were divided into two treatment groups of 12 samples. The first treatment group consisted of 12 apples that were exposed to VUV light, while the control treatment did not have any VUV light. All treatment experiments were conducted at 10 °C for 21 days. On day 14, the VUV lights were switched off and the storage containers were opened and the experiment was allowed to continue for a further 7 days.

4.2.5 Ethylene production and respiration rate

The ethylene production rate (EPR) of apples was monitored on each sampling day by transferring apples to sealed hermetic jars (3 L) and the concentration of ethylene was measured at regular intervals using an ICA 56-ethylene analyser (Fricaval 89 S.L, Valencia, Spain). The ethylene production rate was calculated as the amount of ethylene produced per unit mass of the fruit per unit time (μL/kg h).

The respiration rate (RR) of apples was determined by placing a known mass from the treatment and control chamber into a closed system respirometer (developed in-house), which consisted of four glass jars fitted with tubes. Hermetic sealing was achieved with O-rings between the lid and the glass jar. Gas samples (CO_2) were taken after 1 h using a gas analyser (Oxycarb 6, Isolcell, Laives, Italy). The RR was calculated as the amount of CO_2 produced per unit mass of the fruit per unit time (mL/kg h) using Eq. (4.5):

$$R_{CO_2} = \frac{\left(Y_{CO2\,tf} - \frac{Y_{CO2\,ti}}{\Delta t}\right) V_f}{W} \tag{4.5}$$

where $Y_{CO2\,tf}$ and $Y_{CO2\,ti}$ are CO_2 concentration (%) at time t_f (h) and time t_i (h), respectively. R_{CO_2} is RR due to CO_2 production in mL/g h, V_f is the free volume of the containers (mL), and W is the total mass of the product (kg). All measurements were conducted in triplicate.

4.2.6 Firmness

The tissue strength (hardness) of apples was determined as the maximum force required to penetrate the tissue of peeled fruit using a texture analyser (FTA 20, Güss, South Africa). The two opposite sides (left, and right) of the apple were gently peeled, and placed on the platform and a 7.9 mm compression probe was used on each of the sides with a penetration distance of 8.9 mm and a speed of 10 mm/s. All measurements were conducted in triplicate per treatment and tissue strength was expressed in kg.

4.2.7 Colour

Colour changes on each apple fruit were measured based on the Commission International del' Eclairage (CIE) colour system using a digital Chroma-meter (CR 400/410 Konica Minolta Sensing Inc., Japan). Colour calibration of the chroma-meter was performed against a white and black tile background before each measurement. Colour measurements were taken using individual fruit ($n = 3$) and data obtained were averages of individual colour parameters. To describe the measured colour attributes hue angle (h^0), which describes the qualitative attribute of colour shades (0° red-purple and 180° bluish-green), and Chroma (*C**), which denotes the quantitative attribute of colour intensity were calculated (Caleb et al., 2016) using Eqs. (4.6) and (4.7):

$$h^0 = tan^{-1}\left(\frac{b^*}{a^*}\right) \tag{4.6}$$

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \tag{4.7}$$

Where, L^* denotes the lightness, a^* describes red (+)/green (-) and b^* describes yellow (+)/blue(-).

4.2.8 Total soluble solid (TSS) and titratable acidity (TA)

The fruit was processed into juice using a juice extractor (4294 J700, Braun, China) and the juice obtained was used to measure total soluble solids (TSS) and titratable acidity (TA). Total soluble solid was measured using a pocket-calibrated refractometer (PAL-1, ATAGO, and Japan) and the results were expressed as °Brix. The titratable acidity of each fruit was obtained from the titration of 53.7 mL of each fruit juice with 0.333 N of sodium hydroxide (NaOH) at a pH of 8.2, using Crison Titromatic 1S/2B (Crison Instruments, Barcelona, Spain) and the results were expressed as g/100 mL malic acid.

4.2.9 Statistical analysis

Statistical analyses were carried out using STATISTICA software (version 13, StatSoft Inc. Tulsa, USA) where factorial analysis of variance (ANOVA). All treatments were carried out at least in triplicate and results were reported as mean and standard deviation. The significance differences between the mean values were tested by Duncan's multiple range tests ($p \leq 0.05$).

4.3 Results and discussion

4.3.1 Ethylene degradation kinetics

The degradation kinetics of ethylene by the VUV photolysis reactor at different initial concentrations is shown in Fig. 4.2. The kinetic data were well-fitted by the first-order kinetic model, and the observed rate constants are shown in Table 4.1. The degradation removal of ethylene increased from 15.9 to 35.9% with an increase in initial concentration from 7 to 55 ppm and decreased to 28.2% with a further increase to 67 ppm (Table 4.1). The rate constant increased from 0.0036 min^{-1} to 0.0091 min^{-1} when the initial concentration was increased from 7 to 55 ppm. Increasing the concentration from 7 to 55 ppm resulted in more ethylene molecules interacting with the generated photons and hence resulted in higher conversion efficiency. On the other hand, a further increase in ethylene concentration from 55 to 67 ppm resulted in a decrease in the percentage removal and rate constant. This is attributed to the fact that since the number and energy of photons did not change, ethylene molecules obtained less energy as inlet concentration increased resulting in a low rate constant and percentage removal. Additionally, high contents of ethylene might suppress the transmission of 185 nm UV light, thereby reducing the production of the $HO^{\bullet}$ radicals responsible for ethylene oxidation. These results are in accordance with the work of Chang [22] where the authors reported a decrease in ethylene percentage removal from 63 to 40% upon increasing the initial concentration from 20 to 100 ppm. The removal of ethylene by VUV photolysis can be said to be a first-order reaction that is dependent on the initial ethylene concentration. Increasing the ethylene concentration beyond the threshold concentration resulted in decreased percentage removal.

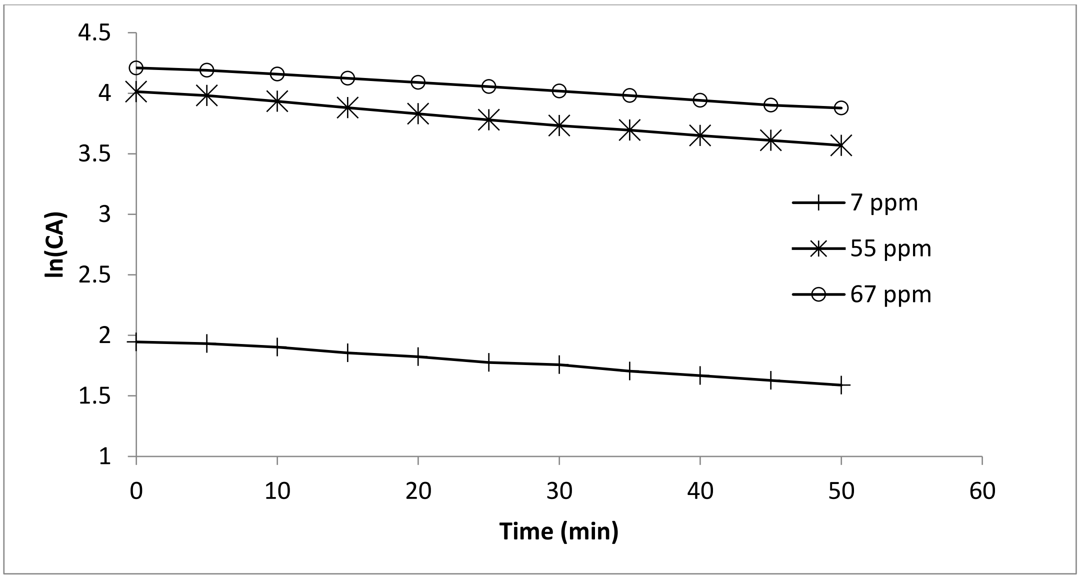


Figure 4.2: Effect of initial concentration on the degradation kinetics of ethylene fitted by the first-order kinetic model in the VUV reactor in batch experiments. Experimental conditions: lamp power 3 W; initial concentrations of ethylene = 7, 55 and 67 ppm; duration 50 minutes

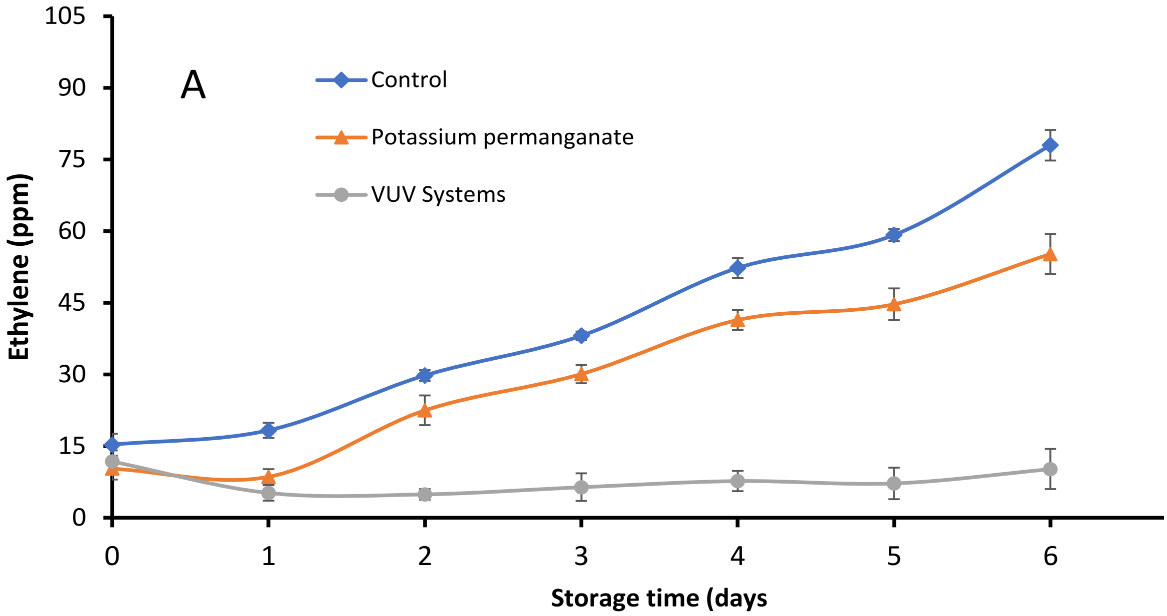
Table 4.1: Removal percentage and kinetic analysis of ethylene degradation in a VUV photolysis system

Ethylene concentration (ppm)	Ethylene removal (%)	Rate constant (min^{-1})	R^2
7	15.9	0.0074	0.9944
55	35.9	0.0091	0.9979
67	28.2	0.0069	0.9972

4.3.2 Ethylene degradation in mixed-fruit storage container

The change in ethylene concentration during the storage period in all three containers containing mixed-fruit and the corresponding percentage of ethylene removal is shown in Fig. 4.3. The VUV system was able to maintain ethylene concentration in the storage chamber to 10 ppm on day 6. In contrast, the ethylene concentration continued to increase in the control and industry practice chambers to values of 78 and 58 ppm respectively. The ethylene concentration accumulated in the control and industry practice chamber is sufficient to produce premature fruit ripening.

The results indicated that ethylene percentage removal was higher in the storage container connected with the VUV photolysis reactor throughout the storage duration. By the end of the storage duration (day 6), the ethylene concentration diminished by 25% for fruits stored under $KMnO_4$ and by 86.9% for fruits stored under the storage container with VUV photolysis reactor compared to the control fruit (Figure. 4.3B). The results obtained in this study are in agreement with the results reported by Pathak [12]. In their study, a percentage removal of 96.28% from a storage chamber of apples connected to a VUV photolysis reactor was reported. The VUV photolysis performed better than potassium permanganate because the reaction in potassium permanganate occurs on the surface which saturates rapidly over time, whereas photolysis occurs in the gas phase and therefore is faster resulting in higher percentage removal. The results from this study show that VUV photolysis could be a great alternative tool for ethylene removal in the storage of a mixed-load fruit.



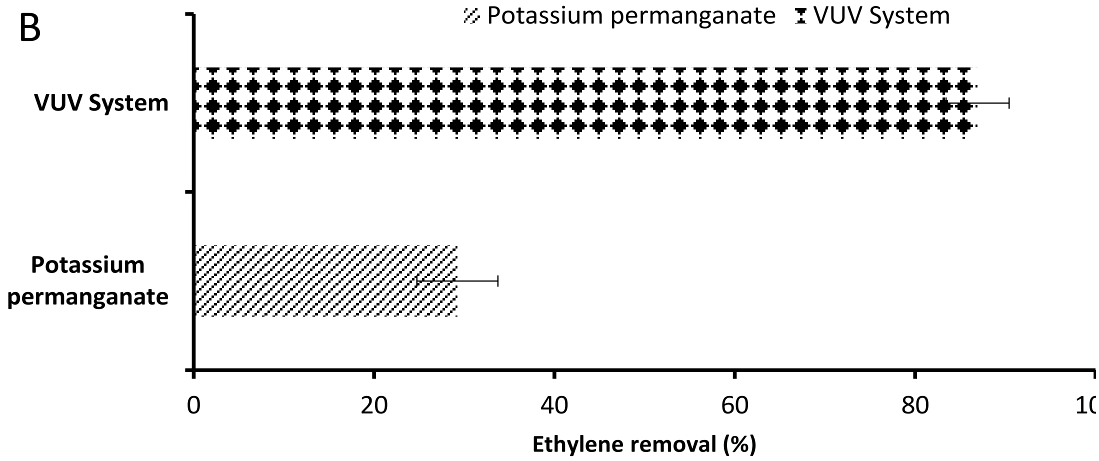


Figure 4.3: Plot of ethylene concentration in different storage chambers at room temperature (25 ± 5 °C) for 6 days (A) and (B) ethylene removal percentage in storage chamber connected with VUV system and potassium permanganate (industry practice)

4.3.3 Changes associated with exposure of apples to direct VUV

4.3.3.1 Ethylene production rate

The ethylene production rates of apples exposed to direct VUV is shown in Fig. 4.4. The results show that the VUV lamp was able to suppress ethylene production during the 14 days of storage. The ethylene production rate of apples under VUV radiation was 2.62 mL $kg^{-1}h^{-1}$ on day 14, while a production rate of 6.66 mL $kg^{-1}h^{-1}$ was achieved from apples in the control storage. When the VUV lamp was turned off, the production rate of ethylene increased by 42.4 % after 3 days suggesting that the VUV lamp was responsible for retarding ethylene production. These results show that the direct exposure of apples to VUV light inhibited ethylene production during storage, which would subsequently delay fruit ripening. Similar results were achieved with UV-C light treatment for mangoes. During the direct exposure of apples, the hydroxyl radicals that are generated react quickly with the ethylene molecules and in such a setup, where the fruits are exposed to direct VUV light, the removal mechanism is by both direct and indirect photolysis . The results showed that apples exposed to direct VUV slowed endogenous ethylene production.

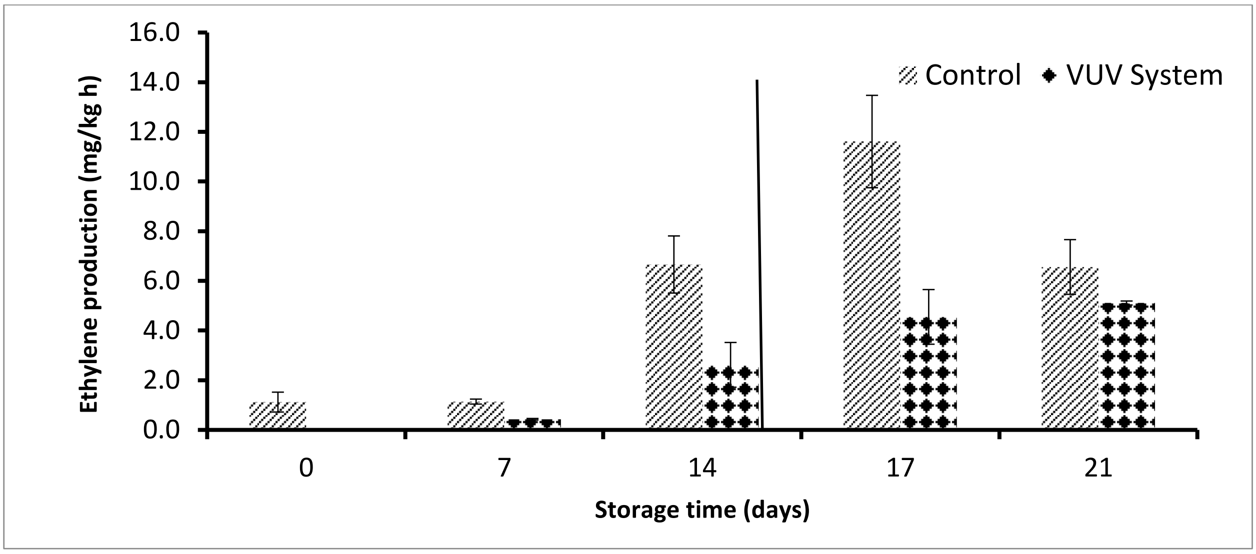


Figure 4.4: Ethylene production rate of apples exposed to direct VUV at 10 for 14 days. The lamps were switched off on day 14 and the storage container was left open

4.3.3.2 Respiration rate

The respiration rate of apples exposed to direct VUV light and those stored under control is shown in Fig. 4.5. The respiration rate ($RRCO_2$) of apples in the control chamber was always high compared to the RR of apples treated with direct VUV. This is in accordance with the ethylene production rates reported above. Ethylene induces the respiratory burst of CO_2 production in climacteric fruits and hence, the removal of ethylene by the VUV lamps resulted in low RR . On the contrary, the RR rate in both the control and treatment chambers decreased after day 14 when the storage containers were opened. The observed decrease in RRs in both storages is attributed to the fact that there was no accumulation of ethylene in both storages as the storages were left open. The results from this study suggest that direct exposure of apples to VUV was able to reduce the RR in closed storage. This demonstrates the potential of the system for maintaining fruit quality as low RR is associated with prolonged shelf-life.

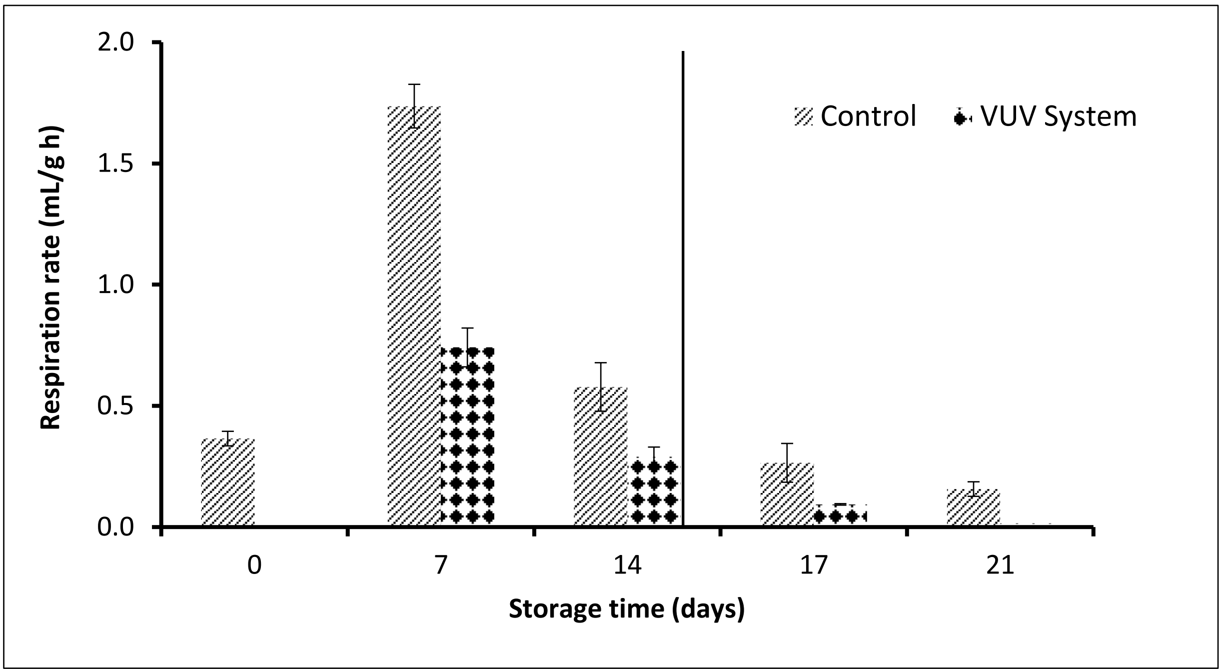


Figure 4.5: Respiration rate of apples exposed to direct VUV at 10 for 14 days. The lamps were switched off on day 14 and the storage container was left open

4.3.3.3 Colour and firmness

The visual change for apples over the 21 days of storage duration is presented in Fig. 4.6. There was no significant difference in the colour of the cut surfaces for apples in the control and apples treated with VUV radiation. On the contrary, the VUV radiation produced alterations in the skin colour of apples resulting in dark skin with dark spots and subsequently losing their commercial value. Vacuum ultraviolet photolysis results in the generation of many different reactive oxygen species, such as hydroxyl radicals and ozone. It can be inferred that ozone could be responsible for damaging the skin colour of the apples. Jia [27] also noticed symptoms of injury and pitted structures on the skin of peaches caused by ozone.

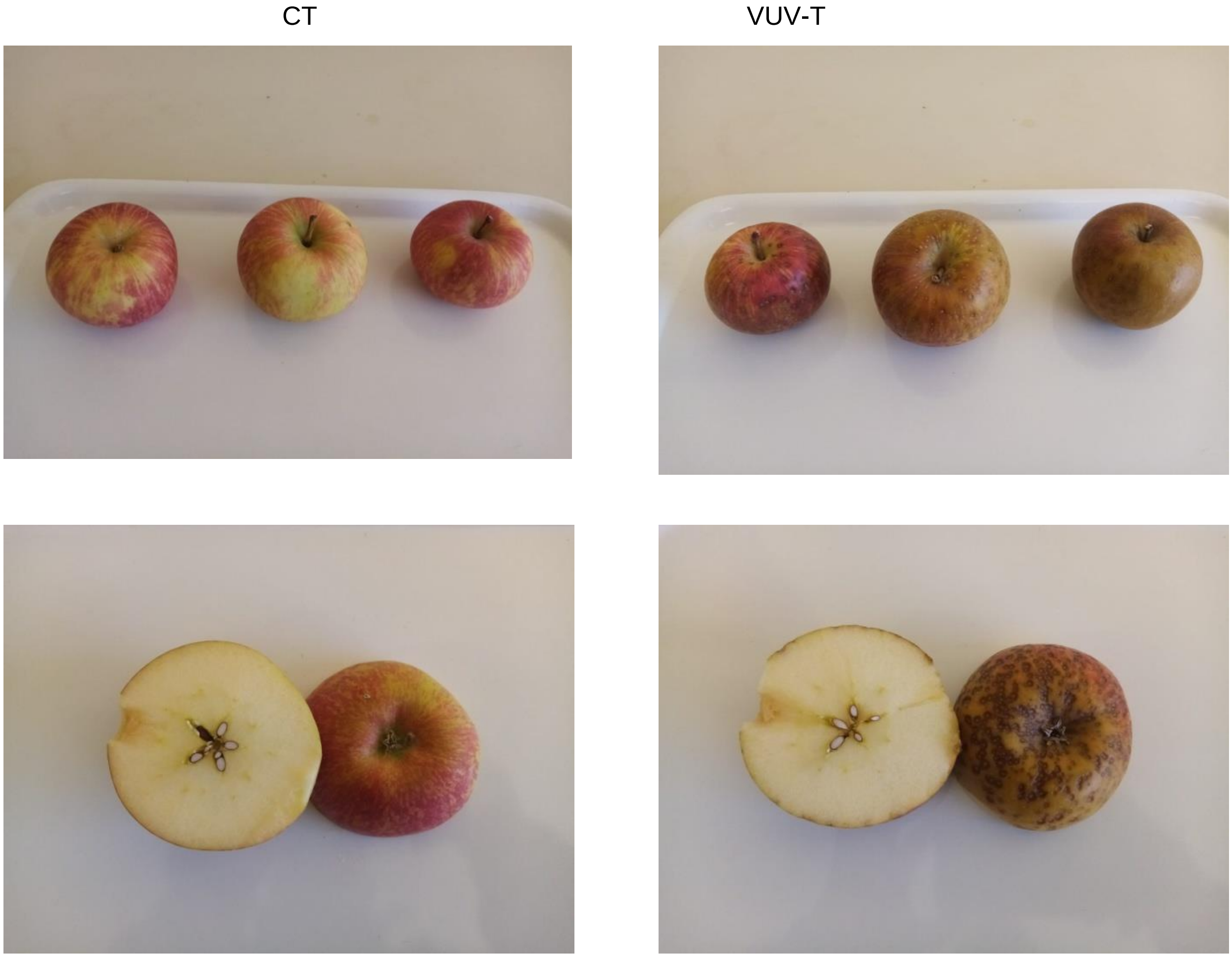


Figure 4.6: Effect of VUV radiation and control treatments on the appearance and longitudinal section photos of apples after 21 days of storage at 10 °C. CT (control treatment) and VUV-T(VUV radiation treatment)

The changes in colour profile of apples exposed to VUV radiation and that in the control chamber are shown in Table. 4.2. Apples stored in the control chamber did not show a significant change in hue angle (*h*°). In contrast, the apples exposed to VUV radiation showed a significant ($p \leq 0.05$) decline in *h*° from 60.73 ± 21.09 to 33.46 ± 9.51. The VUV radiation did not have a significant effect on the colour intensity (C^*). However, there was a significant decrease in the lightness (L^*) parameter of apples exposed to VUV radiation. Since a low value of L^* indicates dark fruit skin, the results show that the apples exposed to VUV radiation were darker than the apples in the control. This was evident from the visual observations (Fig. 4.6). This suggests that prolonged exposure of apples to VUV radiation accelerated chlorophyll degradation resulting in detrimental effects on the fruit's appearance. Although it is reported that the degradation in fruit colour and ethylene production are correlated , the loss in the skin colour of apples in this study was attributed to ozone and the long exposure to VUV radiation since ethylene production was suppressed. These results suggest that ozone production in the storage chamber needs to be monitored and removed. This can be achieved by employing the use of ozone absorbers or catalysts.

Table 4.2: Changes in physicochemical properties in colour, firmness, TTA and TSS of apples under direct exposure to VUV and control treatment at 10 °C for 21 days

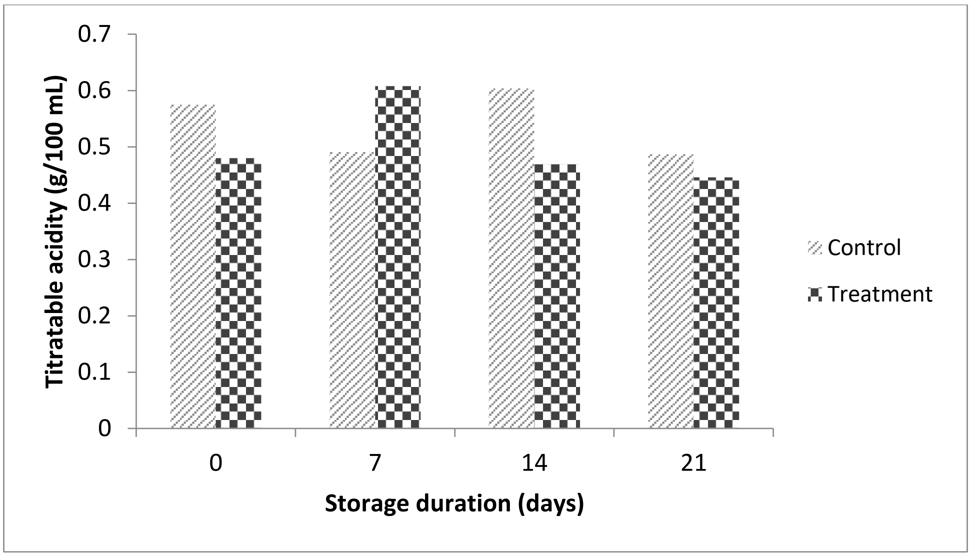
	Control				VUV treatment			
Quality parameter	**Day 0**	**Day 7**	**Day 14**	**Day 21**	**Day 0**	**Day 7**	**Day 14**	**Day 21**
C^*	35.48 ± 3.78	33.72 ± 4.59	34.82 ± 2.16	37.43 ± 2.76	31.93 ± 3.42	31.35 ± 3.65	32.31 ± 3.89	33.46 ± 4.07
$h°$	55.20 ± 24.72	64.26 ± 22.30	55.96 ± 17.92	54.38 ± 20.50	60.73 ± 21.09	58.84 ± 22.19	66.46 ± 17.04	33.46 ± 9.51
L	51.00 ± 9.98	54.54 ± 11.63	53.70 ± 8.20	53.89 ± 10.57	55.13 ± 7.61	50.32 ± 11.22	49.84 ± 8.27	50.43 ± 5.13
Firmness (kg)	6.78 ± 0.80	6.76 ± 0.8	6.74 ± 0.91	6.22 ± 0.620	6.75 ± 0.711	6.23 ± 0.512	6.39 ± 1.08	5.72 ± 0.541

The firmness of apples in both treatments declined during storage (Table. 4.2). However, the firmness of apples under VUV radiation was significantly ($p \leq 0.05$) lower than those in the control. During the storage duration, the firmness of apples declined from the initial value of 6.75 ± 0.711 kg on day 0 to 5.72 ± 0.541 kg and on day 21 for VUV radiation and control samples, respectively. The firmness of fruits can be correlated to the degraded ethylene during storage. Although VUV radiation was successful in removing ethylene, the loss in firmness of apples under VUV radiation reported in this study could be attributed to the deterioration of cell wall compounds by VUV radiation. On the other hand, the firmness of apples in the control did not change significantly although high ethylene accumulation was reported. This could be attributed to the effect of the low temperature at which the study was conducted. The results from this study show that although direct VUV exposure was successful in removing ethylene from storage, it had a negative impact on the firmness of apples.

4.3.3.4 Total soluble solid (TSS) and titratable acidity (TA)

The total soluble solids (TSS) and titratable acidity (TA) of apples under different treatments are shown in Figure. 4.7. The level of TA decreased from 0.575 - 0.487 g/100 mL for apples in control and from 0.480 - 0.446 g/100 mL for apples under VUV radiation. The decrease in TA for apples under different treatments was not significant ($p \geq 0.05$), but the apples in the control samples showed a high decrease. Increased CO_2 and ethylene production, observed in the control chamber, may trigger the transformation of organic acids into sugars resulting in decreasing TA during apple ripening [33]. There was no significant decrease in the TA of apples exposed to VUV radiation. This could be attributed to the beneficial effect of continuous removal of ethylene around the fruit vicinity.

The TSS content for apples in control increased from an initial value of 14.2% to 15.1 % on day 7 of storage and then decreased to 13.9% on day 14. The increase in TSS content during the ripening of fruits and the decrease after attaining peak levels is a result of natural fruit ripening and senescence processes that are typical of postharvest change . Similarly, the initial increase in TSS of apples in the control chamber is attributed to the presence of accumulated ethylene causing ripening, which increases the sugar content. The increase in TSS for apples under VUV radiation was from 14.4% to 14.6% on day 7 and then decreased to 13.9% on day 14. The results from this study show that the degradation of ethylene by VUV radiation had a beneficial effect in maintaining TSS and TA for apples.



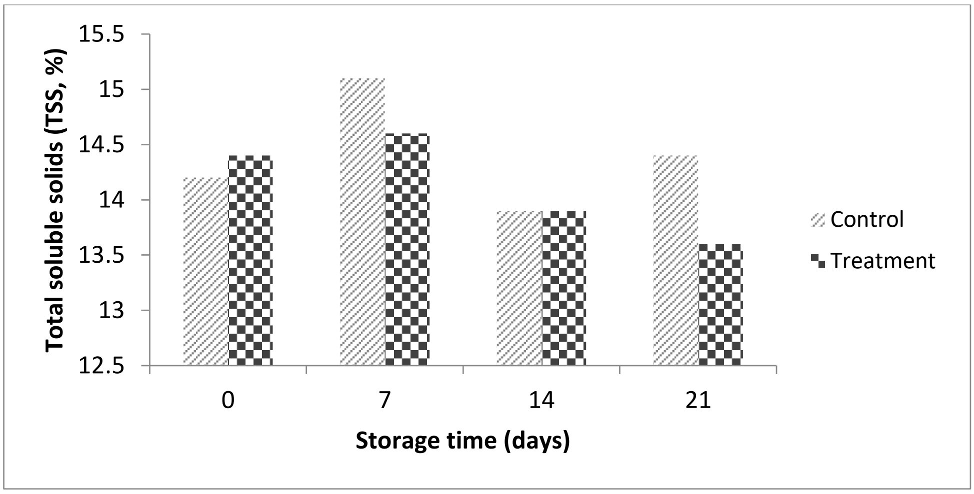


Figure 4.7: Changes in titratable acidity (TA, g/100 mL) (A) and total soluble solids (TSS, %) (B) for apples under control and VUV radiation treatment during the 21 days of storage at 10 °C

4.3.4 Prediction of loss of firmness of apples using vacuum ultraviolet photolysis

The linear relationship observed in Figure 4.8 (A and B) was used to predict the shelf-life of apple fruit under the two different storages. According to Bhosale and Sundaram (2010), apples with firmness below 49N are deemed unmarketable as 49N is the lower acceptable quality limit for firmness. This lower limit (49N) was used to predict the shelf-life of apples under the two different storages. The shelf-life of apples in the control and treatment was predicted to be 32 and 78 days, respectively. According to the model, the VUV photolysis reactor could extend the shelf-life of apples by 46 days.

A first-order kinetic model was used to describe the decrease in firmness of apples in the two different storages and the results are shown in Figure 4.8 (C and D). The results show that the rate constant of apples in the control and treatment was 0.0063 day^{-} and 0.026 day^{-}, respectively. The higher value of the rate constant observed in the control is due to apple softening which decreased quickly during the ripening process because of accumulated ethylene, while the lower value of the rate constant in treatment is correlated with a slow ripening process as a result of the continuous removal of ethylene. Cárdenas-Pérez et al. (2017) used the Weibull model to describe the firmness kinetics of ‘Golden Delicious’ apples. In contrast to the empirical first-order kinetics model (n = 1) proposed in this study, the authors reported a fractional reaction order of 0.57. The difference in the reaction orders between the two studies could be attributed to the different cultivars used and the storage conditions. Cárdenas-Pérez et al. (2017) stored the apples at 25 °C which could have accelerated complex enzymatic reactions, resulting in a fractional reaction order.

Values of R^2 greater than 0.84 were found in all fitted kinetic models. The low values of R^2 imply that the model could not predict the experimental data well. The lack of the model to predict the experimental data could be attributed to many factors, the most prominent one being the omission of the role of enzymes on firmness degradation kinetics. Billy et al. (2008) suggested that fruit softening during storage is a complex process that involves the action of enzymes and proteins which are responsible for firmness loss. Furthermore, it is reported that the activity of such enzymes is regulated by ethylene (Matabura, 2022). Therefore, the poor correlation between the model and experimental data observed in this study could be attributed to the omission of the reaction kinetics of firmness-related enzymes in the model development. This implies that future models should consider the role of firmness-related enzymes on the firmness degradation kinetics and the role of ethylene in regulating these enzymes.

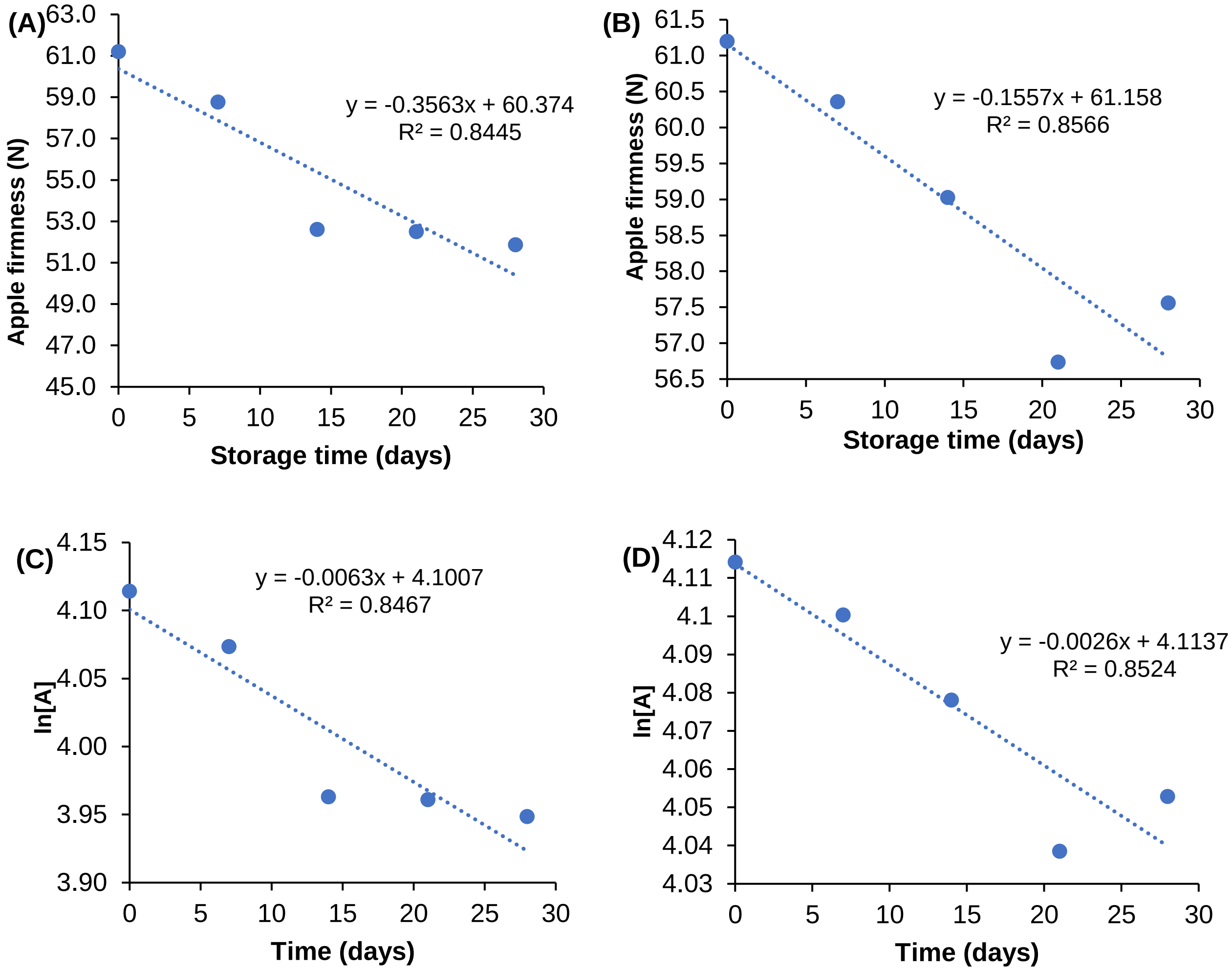


Figure 4.8: Changes in firmness of apple fruit during 28-day storage at 15 °C A and B: loss in firmness in control and treatment respectively, and C and D: first-order kinetic model in control and treatment, respectively

4.4 Conclusion

This study investigated the potential of a VUV photolysis reactor for the removal of ethylene during the storage of mixed fruit. The effect of direct VUV exposure on the physicochemical properties of apples was also examined. The results indicated that the kinetics of ethylene degradation by VUV photolysis followed a first-order kinetic model. Additionally, the VUV reactor reduced ethylene concentration in the mixed-fruit storage container by 86.9%, compared to 47% achieved by $KMnO_4$. The use of VUV radiation effectively maintained a low ethylene production rate and respiration rate, suggesting it is an efficient technology for prolonging the shelf life of apples. There were no significant changes in the TSS and TA of treated apples. However, continuous direct VUV exposure damaged the apple skins and reduced their firmness. The firmness of apples under both storage conditions decreased linearly over time, but apples in the control group lost firmness at a rate 2.3 times higher than those in the treatment group. The rate of firmness loss was observed to follow a first-order kinetic model. The findings from this study demonstrate that VUV photolysis is a promising technique for ethylene removal in mixed-fruit storage environments and could offer a better solution for maintaining the postharvest quality of fruit. Future studies should focus on optimizing the direct exposure of fruit to VUV radiation. Finally, the reactor should be designed with an ozone scrubber to remove residual ozone.

4.5 Summary

This chapter addressed one of the main objectives of the thesis, i.e. to evaluate the efficiency of the VUV photolysis reactor in degrading ethylene across different initial ethylene concentrations. Moreover, it explored the potential application of this reactor in fruit storage, scrutinizing the essential physicochemical quality attributes of the fruit. The degradation of ethylene was fitted to a first-order kinetic model. The outcomes of this section convincingly illustrated the efficacy of the proposed VUV photolysis reactor in ethylene degradation while simultaneously maintaining the overall quality of the fruit. The results obtained in this chapter serve as a crucial foundation and motivation for the subsequent findings and conclusions presented in Chapters 5 and 6.

Reference

Palou, L.S., et al., *Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes.* Postharvest Biology and Technology 2003. **27**(27): p. 243-254.

Saltveit, M.E., *Effect of ethylene on quality of fresh fruits and vegetables.* Postharvest Biology and Technology, 1999. **15**(15): p. 279-292.

Pathak, N., et al., *Photocatalytic and Photochemical Oxidation of Ethylene: Potential for Storage of Fresh Produce—a Review.* Food Bioprocess Technology, 2017. **10**(10): p. 982-1001.

Mabusela, B., et al., *Trends in ethylene management strategies: Towards mitigating postharvest losses along the South African value chain of fresh produce - A Review.* 2021: p. In press.

Aprilliani, F., Warsiki, and A. Iskandar, *Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material.* IOP Conference Series: Earth and Environmental Science, 2018. **141**(141): p. IOP Conference Series: Earth and Environmental Science.

Smilanick, J.L., *Use of ozone in storage and packing facilities. In: Paper Presented at the Washington Tree Fruit Postharvest Conference.* 2003.

Zhu, Z., et al., *Electrospun Nanofibers Containing TiO2 for the Photocatalytic Degradation of Ethylene and Delaying Postharvest Ripening of Bananas.* Food and Bioprocess Technology, 2019. **12**.

Duque, L.F., et al., *Development of a New Essential Oil-Based Technology to Maintain Fruit Quality in Tomato.* Horticulturae, 2021. **7**(9): p. 303.

Keller, N., et al., *Ethylene Removal and Fresh Product Storage: A Challenge at the Frontiers of Chemistry. Toward an Approach by Photocatalytic Oxidation.* Chemical Reviews, 2013. **113(7)**: p. 5029-5070.

Basso, A., R.D.F.P.M. Moreira, and H.J. José, *Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening.* Journal of Photochemistry & Photobiology A: Chemistry 2018. **367**(367): p. 294-301.

Pathak, N., et al., *Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage.* Biosystems Engineering, 2017. **159**(159): p. 33-45.

Pathak, N., et al., *Efficacy of photocatalysis and photolysis systems for the removal of ethylene under different storage conditions.* Posthavest Biology and Technology, 2019. **147**(147): p. 68-77.

Mabusela, B., et al., *Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of Fruit and Vegetables Along the Value Chains: a Review.* Food and Bioprocess Technology, 2021: p. 1 - 19.

Cheng, Z.-W., et al., *Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media.* Separation and Purification Technology, 2011. **77**(77): p. 26-32.doi:10.1016/j.seppur.2010.11.014.

Huang, H., et al., *Efficient degradation of gaseous benzene by VUV photolysis combined with ozone-assisted catalytic oxidation: Performance and mechanism.* Applied Catalysis B: Environmental, 2016. **186**: p. 62-68.

Mahmoudkhani, F., et al., *Benzene degradation in waste gas by photolysis and photolysis-ozonation: experiments and modeling.* Frontiers in Environmental Science, 2016. **10(6)**(10(6)): p.:DOI 10.1007/s11783-016-0876-4.

Kang, I.-S., J. Xi, and H.-Y. Hu, *Photolysis and photooxidation of typical gaseous VOCs by UV Irradiation: Removal performance and mechanisms.* Frontiers of Environmental Science and Engineering, 2018. **12(3): https://doi.org/10.1007/s11783-018-1032-0**.

Mortazavian, S., A. Saber, and D.E. James, *Optimization of Photocatalytic Degradation of Acid Blue 113 and Acid Red 88 Textile Dyes in a UV-C/TiO2 Suspension System: Application of Response Surface Methodology (RSM).* Catalysts, 2019. **9**(4): p. 360.

Caleb, O.J., et al., *Hot water dipping: Impact on postharvest quality, individual sugars, and bioactive compounds during storage of 'Sonata' strawberry.* Scientia Horticulturae, 2016. **210**: p. 150-157.

Gómez Pacheco, C., et al., *Tetracycline degradation in aqueous phase by ultraviolet radiation.* Chemical Engineering Journal, 2012.

Yao, H., et al., *Effect of Fe(II/III) on tetracycline degradation under UV/VUV irradiation.* Chemical Engineering Journal, 2016. **308**.

Chang, K.-L., et al., *Removal of Ethylene and Secondary Organic Aerosols Using UV-C254 + 185 nm with TiO_2 Catalyst.* Aerosol and Air Quality Research, 2013. **13**: p. 618-626. doi: 10.4209/aaqr.2012.07.0195.

Pristijono, P., J.B. Golding, and M.C. Bowyer, *Postharvest UV-C Treatment, Followed by Storage in a Continuous Low-Level Ethylene Atmosphere, Maintains the Quality of 'Kensington Pride' Mango Fruit Stored at 20 ^{0}C.* Horticulturae, 2018. **5(1)**(5(1)): p. doi:10.3390.

Huang, H., et al., *Recent Development of VUV-Based Processes for Air Pollutant Degradation.* Frontiers in Environmental Science, 2016. **4**(4).

Zagory, D., *Ethylene-removing packaging*, in *Active Food Packaging*, M.L. Rooney, Editor. 1995, Springer US: Boston, MA. p. 38-54.

Fagundes, C., et al., *Effect of active modified atmosphere and cold storage on the postharvest quality of cherry tomatoes.* Postharvest Biology and Technology, 2015. **109**: p. 73-81.

Jia, X., et al., *Combination of Low Fluctuation of Temperature with TiO_2 Photocatalytic/Ozone for the Quality Maintenance of Postharvest Peach.* Foods, 2020. **9(2):234**(9(2):234).

Lourenço, R.E.R.S., et al., *Photodegradation of ethylene by use of TiO2 sol-gel on polypropylene and on glass for application in the postharvest of papaya fruit.* Environ Sci Pollut Res, 2016. DOI 10.1007/s11356-016-8197-5.

Cheng, Y., et al., *Effects of 1-MCP on chlorophyll degradation pathway-associated genes expression and chloroplast ultrastructure during the peel yellowing of Chinese pear fruits in storage.* Food Chemistry, 2012. **135**(2): p. 415-422.

Zhang, W. and W. Jiang, *UV treatment improved the quality of postharvest fruits and vegetables by inducing resistance.* Trends in Food Science & Technology, 2019. **92**: p. 71-80.

Siti Amirah, M.Z., et al., *THE EFFECTS OF CHARCOAL FROM DIFFERENT AGRICULTURAL WASTES IN REDUCING ETHYLENE PRODUCTION OF BERANGAN BANANA (Musa sp. AAA Berangan).* Proceedings of The International Conference of FoSSA Jember, August 1st - 3rd, 2017: p. 201-210.

Nsumpi, A.N., Z.A. Belay, and O.J. Caleb, *Good intentions, bad outcomes: Impact of mixed-fruit loading on banana fruit protein expression, physiological responses and quality.* Food Packaging and Shelf Life, 2020. **26**: p. 100594.

Bruijn, J.D., et al., *Effect of Doping Natural Zeolite with Copper and Zinc Cations on Ethylene Removal and Postharvest Tomato Fruit Quality.* Chemical engineering transactions, 2019. **75**: p. 265-270.

CHAPTER FIVE:

IMPACT OF VACUUM ULTRAVIOLET (VUV) PHOTOLYSIS REACTOR ON PROTEOMIC CHANGES OF APPLE (*FUJI)* FRUIT DURING POSTHARVEST STORAGE AT LOW TEMPERATURE

Mabusela, B., Belay, Z., Husselmann, L.H.H., Godongwana, B., & Caleb, O Proteomic Changes Associated with Ethylene Removal by Vacuum Ultraviolet (VUV) Photolysis for Apple Fruit During Cold Storage. **Under Review.**

5. IMPACT OF VACUUM ULTRAVIOLET (VUV) PHOTOLYSIS REACTOR ON PROTEOMIC CHANGES OF APPLE (FUJI) FRUIT DURING POSTHARVEST STORAGE AT LOW TEMPERATURE

Abstract

Ethylene plays a crucial role in the ripening of climacteric fruits, while prolonged exposure to ethylene may lead to excessive ripening. The presence of ethylene in apple storage not only affects physiological changes but also alters, either directly or indirectly, the activity of critical proteins with a crucial role in apple ripening. This study aimed to investigate the efficacy of the VUV photolysis reactor in ethylene removal and the subsequent impact on proteomic changes in apple fruit. Proteomic analysis revealed a total of 48 proteins, with 29, 17 and 44 proteins on day 0, treatment and control respectively. The apple fruit in control exhibited 18 unique proteins induced by ethylene accumulation, involved in cell wall modification, firmness, and ethylene synthesis. The VUV photolysis reactor, on the other hand, suppressed remarkably the expressions of proteins responsible for cell wall degradation and ethylene synthesis. The results suggested that the VUV photolysis reactor was successful in reducing ethylene production, which in turn suppressed the expression of the proteins responsible for accelerated ripening in apple fruit. By mitigating ethylene-related effects, this technology offers a viable solution to preserve fruit quality, enhance shelf life, and meet the demands of the market for high-quality produce.

Keywords: Ripening, senescence, proteomic changes, postharvest storage, fruit quality

5.1 Introduction

Apple (*Malus domestica*) is one of the most economically important and widely cultivated horticultural fruit crops worldwide (Zhang et al., 2015). In South Africa, apples contributed approximately 31.3% (USD 320 million) of the total gross value for deciduous fruits in 2018/2019 (Department of Agriculture, 2022). As a climacteric fruit, there is a concomitant burst of ethylene and a sudden rise in respiration at the onset of apple ripening (Li et al., 2017) . Unproperly managed ethylene during storage could increase pathogen vulnerability, induce physiological disorders, as well as senescence, and lead to a reduction in the postharvest life of fresh produce. While ethylene is beneficial for uniform ripening of fruit, in commercial stores, accumulated ethylene is routinely scrubbed from the atmosphere (Schaffer et al., 2007) to preserve freshness and reduce spoilage of fruit. The detrimental effects of ethylene accumulation in fruit storage result in significant economic loss for the apple industry.

Ethylene is a plant hormone that plays a key role in fruit ripening by influencing a series of biochemical and physiological changes (Zheng et al., 2013). These changes encompass the softening, color change, and flavor development that characterize ripe fruits. To control fruit ripening and prolong post-harvest shelf life, several ethylene removal techniques have been developed. These techniques include ethylene inhibitors by 1-Methylcyclopropen (1-MCP) (Lien et al., 2018; Sardabi et al., 2014), scavengers like potassium permanganate (Alonso Salinas et al., 2022; Álvarez-Hernández et al., 2020; Aprilliani et al., 2018a), photocatalytic oxidation (Basso et al., 2018; L. Chen et al., 2021; de Chiara et al., 2015), and absorbents (De Bruijn et al., 2019). These techniques have demonstrated promising results in reducing ethylene levels, thereby delaying physiological changes associated with ripening, such as firmness, weight loss, total soluble solids (TSS), titratable acidity (TTA), color changes, ethylene production, and respiration rate (RR). However, there is still limited research regarding the interaction between ethylene removal techniques and the proteins involved in fruit ripening. These proteins encompass enzymes associated with ethylene biosynthesis and proteins that regulate various ripening processes, including cell wall degradation and pigment formation. The impact of ethylene removal techniques on the expression of these proteins and how it influences fruit ripening remains unclear. Studies have shown that exposure to ethylene leads to an increased number of unique proteins in apples (Zheng et al., 2013), and bananas exposed to ethylene exhibit alterations in proteins linked to pathogen resistance, cell wall metabolism, ethylene biosynthesis, and allergens (Du et al., 2016). Therefore, it is crucial to investigate the removal of ethylene and its effects on protein changes related to fruit ripening.

This study proposes the use of vacuum ultraviolet photolysis (VUV) as a method for ethylene removal. Photolysis uses UV light sources, specifically low-pressure and medium-pressure mercury lamps, which emit approximately 85% UV light at 254 nm and 15% UV light at 185 nm. The high-energy photons at 185 nm are capable of decomposing oxygen and water molecules in the air, generating highly reactive oxygen species (ROS). These reactive species play a crucial role in oxidizing ethylene into carbon dioxide and water. The application of VUV photolysis for ethylene removal and its potential for shelf-life extension for fruit has been previously investigated (Mabusela et al., 2023; Pathak et al., 2017). However, the efficacy of VUV photolysis on the interaction between ethylene removal and the proteins associated with fruit ripening remains unknown. Thus, the aim of this study was to investigate proteomic changes linked to the removal of ethylene by VUV photolysis and its subsequent effects on apple ripening during postharvest storage.

5.2 Materials and methods

5.2.1 Plant material and storage experiments

All fruit samples ('Fuji' apples) used in this study were obtained at commercial maturity from a fresh fruit retail market, in Stellenbosch, South Africa. Fruits were transported under cool conditions and in a ventilated vehicle to the Agri-Food Systems and Omics Laboratory, Agricultural Research Council (ARC) Infruitec-Nietvoorbij, Stellenbosch, South Africa. On arrival, samples were sorted carefully to ensure uniformness and eliminate damaged or decayed fruit. Fruit surfaces were disinfected by dipping in NaOCl solution (≈ 200 mg/L) and stored at 5 ℃ before the start of the full experiment.

Storage investigation of apples was conducted using 30 L plastic chambers. A total of 74 uniform 'Fuji' apples were divided into two treatment groups. The first treatment group consisted of apples stored without any ethylene removal strategy, which served as a control. The second group consisted of apples stored in a chamber connected to the VUV photolysis reactor for continuous removal of ethylene (treatment). The VUV photolysis reactor consisted of three UV lamps (3W each) with major radiation at 254 nm and minor radiation at 185 nm. The storage chambers were placed inside a walk-in, temperature-regulated cold room maintained at 15 ℃ for 28 days. For the treatment experiment, only the chamber was placed inside the cold room and air was circulated through the reactor, which was placed outside the cold room. Each setup was conducted in triplicate. The ethylene concentration in the gas phase inside the chambers was monitored using ICA 56-ethylene analyser (Fricaval 89 S.L, Valencia, Spain).

5.2.2 Fruit respiration and ethylene production

The respiration rate (RR) and ethylene concentration of apples were determined by placing a known mass from the treatment and control chamber into a closed system respirometer (developed in-house), which consisted of three glass jars fitted with tubes. Hermetic sealing was achieved with O-rings between the lid and the glass jar. Apple fruits were then placed in glass jars and allowed to acclimatize for an hour at ambient temperature. Gas samples (CO_2) were taken after 1 h using a gas analyser (Oxycarb 6, Isolcell, Laives, Italy). RR was calculated as the amount of CO_2 produced per unit mass of the fruit per unit time (mL/kg h) using Eq. (5.1). The concentration of ethylene was measured at regular intervals using an ICA 56-ethylene analyser (Fricaval 89 S.L, Valencia, Spain). The ethylene production rate was calculated as the amount of ethylene produced per unit mass of the fruit per unit time (ppm/kg h).

$$R_{\mathrm{CO2}} = \frac{\left(Y_{CO2\,tf} - \frac{Y_{CO2\,ti}}{\Delta t}\right) V_f}{W} \tag{5.1}$$

where, $Y_{CO2\,tf}$ and $Y_{CO2\,ti}$ are CO_2 concentration (%) at time t_f (h) and time t_i (h), respectively. R_{CO2} is RR due to CO_2 production in mL/g h, Vf is the free volume of the containers (mL), and W is the total mass of the product (kg). All measurements were conducted in triplicate.

5.2.3 Texture

The fruit tissue strength (hardness) of apples was determined as the maximum force required to penetrate the tissue of peeled fruit using a texture analyser (FTA 20, Güss, South Africa). Opposite sides (left, right) of the apple were gently peeled, and placed on a texture analyser and a 7.9 mm compression probe was used on each of the sides with a penetration distance of 8.9 mm and a speed of 10 mm/s. All measurements were conducted in triplicate per treatment and tissue strength was expressed in kg.

5.2.4 *Protein extraction*

For the sample preparation, the apples were peeled, and immediately flash-frozen using liquid nitrogen, followed by storage at -20 ℃ until further use. A modified SDS/phenol protein extraction method (W. Wang et al., 2006) was used to extract proteins. One gram of the frozen apple pulp was ground to powder with liquid nitrogen using a mortar and pestle. The samples were then homogenized with 200 mg of PVPP and 4ml 10% TCA/Acetone (w/v) and centrifuged for 4 min at 4 °C at 13 300 X g. Once the supernatants were discarded, the pellets were then washed with 80% methanol containing 0.1 M acetate once and an additional 3 times with 80% acetone containing 5mM DTT (by centrifuging at 13 000 X g at 4°C for 4 min). The pellets were solubilised with SDS buffer (30% sucrose, 2% SDS, 0.1M Tris-HCl (pH 8.8) and 5% beta-mercaptoethanol), vortexed for ~20 min. An equal volume of buffered phenol was added to the SDS solution, vortexed again and centrifuged at 4 ℃ for 20 min at 13 300 X g. The phenol phase of each sample was transferred to fresh 15 ml Greiner tubes, 4 times the volume of 80% methanol acetate was added and stored at -20 ℃ overnight for precipitation. Each sample was transferred to fresh 2ml Eppendorf tubes (3 replicates per treatment and centrifuged at 13 000 X g at 4 ℃ for 20 minutes. The supernatants were discarded, and the pellets were washed with ice-cold methanol (100% v/v) and ice-cold acetone (80% v/v) respectively and allowed to air dry. Two sets of samples were prepared i.e. one set of the air-dried pellets was resuspended in 7M urea, vortexed for ~1 hour and left in -20 ℃ storage until further use. The other set of pellets was covered with parafilm and stored at -20 ℃ to be used for on-bead digestion.

5.2.5 Qualitative analysis: 1D SDS-PAGE

A 1D SDS-PAGE was prepared to visualise the quality and integrity of the proteins in the samples by separating them according to their molecular weight (MW). The protein samples (10µg) were added to 2µl of SDS loading dye and boiled at 95 ℃ for 5 min then put on ice. For the 1D gels, the Mini–Protean III® Cell gel casting system Bio–Rad) was used with 12% resolving gels and 5% stacking gel prepared according to the manufacturer’s manual (Bio-Rad). The gels were electrophoresed at 120 V until the dye ran out from the bottom of the gels (1-2 hours). The gels were stained with Coomassie Brilliant Blue and destained with destaining buffer (10% acetic acid and 1% glycerol) until bands were visible.

5.2.6 Protein pellet solubilisation

All protein pellets were first solubilised in 50 mM Tris containing 2 % SDS (Sigma) and 4 M urea (Sigma) by vortexing for 30 minutes. Samples were quantified using the Thermo-Fischer BCA kit following the manufacturer's instructions. Approximately 50 µg of protein was aliquoted for trypsin digestion.

5.2.7 *On-bead digest*

All reagents are analytical grade or equivalent. Samples were re-suspended in 50 mM ammonium bicarbonate (Sigma) before reduction with 10 mM dithiothreitol (DTT) (Sigma) for 30 minutes at room temperature. This step was followed by an alkylation with 30 mM iodoacetamide at room temperature in the dark. After the reduction and alkylation of the protein samples, the samples were diluted with an equal volume of binding buffer (200 mM sodium acetate, 30 % acetonitrile, pH 4.5).

The protein solution was added to MagResyn (Resyn Biosciences) HILIC magnetic particles prepared according to the manufacturer's instructions and incubated overnight at 4 °C. After binding, the supernatant was removed and the magnetic particles were washed twice with washing buffer (95% acetonitrile). After washing, the magnetic particles were suspended in 50 mM ammonium bicarbonate containing trypsin (New England Biosystems) to a final ratio of 1:50. After overnight incubation at 37 ℃, the peptides were removed from the beads and collected in a fresh tube. The adsorbed peptides were removed by incubating them for 3 minutes at room temperature in 20 µL 1% TFA.

Residual digest reagents were removed using an in-house manufactured C_{18} stage tip (Empore Octadecyl C_{18} extraction discs; Supelco). The samples were loaded onto the stage tip after activating the C_{18} membrane with 30 µL methanol (Sigma) and equilibration with 30 µL 2 % acetonitrile: water; 0.05 % TFA. The bound sample was washed with 30 µL 2 % acetonitrile: water; 0.1 % TFA before elution with 30 µL 50 % acetonitrile: water 0.05 % TFA. The eluate was evaporated to dryness. The dried peptides were dissolved in 2 % acetonitrile: water; 0.1 % FA for LC-MS analysis at Central Analytical Facility (CAF) Stellenbosch University.

5.2.8 Liquid chromatography

Dionex nano-RSLC

The method for LC–MS/MS analysis was adapted from (Hooijberg et al., 2018) Liquid chromatography was performed on a Thermo Scientific Ultimate 3000 RSLC equipped with a 5mm x 300 µm C_{18} trap column (Thermo Scientific) and a CSH 25cmx75 µm 1.7 µm particle size C_{18} column (Waters) analytical column. The solvent system employed was loading: 2 % acetonitrile:water; 0.1 % FA; Solvent A: 2 % acetonitrile:water; 0.1 % FA and Solvent B: 100 % acetonitrile:water. The samples were loaded onto the trap column using loading solvent at a flow rate of 2 µL/min from a temperature-controlled autosampler set at 7 ℃. Loading was performed for 5 min before the sample was eluted onto the analytical column. The flow rate was set to 250 nL/minute and the gradient generated as follows: 5.0 % -35 %B over 60 minutes and 35-50 %B from 60-75 minutes. Chromatography was performed at 40 ℃ and the outflow was delivered to the mass spectrometer through a stainless-steel nano-bore emitter.

5.2.9 Mass spectrometry

Mass spectrometry was performed using a Thermo Scientific Fusion mass spectrometer equipped with a Nanospray Flex ionization source. The sample was introduced through a stainless steel emitter. Data was collected in positive mode with spray voltage set to 1.8kV and ion transfer capillary set to 280 ℃. Spectra were internally calibrated using polysiloxane ions at m/z = 445.12003 and 371.10024. MS1 scans were performed using the orbitrap detector set at 120 000 resolution over the scan range 350-1650 with AGC target at 3 E5 and maximum injection time of 50 ms. Data was acquired in profile mode.

MS2 acquisitions were performed using monoisotopic precursor selection for ions with charges +2-+7 with error tolerance set to +/- 10ppm. Precursor ions were excluded from fragmentation once for 60 seconds. Precursor ions were selected for fragmentation in HCD mode using the quadrupole mass analyser with HCD energy set to 30 %. Fragment ions were detected in the orbitrap mass analyzer set to 30,000 resolution. The AGC target was set to 5E4 and the maximum injection time to 80 ms. The data was acquired in centroid mode.

5.2.10 Data Analysis

The raw files generated by the mass spectrometer were imported into Proteome Discoverer v1.4 (Thermo Scientific) and processed using the Sequest and Amanda algorithms. Database interrogation was performed against a concatenated database created using the UniProt "Rosaceae". Semi-tryptic cleavage with 2 missed cleavages was allowed. Precursor mass tolerance was set to 10 ppm and fragment mass tolerance was set to 0.02 Da. Deamidation (NQ), oxidation (M) and acetylation of protein N-terminal were allowed as dynamic modifications and thiomethyl of C as a static modification. Peptide validation was performed using the Target-Decoy PSM validator node. The search results were imported into Scaffold Q+ for further validation (www.proteomesoftware.com). The result files (.sf3) generated from Scaffold Q+ were imported into Scaffold 5 (version 5.1.2). Analysis in Scaffold 5 was performed with parameters set at 1% FDR, minimum 2 peptides and 95% peptide match threshold. Data was exported to Excel and filtered based on >95% protein identification probability and significant proteins (p-value < 0.05).

5.2.1Statistical analysis

Statistical analyses were carried out using STATISTICA software (version 13, StatSoft Inc. Tulsa, USA) where factorial analysis of variance (ANOVA). All treatments were carried out at least in triplicate and results were reported as mean and standard deviation. The significance differences between the mean values were tested by Duncan's multiple range tests ($p \leq 0.05$).

5.3 Results and discussion

5.3.1 Physiological characteristics of apple fruit ripening

The results depicted in Figure 6.1A illustrate the ethylene production rate within the different storage conditions. As the storage period increased in both storages, the ethylene production rate exhibited an initial increase followed by a subsequent decrease. Notably, treated apples displayed a significantly lower ($p < 0.05$) ethylene concentration compared to untreated apples. The treated samples consistently exhibited a 50% lower ethylene concentration than the control. Since the abundance of ethylene correlates with accelerated ripening (Alexander & Grierson, 2002), the use of the VUV photolysis reactor effectively delayed the ripening of apples.

Similarly, the respiration rate (RR) of the treated apples remained consistently lower ($p < 0.05$) than that of the control apples throughout the storage period, as shown in Figure 5.1B. The elevated RR in the control group corresponded with the increased ethylene production rate. These findings align with a study by Fonseca et al. (2021), where a lower RR was observed in relation to ethylene production rate in papaya wrapped in gelatin-TiO_2-coated EPE foam nets. Increased ethylene production rate and RR are known to accelerate fruit ripening (J. Li et al., 2019). In the present study, the use of a VUV photolysis reactor effectively reduced ethylene production and RR and thus delayed the ripening of apples.

Figure 5.1C demonstrates that the treated apples exhibited significantly higher ($p < 0.05$) firmness compared to the untreated apples. The delayed fruit softening observed in the treated apples can be attributed to the lower ethylene levels in the treated samples, as fruit softening is closely associated with ethylene levels (Hrazdina et al., 2003). A positive correlation between ethylene removal by photocatalysis and firmness retention was also reported by Zhu et al. (2019). Thus, the results demonstrate that the VUV photolysis reactor can delay ripening, prevent softening, and extend the shelf life of apple fruit.

The ratio of total soluble solids to total titratable acidity (TSS/TTA), which is used to express the equilibrium between sweetness and acidity, is shown in Fig. 5.1D. No significant difference in the TSS/TTA ratio was observed between the two storage conditions during the first 20 days. However, after 28 days of storage, the untreated apples had a significantly ($p< 0.05$) higher ratio of TSS/TTA compared to treated apples. Generally, as the fruit ripens, TSS increases while TTA declines. This phenomenon occurs because ethylene promotes the conversion of starches into sugars while reducing acidity. The successful removal of ethylene by the VUV photolysis reactor hindered the conversion of starches to sugars, resulting in lower sugar content (TSS), while maintaining higher levels of acidity (TTA). Consequently, the treated apples exhibited a lower ratio of TSS/TTA.

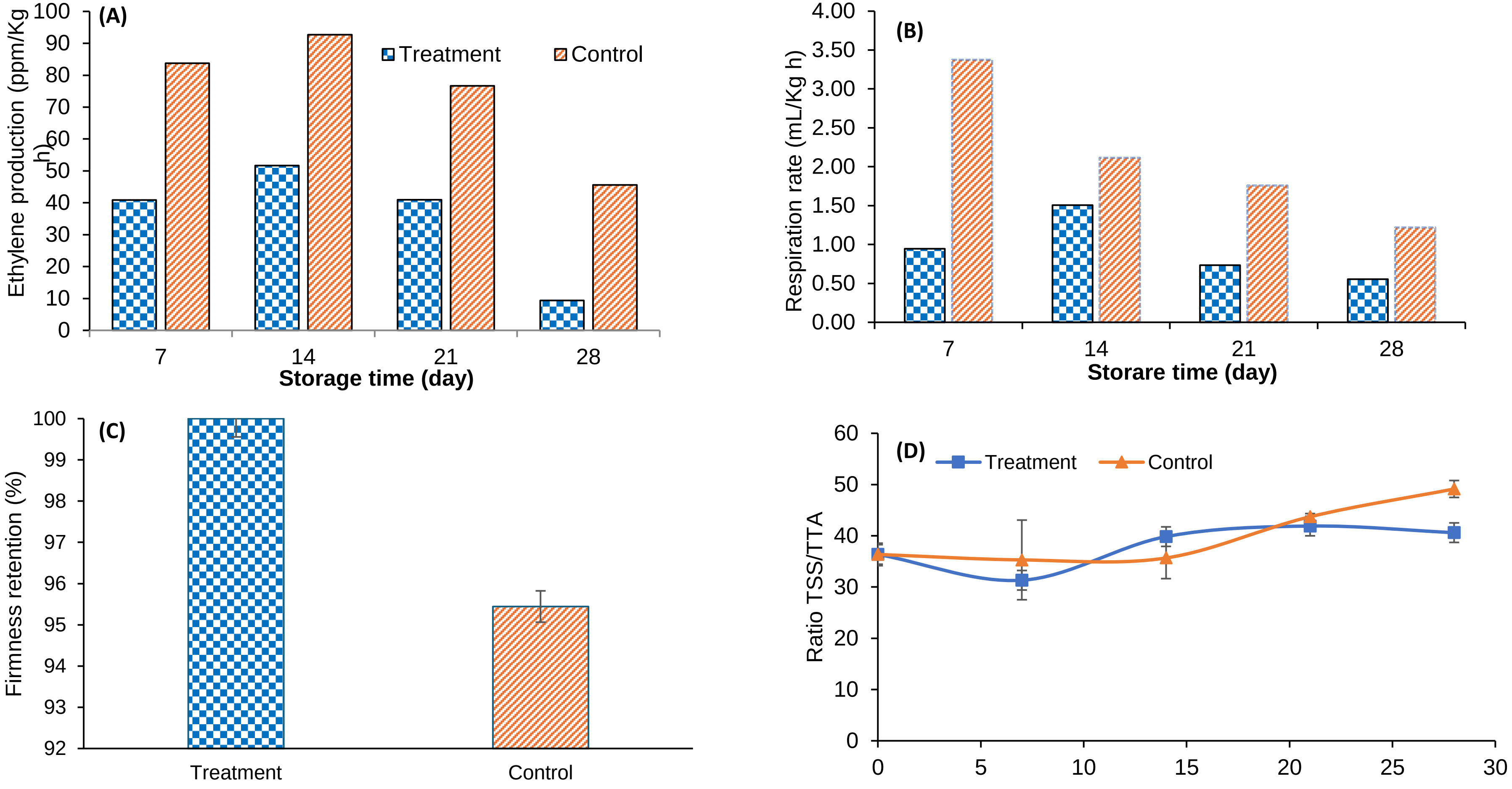


Figure 5.1: Postharvest physiological quality indices of apples during ripening under different treatments after 28 days. A: Changes in ethylene ethylene production rate; B: changes in respiration rate; C: Firmness retention, and D: ratio of TSS/TTA

5.3.2 Protein identification in apples under different storage

To assess the changes in protein, protein extracts from fruit samples taken at control-28 and VUV treatment-28 were compared to samples taken at day 0 (reference) and comparatively evaluated by 1D SDS-PAGE. After 1D SDS-PAGE, a total of 757 proteins were identified and quantified in apple fruit with relative molecular mass ranging between 10 – 422 kDa. These proteins were further filtered for an abundance threshold >95% for a protein to be considered a true protein, and anything without a molecular weight was eliminated. Further filtering was done in Scaffold 5 with parameters set at 1% false discovery rate (FDR), minimum 2 peptides and 95% peptide match threshold. Furthermore, >95% protein identification probability and significant proteins (p-value < 0.05) were applied to identify significantly changed (up- and down-regulated) proteins.

Based on these stringent set parameters, the significantly upregulated and downregulated proteins in control and VUV-treated apples after 28 days of storage were compared to day 0 (baseline). Figure 5.2A illustrates the significantly expressed proteins at day 0 (baseline) and after 28 days of storage for both control and treated samples, and their quantitative profile is shown in Table 5.1. At day 0, approximately 29 proteins were significantly identified, while after 28 days of storage, about 17 and 44 proteins were significantly identified in treated and control apple tissue, respectively. The increased number of proteins detected in control apples is attributed to the effect of ethylene which induced a group of proteins. Similar findings were reported by Zheng et al. (2013) , who observed an increased number of proteins in apples exposed to ethylene.

Figure 5.2 B shows the proteins that were common and/or unique in each of the treatments. There was a significant difference in protein content between the treated and control apple, with 18 unique proteins identified in the control and no unique proteins detected in the treated apple fruit. On the other hand, 14 proteins that were present at day 0 were also present in both control and treated apples after 28 days of storage. Notably, only one protein was common to both control and treated apples.

Among the 18 unique proteins identified in control apple fruit, some, such as NAD(P)H dehydrogenase (quinone) 1.6.5.2 and malic enzymes, are associated with changes in fruit respiration, firmness, and soluble solids (Shi et al., 2014). The presence of these proteins was expected, considering the significant increase in ethylene production in the control apples and the changes in firmness and TSS/TTA ratio as shown in Figure 6.1. In addition, it was observed that 15 proteins were initially present in relatively low quantities at day 0 but exhibited an increase in abundance after 28 days in the control apples.

In the treatment group, a total of 10 proteins were conserved (did not change in quantity) compared to day 0. Some of these proteins included malate dehydrogenase and PMEI domain-containing proteins. Malate dehydrogenase, known to be related to fruit softening in apples, exhibited relatively high levels in control apples compared to treated apples. The downregulation of this protein in treated apples indicates that fruit ripening was slowed down by the VUV treatment.

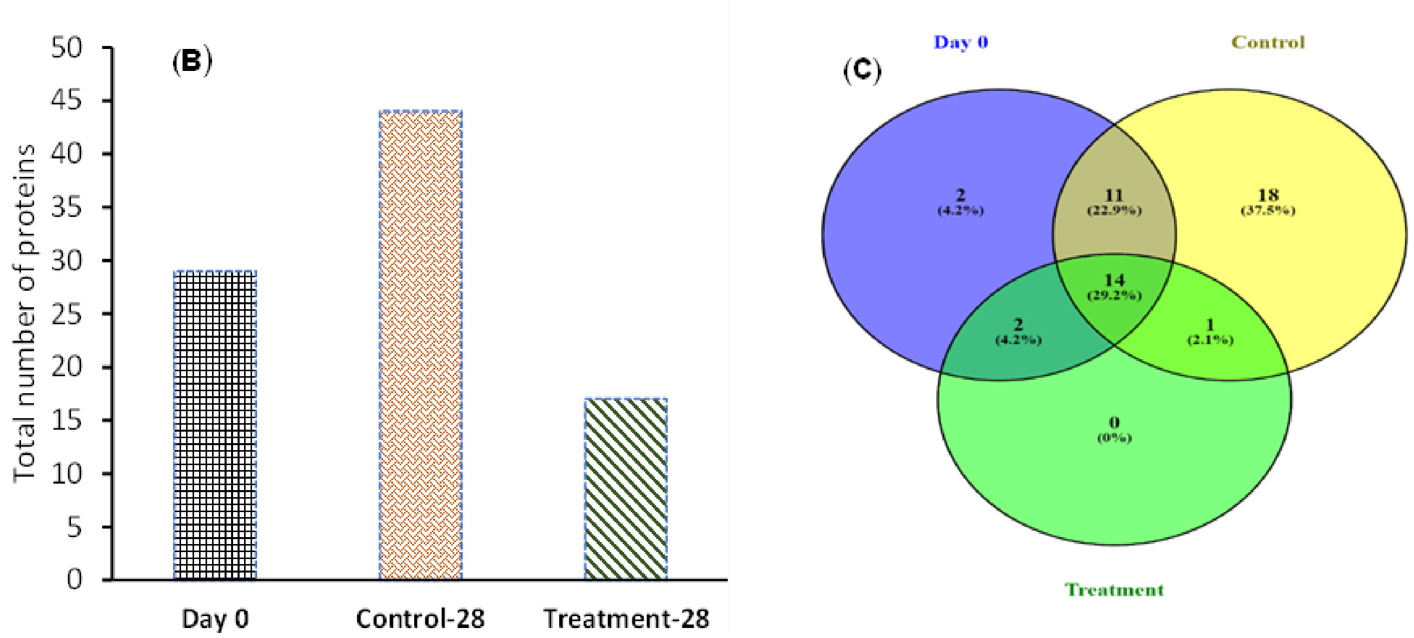


Figure 5.2: Identification of significant proteins identified in different storages. A: Total number of proteins identified in different storage treatments and B: Venn diagram showing common and unique proteins in the control 28 and treatment 28 in comparison with day 0

Table 5.1: List of proteins that changed significantly in apple fruit stored in control (no ethylene management) and in treatment (with ethylene management). Fasta sequences for significant proteins were obtained from www.uniprot.org

			Protein present (%)			Quantitative profile		
Protein name	**Accession Number**	**Molecular Weight (kDa)**	**Day 0**	**Control**	**Treatment**	**Day 0**	**Control**	**Treatment**
Phospho-N-acetylmuramoyl-pentapeptide-transferase homolog	A0A498JUX9_MALDO [3]	85	-	100.00	-	-	High	-
J domain-containing protein	A0A498J2W5_MALDO	41	-	99.67	-	-	High	-
Pyruvate kinase, 2.7.1.40	A0A498IKR9_MALDO [4]	54	100.00	100.00	-	Low	High	-
MFS domain-containing protein	A0A498IM89_MALDO	61	99.50	99.33	98.67	Low	Low	High
Adenosylhomocysteinase	A0A498K2R9_MALDO [3]	53	100.00	100.00	100.00	Low	High	Low
RNA helicase, 3.6.4.13	A0A498IJ30_MALDO	67	-	96.00	-	-	High	-
Ubiquitin receptor RAD23, DNA repair protein RAD23	A0A498HFT4_MALDO	37	-	99.67	-	-	High	-
Usp domain-containing protein	A0A498HK42_MALDO [2]	18	100.00	100.00	95.33	Low	Low	High
PMEI domain-containing protein	A0A498I0A4_MALDO [2]	22	100.00	-	100.00	High	-	High
Malic enzyme	A0A498KLG6_MALDO [5]	70	-	100.00	-	-	High	-
Beta-amyrin 28-oxidase-like	A0A498JUT2_MALDO [3]	163	-	100.00	-	-	High	-
WHY domain class transcription factor	D9ZJE6_MALDO [2]	34	100.00	100.00	-	Low	High	-

Stromal 70 kDa heat shock-related protein, chloroplastic	A0A498HWF0_MALDO [4]	193	100.00	100.00	-	Low	High	-

Protein name	Accession Number	Molecular Weight (kDa)	Protein present (%) Day 0	Control	Treatment	Quantitative profile Day 0	Control	Treatment
Inorganic diphosphatase, 3.6.1.1	A0A498KJF1_MALDO [7]	97	-	100.00	-	-	High	-
Glucosylceramidase	A0A498HRR3_MALDO [3]	131	100.00	100.00	100.00	Low	High	Low
Alpha-mann_mid domain-containing protein	A0A498J6Q4_MALDO [6]	176	95.50	100.00	100.00	Low	High	Low
Glutaredoxin-dependent peroxiredoxin, 1.11.1.25	A0A498ID23_MALDO [2]	24	-	100.00	-	-	High	-
Cysteine proteinase inhibitor	A0A498KFH3_MALDO [3]	117	100.00	100.00	-	High	High	-
Peptidylprolyl isomerase, 5.2.1.8	A0A343U702_MALDO	12	-	100.00	-	-	High	-
Non-specific lipid-transfer protein precursor	Q2V6D8_MALDO [3]	11	96.67	-	-	Low	-	-
Cupin type-1 domain-containing protein	A0A498J9F4_MALDO [4]	37	100.00	100.00	-	Low	Low	-
Vesicle-associated membrane protein 711	A0A498JAD8_MALDO [2]	23	98.00	100.00	-	High	High	-
ABC1 domain-containing protein	A0A498J4L4_MALDO [3]	148	100.00	100.00	-	Low	High	-
High molecular weight heat shock protein	Q9M6R1_MALDO [7]	71	100.00	100.00	100.00	High	High	Low
Aldedh domain-containing protein	A0A498I194_MALDO	59	-	100.00	-	-	High	-
Diadenosine tetraphosphate synthetase, 6.1.1.14, 7.1.1.8	A0A498IFG8_MALDO [5]	117	100.00	98.00	100.00	Low	High	Low

Ribosomal_L18e/L15P domain-containing protein	A0A498IMC9_MALDO [5]	21	-	100.00	-	-	High	-
40S ribosomal protein S3a	A0A498HJW5_MALDO [5]	80	-	92.67	-	-	High	-

			Protein present (%)			Quantitative profile		
Protein name	**Accession Number**	**Molecular Weight (kDa)**	**Day 0**	**Control**	**Treatment**	**Day 0**	**Control**	**Treatment**
Alpha-mannosidase, 3.2.1.24	A0A498J6W9_MALDO	151	-	100.00	-	-	High	-
Profilin	B0B0N5_MALDO [4]	14	97.00	100.00	99.50	Low	High	Low
Nucleoside diphosphate kinase, 2.7.4.6	A0A498I3I1_MALDO [3]	53	-	98.67	-	-	High	-
GTP-binding nuclear protein	A0A498HV09_MALDO [3]	30	100.00	100.00	100.00	Low	High	Low
acylaminoacyl-peptidase, 3.4.19.1	A0A498HP27_MALDO [2]	82	-	99.00	-	-	High	-
L-arabinokinase	A0A498JEV1_MALDO [2]	110	100.00	99.33	100.00	High	Low	High
phosphoenolpyruvate carboxykinase (ATP), 4.1.1.49	A0A498JA17_MALDO [4]	74	100.00	100.00	-	Low	High	-
Programmed cell death protein 4	A0A498I6A6_MALDO [2]	78	99.67	100.00	96.50	High	Low	Low
malate dehydrogenase	A0A498K9H0_MALDO [7]	188	100.00	100.00	100.00	Low	High	Low
ABC transporter domain-containing protein	A0A498KGY4_MALDO [11]	97	95.00	100.00	-	Low	High	-
DEAD-box ATP-dependent RNA helicase 38	A0A498I4U0_MALDO	63	99.50	-	99.67	Low	-	High
F-box domain-containing protein	A0A498J4M9_MALDO [5]	78	-	100.00	-	-	High	-

60S ribosomal protein L9	A0A498JKE2_MALDO	25	100.00	100.00	-	Low	High	-
PH domain-containing protein	A0A498HA84_MALDO [3]	57	-	99.67	-	-	High	-
Fasciclin-like arabinogalactan protein 2	A0A498J7G9_MALDO [2]	48	-	99.00	99.50	-	High	Low

			Protein present (%)			**Quantitative profile**		
Protein name	**Accession Number**	**Molecular Weight (kDa)**	**Day 0**	**Control**	**Treatment**	**Day 0**	**Control**	**Treatment**
Heat shock 70 kDa protein, mitochondrial	A0A498IU20_MALDO [3]	73	100.00	100.00	100.00	High	Low	High
transketolase, 2.2.1.1	A0A498JIB6_MALDO [4]	133	100.00	100.00	100.00	Low	High	Low
Calnexin homolog	A0A498JQN8_MALDO [3]	61	100.00	-	-	High	-	-
Alpha-1,4 glucan phosphorylase, 2.4.1.1	A0A498KD22_MALDO [2]	96	97.00	100.00	-	Low	High	-
NAD(P)H dehydrogenase (quinone), 1.6.5.2	A0A498IW71_MALDO [3]	22	-	98.00	-	-	High	-

5.3.3 Proteins related to ethylene biosynthesis

Ethylene plays a crucial role in the ripening of climacteric fruits, characterized by an initial burst of ethylene followed by a peak in respiration (Shi et al., 2014). It is well known that reduced ethylene levels lead to delayed fruit softening (Hrazdina et al., 2003). Therefore, it is not surprising that the identification of the ethylene biosynthetic enzyme, S-adenosylmethionine synthase (SAM synthase), was only detected in the control apple fruit, although its presence was not significant ($p>0.05$). Conversely, the absence of SAM synthase in the treated samples implies a hindered ethylene production, which aligns with the low ethylene production rate shown in Figure 5.1A, thus slowing down the softening of treated apples. Marondedze and Thomas (2012) also reported a low abundance of SAM synthase in high-firmness hypanthium. The quantitative abundance of other proteins involved in ethylene biosyntheses, such as malic enzymes, beta-amyrin 28-oxidase-like enzymes, ribosomal_L18e/L15P domain-containing protein, NAD(P)H dehydrogenase (quinone) and F-box domain-containing protein (Table 5.1), were relatively high in control apples. The elevated abundance of these proteins in the control apples corresponds to the high levels of ethylene observed in this treatment because of the absence of an ethylene management system. Malic enzyme plays a role in ethylene biosynthesis by catalyzing the conversion of malate to pyruvate, a precursor for ethylene production. Its increased presence in the control is associated with enhanced ethylene production. An increased abundance of malic enzymes in apples exposed to ethylene was also reported by Zheng et al. (2013) . The abundance of F-box domain-containing protein, known to regulate ethylene signaling (Potuschak et al., 2003), also correlates with the increased production of ethylene in the control. Also, the presence of Fasciclin-like arabinogalactan protein 2 (FLA2), a type of arabinogalactan protein (AGP) found in apples, was quantitatively high in control apples and low in treated apples. It is reported that 1-aminocyclopropane-1-carboxylic acid (ACC), a precursor of ethylene synthesis, might be involved in cell wall formation associated with AGPs (Lin et al., 2022). Lastly, NAD(P)H dehydrogenase (quinone) is responsible for ethylene activation (Marhavý et al., 2019). Its increase indicated that the synthesis of ethylene was increased, which accelerated the ripening process of apples in the control treatment. The identification of these proteins in high abundance not only confirmed the results of increased ripening but also indicated that ethylene is responsible for inducing the proteins responsible for ethylene biosynthesis. These results indicate that the removal of ethylene by the VUV system had a positive impact on suppressing the proteins that are responsible for ethylene biosynthesis thereby reducing the ripening process of apples.

5.3.4 Cell wall modification enzymes

The reduction in fruit firmness that occurs during ripening is partially regulated by the activity of cell wall-degrading enzymes, which induce biochemical and structural alterations in cell walls (Shi et al., 2014). One protein associated with cell wall modification, 40S ribosomal protein S3a, was found in high abundance in the control sample. The presence of this protein in the control apples aligns with the observed decrease in firmness and high ethylene production (Figure 6.1C). This finding is consistent with the study by Zhang et al. (2015), who reported that elevated levels of 40S ribosomal protein S3a were correlated with ethylene production. On the other hand, this protein was absent in treated apples, where ethylene was continuously degraded.

Another important protein involved in cell wall modification is pectin methylesterase inhibitors (PMEI), which were identified in the baseline (day 0) and VUV-treated apples. PMEI plays a crucial role in cell wall modification by inhibiting the activity of pectin methylesterase (PME) during plant growth and development. PME itself plays a vital role in regulating cell wall loosening and cell expansion in apples (M. Li et al., 2016). The presence of PMEI at day 0 and in treated apples suggests that the cell wall integrity of apples was preserved, resulting in high firmness (Figure 5.1C). These findings align with the study by Bu et al. (2013) , where the authors demonstrated that inhibition of ethylene production decreased PME activity and consequently delayed tomato fruit softening. This was also confirmed by Shinga and Fawole (2023) who reported that the inhibition of ethylene production and RR reduced the increase of cell wall degrading enzymes such as PME. These results demonstrate that the VUV photolysis reactor effectively suppressed the proteins responsible for cell wall degradation by removing ethylene from the storage.

5.4 Conclusion

The VUV photolysis reactor was efficient in degrading ethylene and postponing the ripening of apples at the studied storage conditions. Apples stored in the VUV photolysis-connected storage exhibited lower ethylene production and respiration rate, higher firmness, and a lower ratio of TSS/TTA compared to apples in the control storage without an ethylene removal technique. The proteomic analysis identified a total of 48 significant proteins, with 29 proteins detected in the baseline samples (day 0), 17 proteins in VUV-treated apples, and 44 proteins in the control group. Notable differences in protein expression were observed between the control and treated apples during postharvest storage. The results showed that the VUV photolysis reactor's ability to efficiently remove ethylene played a significant role in suppressing the activity of ethylene biosynthesis and cell wall-degrading enzymes, consequently delaying the ripening process of apples. It can be concluded that the VUV photolysis technique holds a significant potential for application in postharvest management. By mitigating ethylene-related effects, this technology offers a viable solution to preserve fruit quality, enhance shelf life, and meet the demands of the market for high-quality produce. Future studies aimed at elucidating the precise mechanisms by which ethylene induces these protein expression alterations will be developed. Understanding these underlying mechanisms will provide valuable insights into the complex regulatory processes involved in ethylene-mediated proteomic changes and enable the development of postharvest technologies for enhanced postharvest management of fruits.

5.5 Summary

This chapter delved into assessing the effectiveness of a vacuum ultraviolet (VUV) photolysis reactor in inhibiting the proteins accountable for ethylene biosynthesis and cell wall degradation. The outcomes revealed that the VUV photolysis reactor successfully downgraded a significant portion of the proteins associated with the acceleration of apple ripening. Beyond ethylene removal, the reactor demonstrated efficacy in reducing the proteins and enzymes responsible for hastening the ripening process. This chapter serves as a sequential continuation of Chapters 3 and 4.

References

Alexander, L., & Grierson, D. (2002). Ethylene biosynthesis and action in tomato: A model for climateric fruit ripening. *Journal of Experimental Botany*, *53*, 2039–2055. https://doi.org/10.1093/jxb/erf072

Alonso Salinas, R., Motos, J. R., Núñez-Delicado, E., Gabaldon, J., & López-Miranda, S. (2022). Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures. *Agronomy*, *12*, 616. https://doi.org/10.3390/agronomy12030616

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., Ventura-Sobrevilla, J. M., & Martínez-Hernández, G. B. (2018). Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food and Bioprocess Technology*, *11*(3), 511–525. https://doi.org/10.1007/s11947-018-2076

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Miranda-Molina, F. D., & Artés-Hernández, F. (2020). Postharvest quality retention of apricots by using a novel sepiolite–loaded potassium permanganate ethylene scavenger. *Postharvest Biology and Technology*, *160*, 111061. https://doi.org/https://doi.org/10.1016/j.postharvbio.2019.111061

Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R., & Anderson, W. A. (1995). UV oxidation for drinking waterfeasibility studies for addressing specific water quality issues. *Proceedings of the AWWA WQTC, New Orleans, LA*, 18811898.

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018a). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1). https://doi.org/10.1088/1755-1315/141/1/012003

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018b). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1), 012003. https://doi.org/10.1088/1755-1315/141/1/012003

Basso, A., de Fátima Peralta Muniz Moreira, R., & José, H. J. (2018). Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening. *Journal of Photochemistry and Photobiology A: Chemistry*, *367*, 294–301. https://doi.org/10.1016/j.jphotochem.2018.08.027

Bu, J., Yu, Y., Aisikaer, G., & Ying, T. (2013). Postharvest UV-C irradiation inhibits the production of ethylene and the activity of cell wall-degrading enzymes during softening of tomato (Lycopersicon esculentum L.) fruit. *Postharvest Biology and Technology*, *86*, 337–345. https://doi.org/10.1016/j.postharvbio.2013.07.026

Chang, K.-L., Sekiguchi, K., Wang, Q., & Zhao, F. (2013). Removal of Ethylene and Secondary Organic Aerosols Using UV-C-254 (+) (185) (nm) with TiO2 Catalyst. *Aerosol and Air Quality Research*, *13*, 618–626. https://doi.org/10.4209/aaqr.2012.07.0195

Chen, F., Yang, Q., Pehkonen, S. O., & Ray, M. B. (2004). Modeling of Gas-Phase Photodegradation of Chloroform and Carbon Tetrachloride. *Journal of the Air & Waste Management Association*, *54*(10), 1281–1292. https://doi.org/10.1080/10473289.2004.10470991

Chen, L., Xie, X., Song, X., Luo, S., Ye, S., & Situ, W. (2021). Photocatalytic degradation of ethylene in cold storage using the nanocomposite photocatalyst MIL101(Fe)-TiO2-rGO. *Chemical Engineering Journal*, *424*, 130407. https://doi.org/https://doi.org/10.1016/j.cej.2021.130407

Cheng, Z.-W., Jiang, Y.-F., Zhang, L.-L., Chen, J.-M., & Wei, Y.-Y. (2011). Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. *Separation and Purification Technology*, *77*(1), 26–32. https://doi.org/https://doi.org/10.1016/j.seppur.2010.11.014

Chou, M.-S., & Chang, K.-L. (2007). UV/ozone degradation of gaseous hexamethyldisilazane (HMDS). *Chemosphere*, *69*(5), 697–704. https://doi.org/https://doi.org/10.1016/j.chemosphere.2007.05.040

De Bruijn, J., Gómez, A. E., Melín, P., Loyola, C., Solar, V. A., & Valdés, H. (2019). Effect of doping natural zeolite with copper and zinc cations on ethylene removal and postharvest tomato fruit quality. *Chemical Engineering Transactions*, *75*, 265–270. https://doi.org/10.3303/CET1975045

de Chiara, M. L. V., Pal, S., Licciulli, A., Amodio, M. L., & Colelli, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO2/SiO2 nanocomposites: Effects on the ripening of mature green tomatoes. *Biosystems Engineering*, *132*, 61–70. https://doi.org/10.1016/j.biosystemseng.2015.02.008

Department of Agriculture, F. and F. (2022). *A PROFILE OF THE SOUTH AFRICAN APPLE MARKET VALUE CHAIN 2020*. www.dalrrd.gov.za

Du, L., Song, J., Forney, C., Palmer, L. C., Fillmore, S., & Zhang, Z. (2016). Proteome changes in banana fruit peel tissue in response to ethylene and high-temperature treatments. *Horticulture Research*, *3*. https://doi.org/10.1038/hortres.2016.12

Feiyan, C., Pehkonen, S. O., & Ray, M. B. (2002). Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. *Water Research*, *36*(17), 4203–4214. https://doi.org/https://doi.org/10.1016/S0043-1354(02)00140-9

Fonseca, J. de M., Pabón, N. Y. L., Nandi, L. G., Valencia, G. A., Moreira, R. de F. P. M., & Monteiro, A. R. (2021). Gelatin-TiO2-coated expanded polyethylene foam nets as ethylene scavengers for fruit postharvest application. *Postharvest Biology and Technology*, *180*, 111602. https://doi.org/https://doi.org/10.1016/j.postharvbio.2021.111602

Hooijberg, E. H., Miller, M., Cray, C., Buss, P., Steenkamp, G., & Goddard, A. (2018). Serum protein electrophoresis in healthy and injured southern white rhinoceros (Ceratotherium simum simum). *PLoS ONE*, *13*(7). https://doi.org/10.1371/journal.pone.0200347

Hrazdina, G., Kiss, E., Galli, Z., RosenField, C., Norelli, J. L., & Aldwinckle, H. S. (2003). DOWN REGULATION OF ETHYLENE PRODUCTION IN “ROYAL GALA” APPLES. *Acta Horticulturae*, *628*, 239–251. https://doi.org/10.17660/ActaHortic.2003.628.29

Huang, H., Huang, H., Zhang, L., Hu, P., Xu, Y., Ye, X., Liang, X., Chen, J., & Ji, M. (2014). Photooxidation of Gaseous Benzene by 185 nm VUV Irradiation. *Environmental Engineering Science*, *31*(8), 481–486. https://doi.org/10.1089/ees.2014.0100

Kader, A. A. (1985). Ethylene-induced Senescence and Physiological Disorders in Harvested Horticultural Crops. *HortScience*, *20*(1), 54–57 https://doi.org/10.21273/HORTSCI.20.1.54

Khedr, E., & Al-Khayri, J. (2023). Synergistic Effects of Tragacanth and Anti-ethylene Treatments on Postharvest Quality Maintenance of Mango (Mangifera indica L.). *Plants*, *12*, 1887. https://doi.org/10.3390/plants12091887

Kim, K., Chun, I.-J., Suh, J. H., & Sung, J. (2023). Relationships between sensory properties and metabolomic profiles of different apple cultivars. *Food Chemistry: X*, *18*, 100641. https://doi.org/https://doi.org/10.1016/j.fochx.2023.100641

Li, J., Sun, Q., Sun, Y., Chen, B., Wu, X., & Le, T. (2019). Improvement of banana postharvest quality using a novel soybean protein isolate/cinnamaldehyde/zinc oxide bionanocomposite coating strategy. *Scientia Horticulturae*, *258*, 108786. https://doi.org/https://doi.org/10.1016/j.scienta.2019.108786

Li, L., Ban, Z., Limwachiranon, J., & Luo, Z. (2017). Proteomic Studies on Fruit Ripening and Senescence. *Critical Reviews in Plant Sciences*, *36*(2), 116–127. https://doi.org/10.1080/07352689.2017.1355173

Li, M., Li, D., Feng, F., Zhang, S., Ma, F., & Cheng, L. (2016). Proteomic analysis reveals dynamic regulation of fruit development and sugar and acid accumulation in apple. *Journal of Experimental Botany*, *67*(17), 5145–5157. https://doi.org/10.1093/jxb/erw277

Lien, N., Horváth, V., Mai, D., Hitka, G., Zsom, T., & Kókai, Z. (2018). Effect of 1-MCP, ethylene absorber and ozone on melon quality during storage. *Progress in Agricultural Engineering Sciences*, *14*, 101–110. https://doi.org/10.1556/446.14.2018.S1.10

Lin, S., Miao, Y., Huang, H., Zhang, Y., Huang, L., & Cao, J. (2022). Arabinogalactan Proteins: Focus on the Role in Cellulose Synthesis and Deposition during Plant Cell Wall Biogenesis. *International Journal of Molecular Sciences*, *23*, 6578. https://doi.org/10.3390/ijms23126578

Lin, Y.-T., Weng, C.-H., Hsu, H.-J., Huang, J.-W., Srivastav, A. L., & Shiesh, C.-C. (2014). Effect of oxygen, moisture, and temperature on the photo oxidation of ethylene on N-doped TiO2 catalyst. *Separation and Purification Technology*, *134*, 117–125. https://doi.org/https://doi.org/10.1016/j.seppur.2014.07.039

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023). Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics and removal in mixed-fruit storage, and direct exposure to ‘Fuji’ apples during storage. *Journal of Food Science and Technology*. https://doi.org/10.1007/s13197-023-05775-3

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, & Caleb, O. J. (2022). Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of Fruit and Vegetables Along the Value Chains: a Review. *Food and Bioprocess Technology*, *15*(1), 28–46. https://doi.org/10.1007/s11947-021-02703-1

Marhavý, P., Kurenda, A., Siddique, S., Dénervaud Tendon, V., Zhou, F., Holbein, J., Hasan, M. S., Grundler, F. M. W., Farmer, E. E., & Geldner, N. (2019). Single-cell damage elicits regional, nematode-restricting ethylene responses in roots. *The EMBO Journal*, *38*(10), e100972. https://doi.org/https://doi.org/10.15252/embj.2018100972

Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2017). Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage. *Biosystems Engineering*, *159*, 33–45. https://doi.org/https://doi.org/10.1016/j.biosystemseng.2017.04.008

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. https://doi.org/https://doi.org/10.1016/j.postharvbio.2018.09.006

Potuschak, T., Lechner, E., Parmentier, Y., Yanagisawa, S., Grava, S., Koncz, C., & Genschik, P. (2003). EIN3-Dependent Regulation of Plant Ethylene Hormone Signaling by Two Arabidopsis F Box Proteins: EBF1 and EBF2. *Cell*, *115*(6), 679–689. https://doi.org/10.1016/S0092-8674(03)00968-1

Sardabi, F., Mohtadinia, J., Shavakhi, F., & Jafari, A. A. (2014). The Effects of 1-Methylcyclopropen (1-MCP) and Potassium Permanganate Coated Zeolite Nanoparticles on Shelf life Extension and Quality Loss of Golden Delicious Apples. *Journal of Food Processing and Preservation*, *38*. https://doi.org/10.1111/jfpp.12197

Schaffer, R. J., Friel, E. N., Souleyre, E. J. F., Bolitho, K., Thodey, K., Ledger, S., Bowen, J. H., Ma, J. H., Nain, B., Cohen, D., Gleave, A. P., Crowhurst, R. N., Janssen, B. J., Yao, J. L., & Newcomb, R. D. (2007). A genomics approach reveals that aroma production in apple is controlled by ethylene predominantly at the final step in each biosynthetic pathway. *Plant Physiology*, *144*(4), 1899–1912. https://doi.org/10.1104/pp.106.093765

Shenoy, S., Pathak, N., Molins, A., Toncheva, A., Schouw, T., Hemberg, A., Laoutid, F., & Mahajan, P. V. (2022). Impact of relative humidity on ethylene removal kinetics of different scavenging materials for fresh produce industry. *Postharvest Biology and Technology*, *188*, 111881. https://doi.org/https://doi.org/10.1016/j.postharvbio.2022.111881

Shi, Y., Jiang, L., Zhang, L., Kang, R., & Yu, Z. (2014). Dynamic changes in proteins during apple (Malus x domestica) fruit ripening and storage. *Horticulture Research*, *1*. https://doi.org/10.1038/hortres.2014.6

Shinga, M. H., & Fawole, O. A. (2023). Opuntia ficus indica mucilage coatings regulate cell wall softening enzymes and delay the ripening of banana fruit stored at retail conditions. *International Journal of Biological Macromolecules*, *245*, 125550. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2023.125550

Sun, X., Li, C., Yu, B., Wang, J., & Wang, W. (2023). Removal of gaseous volatile organic compounds via vacuum ultraviolet photodegradation: Review and prospect. *Journal of Environmental Sciences*, *125*, 427–442. https://doi.org/https://doi.org/10.1016/j.jes.2022.01.020

Suttikul, T., Nuchdang, S., Rattanaphra, D., Kingkam, W., Moonsrikaew, W., Photsathain, T., & Phalakornkule, C. (2022). Plasma-assisted ethylene removal using silica gel and zeolite in AC dielectric barrier discharge. *Chemical Engineering and Processing - Process Intensification*, *179*, 109066. https://doi.org/https://doi.org/10.1016/j.cep.2022.109066

Taiti, C., Vivaldo, G., Masi, E., Giordani, E., & Nencetti, V. (2023). Postharvest monitoring and consumer choice on traditional and modern apricot cultivars. *European Food Research and Technology*, *249*. https://doi.org/10.1007/s00217-023-04311-z

Wang, J. H., & Ray, M. B. (2000). Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. *Separation and Purification Technology*, *19*(1), 11–20. https://doi.org/https://doi.org/10.1016/S1383-5866(99)00078-7

Wang, W., Vignani, R., Scali, M., & Cresti, M. (2006). A universal and rapid protocol for protein extraction from recalcitrant plant tissues for protomic analysis. *Electrophoresis*, *27*, 2782–2786. https://doi.org/10.1002/elps.200500722

Xie, P., Yue, S., Ding, J., Wan, Y., Li, X., Ma, J., & Wang, Z. (2018). Degradation of organic pollutants by Vacuum-Ultraviolet (VUV): Kinetic model and efficiency. *Water Research*, *133*, 69–78. https://doi.org/https://doi.org/10.1016/j.watres.2018.01.019

Xu, J., Li, C., Liu, P., He, D., Wang, J., & Zhang, Q. (2014). Photolysis of low concentration H2S under UV/VUV irradiation emitted from high frequency discharge electrodeless lamps. *Chemosphere*, *109*, 202–207. https://doi.org/https://doi.org/10.1016/j.chemosphere.2014.01.065

Yu, J., Cai, W., Chen, J., Feng, L., Jiang, Y., & Cheng, Z. (2012). Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. *Journal of Environmental Sciences*, *24*(10), 1777–1784. https://doi.org/https://doi.org/10.1016/S1001-0742(11)61021-8

Zhang, Z., Jiang, S., Wang, N., Li, M., Ji, X., Sun, S., Liu, J., Wang, D., Xu, H., Qi, S., Wu, S., Fei, Z., Feng, S., & Chen, X. (2015). Identification of differentially expressed genes associated with Apple fruit ripening and softening by suppression subtractive hybridization. *PLoS ONE*, *10*(12). https://doi.org/10.1371/journal.pone.0146061

Zheng, Q., Song, J., Campbell-Palmer, L., Thompson, K., Li, L., Walker, B., Cui, Y., & Li, X. (2013). A proteomic investigation of apple fruit during ripening and in response to ethylene treatment. *Journal of Proteomics*, *93*, 276–294. https://doi.org/https://doi.org/10.1016/j.jprot.2013.02.006

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019). Electrospun Nanofibers Containing TiO2 for the Photocatalytic Degradation of Ethylene and Delaying Postharvest Ripening of

Bananas. *Food and Bioprocess Technology*, *12*(2), 281–287. https://doi.org/10.1007/s11947-018-2207-1

CHAPTER SIX:

DEVELOPING A KINETIC MODEL FOR THE DEGRADATION OF ETHYLENE

Published as: **Mabusela, B. P.**, Godongwana, B., Belay, Z. A., & Caleb, O. J. (2024). Ethylene degradation via vacuum ultraviolet photolysis: nth-order kinetic model, energy consumption assessment, and a case study for "Fuji" apples under retail conditions. Food and Bioproducts Processing, 147, 230–238. https://doi.org/10.1016/j.fbp.2024.07.006

6. DEVELOPING A KINETIC MODEL FOR THE DEGRADATION OF ETHYLENE

Abstract

Effective management of ethylene along the value chain is crucial to the regulation of fruit ripening and senescence to reduce postharvest losses. The objectives of this study were to, (i) investigate the degradation kinetics of ethylene using a vacuum ultraviolet (VUV) photolysis reactor at different light intensity (0.0005 mW/m^2, 0.0014 mW/m^2 and 0.0021 mW/m^2) and relative humidity (RH) levels (20 % and 80 %), and (ii) evaluate the economic feasibility of the VUV photolysis system. Kinetic experiments were performed in batch mode with an initial ethylene concentration of 51 mg L^{-1}. The reaction order and rate constant were determined by employing an nth-order kinetic model. Light intensity and RH significantly influenced the kinetic parameters and ethylene degradation ($p < 0.05$). At low light intensity, ethylene degradation followed a zero-order kinetic model, while at high intensity, it followed a fractional-order kinetic model. The developed kinetic models accurately predicted the experimental concentrations (R^2 = 0.9955). The economic feasibility of the VUV photolysis system was assessed using electrical energy per order (*EEO*), which remained below 10 kW m^{-3} order^{-1}, indicating energy efficiency and practical applicability. The chamber equipped with the VUV reactor successfully preserved apple quality (maintaining low TSS/TA ratio and delaying pH increase) during storage for 28 d at 15 ℃ compared to the control. This foundational application of VUV photolysis in ethylene degradation offers promising prospects of upscaling for long-term storage investigation and industry applications.

Keywords: Photooxidation, Fractional n-order kinetics, Electrical energy per order, Storage

6.1 Introduction

Ethylene is a plant hormone that can cause fruit and vegetables to ripen prematurely and make them more susceptible to food waste. While ethylene promotes fruit growth (Suttikul et al., 2022), its presence can pose challenges due to its ability to accelerate decay and deterioration. Although it is recommended to store agricultural products in environments with ethylene concentrations below one ppm, achieving zero ethylene concentrations is of utmost importance to maximize shelf-life and extend the freshness of the stored produce (Pathak, Caleb, Rauh, et al., 2017). Removing ethylene from the storage environment offers several benefits in reducing food loss. It helps to extend shelf-life, maintain firmness, delay color changes, preserve flavor and aroma, reduce pathogen susceptibility, and enhance overall quality control (Álvarez-Hernández et al., 2018). Hence, the effective management of ethylene levels during the storage and transportation of fruit and vegetables is crucial in preventing premature ripening and minimizing food waste.

Conventional technologies, including adsorption, catalytic oxidation, K_2MnO_4 oxidation, and biofilters, have been employed to regulate ethylene concentrations and extend the shelf-life of fruit (Álvarez-Hernández et al., 2020; L. Chen et al., 2021; Shenoy et al., 2022). However, these techniques have significant limitations that hinder their widespread commercial application. Adsorption by adsorbents and K_2MnO_4 is not applicable for long-term storage as they quickly saturate, necessitating frequent replenishment. On the other hand, biological systems are often slow, and finding a readily available substrate is very challenging. Therefore, an alternative ethylene removal technique for long-term storage is needed to maintain the quality of fruit and vegetables.

VUV photolysis has emerged as a promising technology for ethylene removal. Utilizing vacuum ultraviolet light effectively breaks ethylene into less reactive compounds, thereby mitigating its detrimental effects on fruit quality (Mabusela et al., 2022). While VUV photolysis has traditionally been employed to remove organics in aqueous phase applications, its potential in the gas phase has gained significant attention. Researchers have explored its application for treating various volatile organic compounds (VOCs), highlighting its attractive features (Chang et al., 2013; Xu et al., 2014). Given its efficient performance in removing air pollutants, there is a growing interest in harnessing VUV photolysis for postharvest handling and extending the shelf-life of agricultural produce. Pathak et al. (2017) explored the use of VUV photolysis and the impact of different process variables, peculiar in fruit storage, on the efficiency of VUV photolysis. The researchers later applied this technique to store apples and found that the VUV photolysis reduced ethylene concentrations by 96.3% (Pathak et al., 2019). Although the potential application of VUV photolysis has been demonstrated, there still needs to be studies relating to the performance of this technique in the kinetic removal of ethylene. Kinetic studies help provide important information about the ethylene removal rate and the VUV system's efficiency. Such studies can be used to optimize the design and operation of the VUV systems to achieve maximum ethylene removal efficiency.

Thus, this study aims to investigate the degradation kinetics of ethylene using VUV photolysis and assess the efficacy of VUV photolysis in preserving the quality of fruit and reducing food waste. By exploring the kinetic behavior of VUV photolysis, valuable information can be gained to advance the understanding and application of this technique in ethylene removal for enhanced postharvest preservation of apples. Finally, the feasibility of VUV photolysis as an economical and practical alternative technology for removing ethylene was evaluated through the electrical energy per order (E_{EO}) measurement.

6.2 Materials and methods

6.2.1 Ethylene degradation rate

The VUV photolysis reactor consisted of three VUV lamps, each with a power output of 3W, as shown in Figure 6.1. The VUV lamps emitted major radiation at 254 nm, with minor radiation at 185 nm. The reactor lid was constructed from borosilicate glass and featured openings for VUV lamp fittings and a temperature and humidity sensor. The desired lamp power was achieved by manipulating the lamp combination. The moisture in the reactor was controlled by bubbling dry air through a deionized water column. A hygrometer coupled with a temperature sensor measured the humidity and the temperature. Regular ethylene samples were collected from the reactor using an ICA 56-ethylene analyzer (Fricaval 89 S.L, Valencia, Spain). This analyzer incorporated a built-in pump, which returned the gas sample to the reactor to maintain a constant gas volume.

At the beginning of each experiment, the reactor was first purged with air for 20 min to remove any impurities from previous experiments. Subsequently, ethylene from an ethylene standard (100 µL L^{-1}) was allowed to fill the reactor until the desired concentration was achieved. The VUV lamps were switched on when the ethylene concentration in the reactor was stable. Kinetics experiments were conducted by varying lamp power and humidity in the reactor. All experiments were conducted at ambient room temperature and atmospheric pressure.

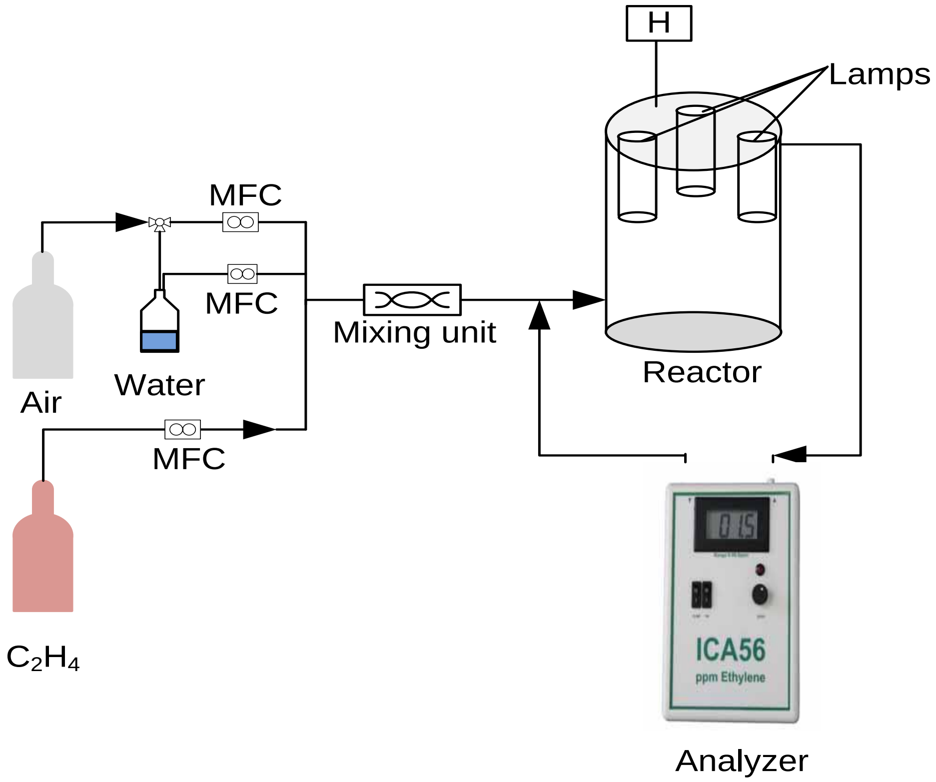


Figure 6.1: Schematic diagram of the experimental batch reactor

6.2.2 Storage experiments of apples

The storage investigation of 'Fuji' apples was conducted using 30 L plastic chambers. A total of 74 uniformly sized apples were divided into two treatment groups. The first group was the control, consisting of apples stored without an ethylene removal strategy. The second group served as the treatment group, storing the apples in a chamber connected to a VUV photolysis reactor for continuous ethylene removal. The storage chambers were placed inside a temperature-regulated walk-in cold room maintained at 15 °C for 28 days; see Mabusela et al. (2023) for a diagram. In the treatment experiment, only the chamber was placed inside the cold room, and the air was circulated through the reactor using a pump. The weight loss during storage was calculated by subtracting the apple weight at specific time points from their initial weight and expressed as a percentage of weight loss.

6.2.3 Kinetic modelling

The photolysis oxidation reaction occurring in a batch reactor can be described by a mass balance equation, specifically an ordinary differential equation (Equation 6.1), which relates the rate of change of ethylene concentration (C_A) with respect to time (t) to the overall kinetic rate expression (r_a) of ethylene in the system.

$$\frac{dC_A}{dt} = r_a \tag{6.1}$$

The oxidation of ethylene by VUV photolysis typically involves two mechanisms: (i) the direct mechanism where the ethylene is directly decomposed by VUV radiation (Equation 6.2), ii) the indirect oxidation where •OH radicals generated through VUV photolysis of another compound (usually a precursor such as water or oxygen) attack ethylene, leading to its oxidation (Equation 3) (Mabusela et al., 2022).

$$C_2H_4 + hv \overset{k_1}{\rightarrow} oxidation\,products \tag{6.2}$$

$$C_2H_4 + \mathrm{OH} \overset{k_2}{\rightarrow} \mathrm{x}C_2H_4 + yCO_2 \tag{6.3}$$

Therefore, the overall photolytic degradation rate (*r_a)* of ethylene can be represented by the following non-elementary expression (Xie et al., 2018):

$$r_a = k_1[C_2H_4]^x + k_2[C_2H_4]^y[OH]_{ss}^z \tag{6.4}$$

where, k_1 and k_2 are the reaction constants for direct and indirect oxidation, respectively; $[C_2H_4]$ is the concentration of ethylene; $[OH]_{ss}$ is the concentration of hydroxyl radicals at steady state; x, y and z are the kinetic order corresponding to ethylene and hydroxyl radicals.

Under high irradiation intensities and considering that •OH radicals have a short estimated shelf-life of approximately 10^{-9} seconds, the rate of the direct photolysis of ethylene is significantly faster than the rate of the reaction between ethylene and •OH radicals $k_1[C_2H_4]^x >>> k_1[C_2H_4]^y[OH]^z$. As a result, the contribution of indirect photolysis to the overall degradation can be ignored when proposing the kinetic model. Therefore, the concentration of ethylene can be expressed as:

$$\frac{dC_{C_2H_4}}{dt} = -k_1[C_2H_4]^x \tag{6.5}$$

Equation 6.5 represents the power law, a mathematical expression used to determine the order (x) of a reaction and the rate constant (k). It is commonly employed in chemical kinetics to analyze reaction rates and understand the underlying mechanisms.

In cases where the rate of indirect photolysis becomes comparable to the rate of direct photolysis, usually at higher RH levels, and assuming that the reaction orders with respect to ethylene concentration for both pathways are equal (x = y), Eq. (6.4) can be simplified and expressed as Eq. (6.6), which is similar to Eq. (6.5):

$$\frac{dC_{C_2H_4}}{dt} = -k_{app}[C_2H_4]^n \tag{6.6}$$

where,

$$k_{app} = k_1 + k_2[OH]_{ss}^z \tag{6.7}$$

In VUV photolysis, most authors assumed 1st and 2nd order degradation kinetics (Cheng et al., 2011; J. H. Wang & Ray, 2000; Yu et al., 2012). However, in this study, a different approach is taken. Instead of assuming a specific order, such as first or second, the reaction is treated as an nth-order reaction. The assumption of an nth-order reaction allows for a more comprehensive analysis of the reaction kinetics. It provides an opportunity to uncover higher-order dependencies and acknowledges that the VUV photolysis process may exhibit more intricate kinetics beyond simple first-and-second order behavior. Thus, Eqs. (6.5) and (6.6) can be solved to obtain ethylene concentration as a function of time. The solution to the equations is as follows:

$$C_A = [C_{AO}^{-n+1} - (n-1)kt]^{\frac{1}{-n+1}} \tag{6.8}$$

Eq. (6.8) is developed based on the following conditions of operation and assumptions: (1) negligible temperature change, meaning any temperature-dependent effects on the reaction rate can be neglected, allowing for the use of a single rate constant (k) throughout the reaction; (2) negligible pressure change in the reactor, meaning the volume and gas density do not change and hence the fractional-volume change (ε) is zero; (3) the reaction order is not first-order ($n \neq 1$).

To determine the reaction order (n) and reaction rate constant (k), the experimental data was fitted to Eq. 8. The best set of model parameters was obtained by minimizing the sum of the square of the residual between experimental and predicted values using solver function in MS Excel (Office 2016, Microsoft Corporation).

6.2.4 Electrical energy per order calculation

One of the advantages of VUV irradiation at 185 nm is its energy efficiency, as it consumes a comparable amount of energy to UV irradiation at 254 nm. To optimize ethylene removal, the figure of merit known as 'electrical energy per order' (E_{EO}) is a valuable tool that helps assess the energy consumption in the VUV process. The E_{EO} provides an indirect measure of the relationship between operational costs and the utilization efficiency of electrical energy. In batch operations, the EEO can be calculated using the following formula:

$$E_{EO} = \frac{P \times t \times 10^3}{V \times log\frac{C_0}{C}} \quad (6.9)$$

Where, *P* denotes the total power input (kW), t represents the required reaction time to degrade the contaminant from C_0 to *C* (h), *V* is the reactor volume (l), and C_0 and *C* denote the initial and final concentrations (µL L^{-1}) of the contaminant, respectively.

6.2.5 Statistical analysis

Statistical analyses were carried out using STATISTICA software (version 13, StatSoft Inc. Tulsa, USA). Factorial analysis of variance (ANOVA) was carried out to test the significant effects of lamp power and exposure time on the degradation of ethylene. One-way ANOVA was used to test the effect of relative humidity on the degradation of ethylene. All treatments were carried out at least in triplicate and results were reported as mean and standard deviation. The significance differences between the mean values were tested by Duncan's multiple range tests ($p \leq 0.05$).

6.3 Results and discussion

6.3.1 Effects of lamp power

In this study, the lamp power was varied from 3W to 9W while maintaining a constant ethylene concentration of 51.6 μL L^{-1} and an RH of 20%. The concentration of ethylene at various lamp powers and its removal efficiency are depicted in Figure 6.2. It is evident that at a lamp power of 9W, ethylene was degraded entirely within 16 minutes, and this degradation time increased to 21 minutes at a lamp power of 6W, while it took 42 minutes to degrade ethylene at a lamp power of 3W completely. The conversion efficiency increased from 19.3% to 94.7% as the lamp power increased from 3W and 9W, respectively. These results are consistent with the literature, as Xie et al. (2018) reported an increase in the percentage removal of organic pollutants from 68.7% to 94.8% when the light intensity was increased by a factor of 2.

Higher lamp power leads to the generation of more photons, resulting in enhanced ethylene removal. Since the ethylene concentration remained constant, the ethylene molecules in the 9W experiment received more photons compared to those in the 3W experiment, leading to increased ethylene conversion. Additionally, increasing lamp power accelerates the rate of direct mechanisms and enhances the formation of excited oxygen-reactive species, such as $O(^1D)$, which react with water molecules to generate hydroxyl radicals. These hydroxyl radicals further facilitate the degradation of ethylene (Mabusela et al., 2022).

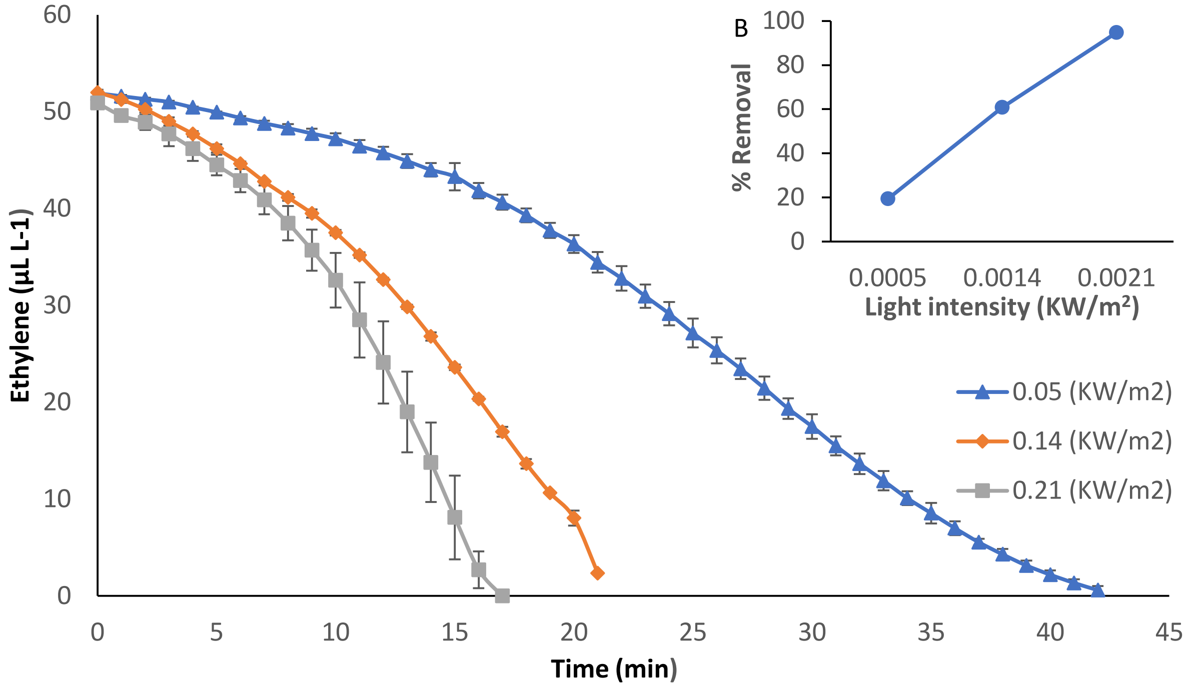


Figure 6.2: Changes in ethylene concentrations and percentage removal at different lamp powers, B: Percentage removal calculated at 15 minutes

6.3.2 Effect of relative humidity

The impact of RH on the removal efficiency of ethylene is presented in Figure 6.3. The ethylene concentration and lamp power were kept constant at 51.6 µL L^{-1} and 9W, respectively. The effect of RH humidity was studied at two levels: 20% and 80%. Increasing RH from 20% to 80% resulted in a significant increase in the removal efficiency of ethylene, from 73% to 95% respectively. As observed in Eq. 6.6, moisture in the system promotes the formation of highly reactive OH radicals that readily react with ethylene leading to enhanced degradation. Previous research by Pathak et al. (2019) demonstrated a corresponding increase in the rate of ethylene degradation with increasing RH in the VUV system. Similarly, studies on benzene removal efficiency under VUV photolysis by Huang et al. (2014) and H_2S removal efficiency by Xu et al. (2014) showed significant increases of 65% and 58%, respectively, when RH was increased. These findings highlight the favorable application of VUV photolysis in postharvest management, as many fruits and vegetables are stored in high-humidity environments.

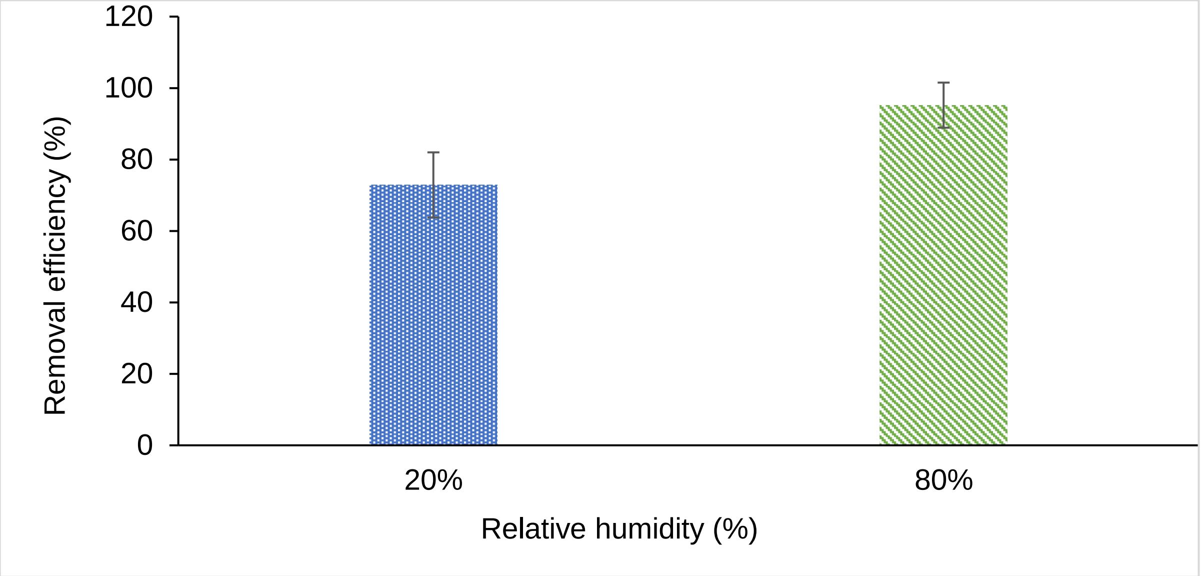


Figure 6.3: Ethylene removal efficiency at two different RH. Ethylene concentration = 51.6 μL L^{-1} and lamp power = 9W.6.3.3 Kinetic analysis of ethylene

6.3.3.1 Effect of lamp power

Table 6.1 presents the rate constants of ethylene degradation at various light intensities. A notable trend was observed: as the lamp power increased from 3W to 9W, the rate constant also significantly increased by 86%. This observation aligns with the well-known dependence of the rate constant in VUV photolysis on lamp power (Y.-T. Lin et al., 2014). Previous studies, such as Chen et al. (2004) on the VUV photolysis degradation of carbon tetrachloride and Chou & and Chang (2007), on the degradation of gaseous hexamethyldisilazane (HMDS), have reported similar trends.

Table 6.1: Kinetic parameters of ethylene degradation at different light intensities (Cao = 51.6 µL L^{-1}, RH = 20%)

Power (W)	Rate constant Zero-order (n = 0)	Fractional order (n =1.17)	R^2	RSME
3	0.497	-	98.30	0.445
6	1.55	-	97.5	1.66
9	-	3.627	99.55	1.69

The degradation of ethylene at lamp power of 3W and 6W followed zero-order kinetics. However, when the lamp power was further increased to 9W, the reaction followed a fractional order with n = 1.17. To assess the accuracies of these kinetic models, Fig. 6.4 shows the deviation between the experimental and theoretical concentrations of ethylene. The model's predictive performance was evaluated using the coefficient of determination (R^2) and Root Mean Square Error (RMSE) shown in Table 6.1. The results indicate that the kinetic models accurately predicted the experimental data well, as demonstrated by the close agreement between the model predictions and the actual measurements. This is further supported by the high R^2 values and low RMSE, indicating the reliability of the kinetic models in representing the experimental observations.

The increase in lamp power likely leads to the generation of additional highly reactive oxygen species, triggering chain reactions and affecting the reaction rate and pathway. This phenomenon likely contributed to the observed shift in the reaction order from zero-order to fractional order.

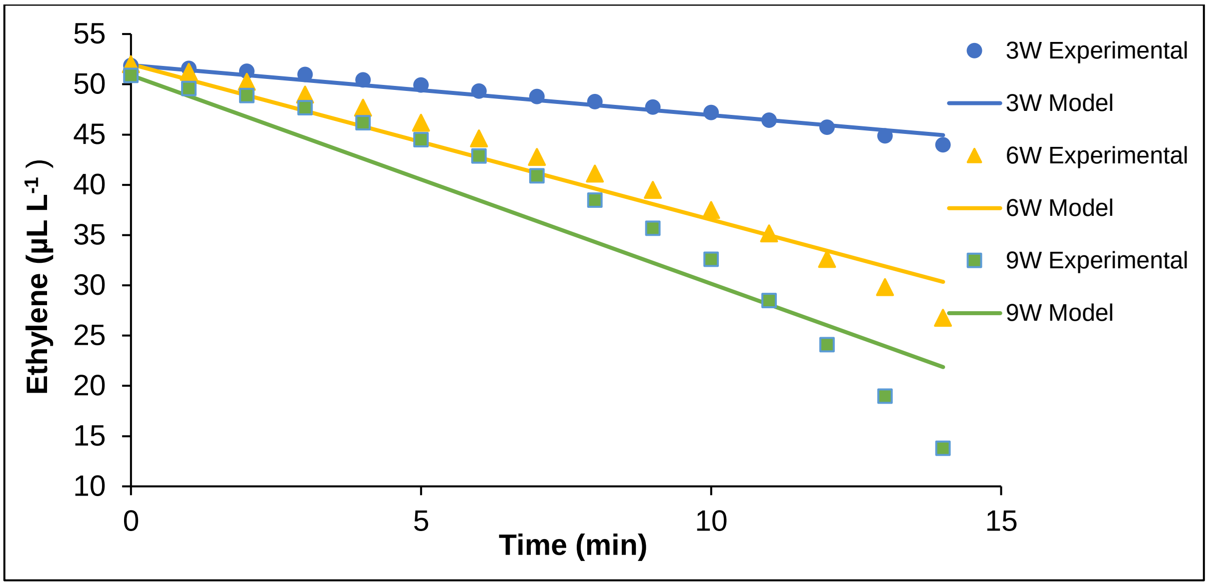


Figure 6.4: The effect of lamp power on ethylene degradation (RH = 20%, C_0 = 51.6 μL L^{-1})

6.3.3.2 Effect of relative humidity

The effect of increasing relative humidity (RH) to 80% on the rate constant and reaction order is depicted in Figure 6.5. Through calculations based on Eq. (6.8), the reaction order was determined to be 0. The experimental data were fitted to the zero-order kinetic model to validate this calculated order, as shown in Figure 6.5. The plot illustrates that the developed kinetic model effectively captured the experimental data at high RH, exhibiting a high coefficient of determination (R^2) of 0.9955. Additionally, comparing the calculated half-life using the proposed kinetic model to the measured half-life resulted in a percentage error of 1.97%, further confirming the excellent fit of the experimental data to the developed kinetic model.

The shift in the reaction order from n = 1.17 to zero-order kinetics upon increasing RH from 20% to 80% suggests a possible change in reaction mechanisms. At low RH humidity, the rate of indirect photolysis is insignificant compared to the direct photolysis rate. However, increasing RH leads to a higher generation of hydroxyl radicals, which actively participate in the further degradation of ethylene, ultimately resulting in a change in the degradation mechanism.

The reaction rate constant at 80% RH increased to 3.627 6 μL L^{-1} s^{-1}. This finding is in accordance with the results of Chou & Chang (2007), who reported a linear increase in the rate constant with RH. A similar trend was also reported in a study conducted by Yu et al. (2012), where the rate constant of dichloromethane at 80% RH was 4.9 times higher than that at 2% RH. Additionally, Feiyan et al. (2002) reported a linear relationship between the rate constant and RH.

These results indicate that increasing RH can significantly impact the reaction kinetics and rate constant during the VUV photolysis of ethylene. The observed shift in the reaction order and the increase in the rate constant suggest alterations in the underlying reaction mechanisms.

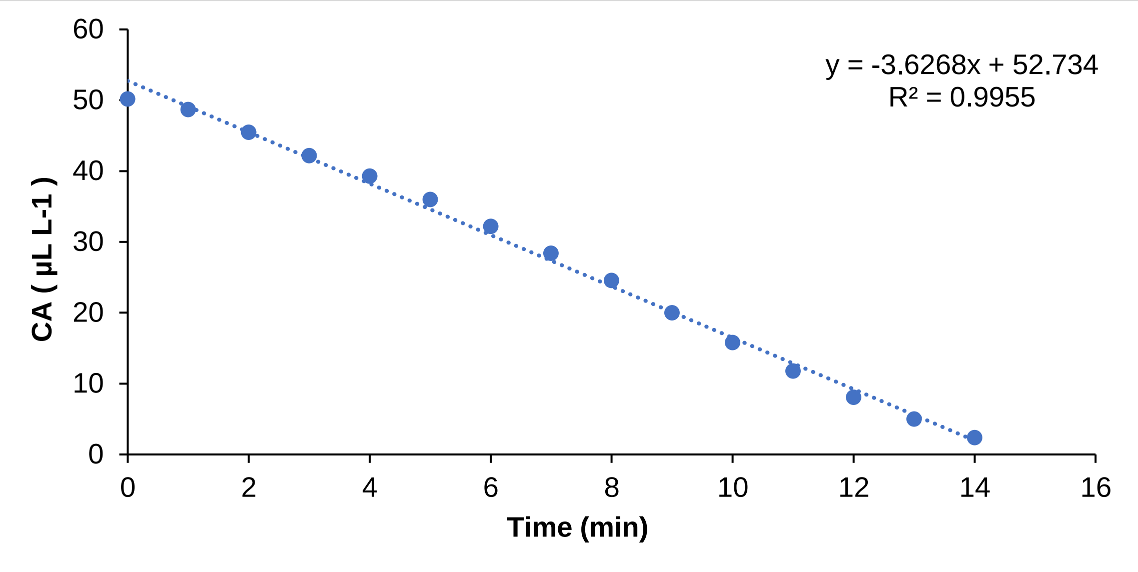


Figure 6.5: **Zero-order kinetic model. Experimental conditions: [C_2H_4] = 51.6 µL L^{-1}, 9W, RH= 80%**

6.3.4 Electrical energy per order

Energy consumption is a significant concern in the long-term operation of VUV photolysis. To optimize ethylene degradation, the figure of merit called 'electrical energy per order' (E_{EO}) is a valuable tool. In this study, E_{EO} was employed to evaluate the energy consumption efficiency of the designed VUV photolysis reactor. Table 6.2 presents the calculated E_{EO} values at different power inputs and under low and high RH conditions. The calculated E_{EO} values ranged from 3.42 to 0.61. Increasing lamp power substantially impacted the E_{EO} values, whereas the range of relative humidity (RH) studied did not have a notable impact on the E_{EO} value. Higher E_{EO} values generally indicate lower system efficiency (Chou & Chang, 2007). The VUV reactor in this study achieved the lowest E_{EO} value of 0.61 kW L^{-1} $order^{-1}$ at 9W lamp power and an RH of 80%. The VUV photolysis appears promising in terms of energy efficiency and is suitable for practical application, especially compared to other VUV reactor systems

(Chou & Chang, 2007). Although increasing the lamp power, which corresponds to higher electrical energy consumption, might not seem the best way to increase the ethylene removal rate, it should be noted that the E_{EO} values obtained in this study are below 10 kW L^{-1} $order^{-1}$, which is typically considered cost-effective for advanced oxidation processes (Andrews et al., 1995). Thus, the VUV photolysis reactor shows promise as a technology for postharvest management to reduce ethylene levels in storage and thereby ultimately minimizing food waste.

Table 6.2: **Comparison of E_{EO} values for ethylene degradation at different light intensities and RHs**

Power Input (W)	RH (%)	E_{EO}
3	20.0	3.423489
6	20.0	1.570788
	20.0	0.752732
9	80.0	0.605668

6.3.5 *Application of VUV photolysis on apple storage*

6.3.5.1 Ethylene accumulation

The negative impact of ethylene accumulation on apple fruit during storage is closely linked to fruit quality and storability, emphasizing the importance of ethylene removal to preserve fruit quality. The amount of ethylene accumulated in both control and VUV reactor-fitted chambers with apples during storage is presented in Figure 6. At the end of day 28, the concentration of ethylene detected in the VUV treatment was significantly ($p < 0.05$) lower than the control chamber, 2.5 µL L^{-1} and 138 µL L^{-1}, respectively. This observation is consistent with the literature, as Pathak et al. (2019) and Mabusela et al. (2023) demonstrated the effectiveness of VUV photolysis in maintaining lower concentration or removing ethylene under different mixed-fruit storage conditions.

Pathak et al. (2019) demonstrated in their work for a storage unit containing apples managed with VUV photolysis reactor a percentage ethylene removal of 96.28%. Similarly, the results from this study showed that the VUV photolysis reactor reduced the ethylene concentration in storage by 98%. These results strongly suggest that apples stored in the treatment chamber are expected to have a considerably longer shelf-life than those in the control chamber. The successful reduction in ethylene concentration by the VUV photolysis reactor highlights its potential for preserving fruit quality and extending the post-harvest shelf-life of apples. Through effective ethylene management, this technology offers promising solutions for mitigating fruit waste and enhancing the overall storage life of perishable produce.

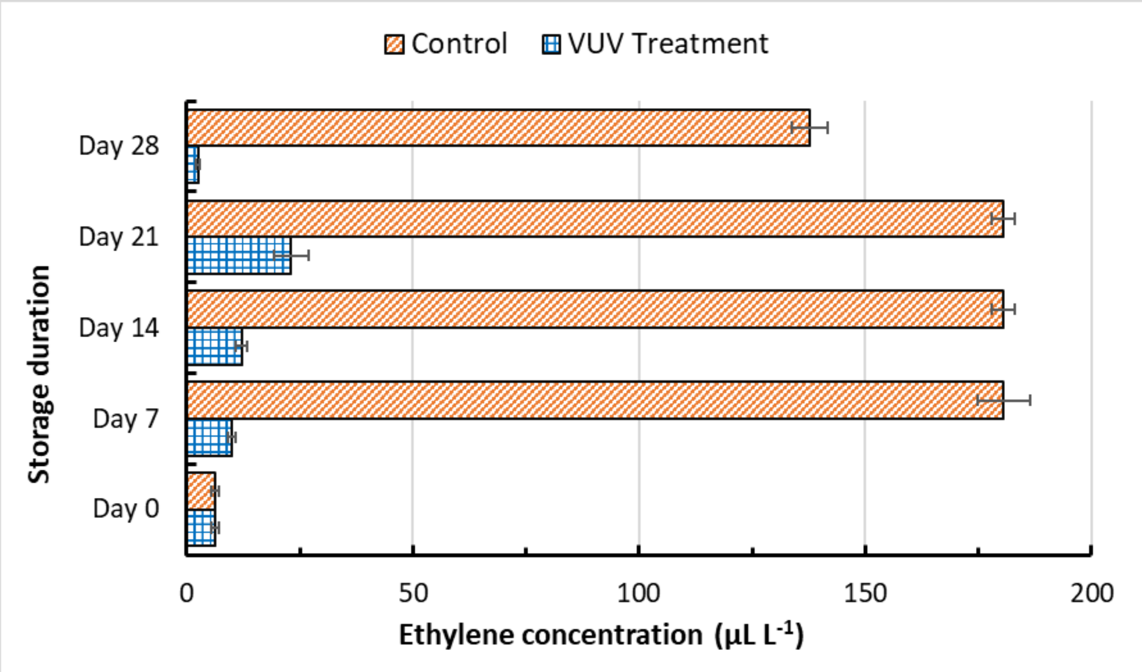


Figure 6.6: Changes in ethylene concentration inside the storage chambers containing 'Fuji' apples stored at 15℃ for 28 d

6.3.5.2 Effects on quality attributes

The results indicate that the pH value of control apples was 3.83 at the end of storage duration, slightly higher than that of treated apples. The pH vlaue of apples can be influenced by the amount of ethylene in storage (Table 6. 3). Since an increase in fruit pH is associated with fruit ripening (Alonso Salinas et al., 2022), the apples in the control were more ripe compared to the treated apples. These findings align with previous research by Sardabi et al. (2014), who reported that ethylene absorber sachets maintained lower pH values in treated apples than in untreated apples. The rise in pH can impact enzyme activities, nutrient availability, and microbial growth, potentially affecting fruit quality. These findings demonstrate the potential of the developed system in effectively delaying fruit ripening by preventing the rise in pH and minimizing weight loss, ultimately reducing vulnerability to decay.

Table 6.3: **Changes in chemical attributes of 'Fuji' apple fruit under different storages at 15 °C for 28 days**

Storage days	TSS (%)		TTA (g/100mL)		TSS/TA		pH	
	Control	**Treatment**	**Control**	**Treatment**	**Control**	**Treatment**	**Control**	**Treatment**
0	12.8 ± 0.14A	12.8 ± 0.14A	0.37 ± 0.01A	0.37 ± 0.01A	34.59 ± 1.15E	34.59 ± 1.15E	3.57 ± 0.05C	3.57 ± 0.05C
7	12.6 ± 0.14A	12.7 ± 0.78A	0.36 ± 0.08AB	0.41 ± 0.02A	35.29 ± 0.15E	31.33 ± 0.75F	3.53 ± 0.02C	3.53 ± 0.01C
14	12.5 ± 0.65AB	12.2 ± 0.57AB	0.35 ± 0.06A	0.31 ± 0.04B	35.67 ± 1.05E	39.84 ± 0.45D	3.82 ± 0.01A	3.71 ± 0.05B
21	12.5 ± 0.06B	11.2 ± 0.11D	0.28 ± 0.003B	0.27 ± 0.03BC	43.72± 0.65B	41.90 ± 1.15BC	3.84 ± 0.04A	3.74 ± 0.02B
28	12.5 ± 0.46AB	11.9 ± 0.17C	0.25 ± 0.01C	0.29 ± 0.004B	49.14 ± 1.45A	40.61 ± 0.33C	3.88 ± 0.01A	3.73 ± 0.00B

Different upper-case letters indicate significant differences at $p < 0.05$.

Comparing the effects of the treatment on the biochemical qualities of the ‘Fuji’ apple, significant differences were observed between treated and control samples. For instance, the TSS value reduced from the initial value of 12.8 ± 0.14 to 11.9 ± 0.17, for 12.5 ± 0.46 and 11.9 ± 0.17, for control and VUV treated samples, respectively, at day 28, demonstrated the highest ($p< 0.05$) reduction under-treated fruit. As presented in Table 6.3, the TA value significantly reduced in both conditions, where the highest reduction of 28% was observed for control fruits, whereas TA value of ‘Fuji’ apples declined by 21% for VUV treatment fruit by the end of storage.

The TSS/TA ratio is commonly used as a good indicator of maturity in various types of fruit, and is a key characteristic of juice quality that impacts consumer acceptability and preferences (Kim et al., 2023; Taiti et al., 2023). Generally, a higher TSS/TA ratio is associated with rapid ripening (Khedr & Al-Khayri, 2023). In this study, a linear increase in TSS/TA was observed during the storage period. However, the TSS/TA ratio increased with the increase in storage time from the initial value of 34.59 ± 1.15 to 49.14 ± 1.45 and 40.61 ± 0.33 for control and VUV treated after the 28-day storage duration. The gradual increase in the TSS/TA ratio in the treated apples could be attributed to the effectiveness of the VUV reactor in removing ethylene from within the chamber.

6.4 Conclusion

This study investigated the degradation kinetics of ethylene using a VUV photolysis reactor under varying lamp power and relative humidity (RH) conditions. The study assumed an nth-order to determine the reaction order, allowing for a flexible kinetics analysis. At low lamp power, the degradation of ethylene followed zero-order kinetics. However, as the lamp power increased, the reaction order shifted to a fractional order of 1.71. This observation indicated that the degradation process becomes more complex and involves higher-order dependencies as the lamp power rises. Furthermore, the rate constant displayed a linear relationship with lamp power, showing that the rate of ethylene degradation increases proportionally with the lamp power. The study also investigated the impact of increasing RH to 80% on the reaction kinetics. It was found that the rate constant increased by 86% at this higher RH level. Moreover, the reaction order decreased from 1.17 to 0, indicating a change in degradation mechanisms. The developed kinetic models successfully fitted the experimental data, demonstrating a strong agreement between the model predictions and actual measurements. This confirms the proposed models' accuracy and reliability in representing ethylene's degradation kinetics under varying conditions. Economic feasibility assessment using a figure of merit revealed favorable E_{EO} values within acceptable limits, indicating the energy efficiency of the VUV photolysis reactor. Additionally, storage application experiments confirmed the reactor's capability to maintain lower ethylene levels. Compared with the control, the VUV system was significantly effective in maintaining the fruit quality and had a significant impact on the TSS/TA ratio and pH during the storage period. Overall, this study demonstrates the effectiveness and promise of VUV photolysis as a technology for ethylene management in fruit storage. It offers the potential to maintain fruit quality and extend its marketability. Further research and system optimization is recommended to enhance this technology's efficiency and practical implementation in postharvest fruit management. Furthermore, this study emphasizes the importance of considering these influential factors when designing and interpreting VUV photolysis reactions, ultimately advancing our knowledge in environmental and chemical engineering applications.

6.5 Summary

This chapter addressed the main objective of the thesis, which was the development of a mathematical kinetic model for ethylene degradation using a VUV photolysis reactor. This research adopts an *n*-th order reaction kinetics approach, unlike other studies found in the literature that use fixed-order models. The n-th order approach accounts for the variable reaction mechanisms under differing conditions, allowing for the possibility of fractional orders. Kinetic experiments reveal the significant impact of lamp power and humidity on ethylene degradation, resulting in distinct kinetic models at varying lamp powers. These models accurately predict experimental outcomes. Moreover, the chapter evaluates the economic viability of the VUV photolysis system, demonstrating its energy efficiency. The proposed kinetic model has valuable implications for designing VUV photolysis reactors, offering superior accuracy compared to the commonly used pseudo-first and second-order models. In conclusion, this chapter provides an essential engineering foundation for the development of mathematical models crucial for scaling up the photolysis reactor effectively.

References

Alexander, L., & Grierson, D. (2002). Ethylene biosynthesis and action in tomato: A model for climateric fruit ripening. *Journal of Experimental Botany*, *53*, 2039–2055. https://doi.org/10.1093/jxb/erf072

Alonso Salinas, R., Motos, J. R., Núñez-Delicado, E., Gabaldon, J., & López-Miranda, S. (2022). Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures. *Agronomy*, *12*, 616. https://doi.org/10.3390/agronomy12030616

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., Ventura-Sobrevilla, J. M., & Martínez-Hernández, G. B. (2018). Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food and Bioprocess Technology*, *11*(3), 511–525. https://doi.org/10.1007/s11947-018-2076-7

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Miranda-Molina, F. D., & Artés-Hernández, F. (2020). Postharvest quality retention of apricots by using a novel sepiolite–loaded potassium permanganate ethylene scavenger. *Postharvest Biology and Technology*, *160*, 111061. https://doi.org/https://doi.org/10.1016/j.postharvbio.2019.111061

Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R., & Anderson, W. A. (1995). UV oxidation for drinking waterfeasibility studies for addressing specific water quality issues. *Proceedings of the AWWA WQTC, New Orleans, LA*, 18811898.

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018a). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1). https://doi.org/10.1088/1755-1315/141/1/012003

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018b). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1), 012003. https://doi.org/10.1088/1755-1315/141/1/012003

Asili, V. (2018). *Mechanistic Model for Ultraviolet Degradation of Light Hydrocarbons in Waste Gas*. University of Calgary.

Asili, V., & De Visscher, A. (2018). Modelling methane and ethane photolysis in waste gas: Optimization of reaction networks. *The Canadian Journal of Chemical Engineering*, *96*(8), 1674–1683. https://doi.org/https://doi.org/10.1002/cjce.23124

Bagheri, M., & Mohseni, M. (2014). Computational fluid dynamics (CFD) modeling of VUV/UV photoreactors for water treatment. *Chemical Engineering Journal*, *256*, 51–60. https://doi.org/https://doi.org/10.1016/j.cej.2014.06.068

Basso, A., de Fátima Peralta Muniz Moreira, R., & José, H. J. (2018). Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening. *Journal of Photochemistry and Photobiology A: Chemistry*, *367*, 294–301. https://doi.org/10.1016/j.jphotochem.2018.08.027

Bu, J., Yu, Y., Aisikaer, G., & Ying, T. (2013). Postharvest UV-C irradiation inhibits the production of ethylene and the activity of cell wall-degrading enzymes during softening of tomato (Lycopersicon esculentum L.) fruit. *Postharvest Biology and Technology*, *86*, 337–345. https://doi.org/10.1016/j.postharvbio.2013.07.026

Chang, K.-L., Sekiguchi, K., Wang, Q., & Zhao, F. (2013). Removal of Ethylene and Secondary Organic Aerosols Using UV-C-254 (+) (185) (nm) with TiO2 Catalyst. *Aerosol and Air Quality Research*, *13*, 618–626. https://doi.org/10.4209/aaqr.2012.07.0195

Chen, F., Yang, Q., Pehkonen, S. O., & Ray, M. B. (2004). Modeling of Gas-Phase Photodegradation of Chloroform and Carbon Tetrachloride. *Journal of the Air & Waste Management Association*, *54*(10), 1281–1292. https://doi.org/10.1080/10473289.2004.10470991

Chen, L., Xie, X., Song, X., Luo, S., Ye, S., & Situ, W. (2021). Photocatalytic degradation of ethylene in cold storage using the nanocomposite photocatalyst MIL101(Fe)-TiO2-rGO. *Chemical Engineering Journal*, *424*, 130407. https://doi.org/https://doi.org/10.1016/j.cej.2021.130407

Cheng, Z.-W., Jiang, Y.-F., Zhang, L.-L., Chen, J.-M., & Wei, Y.-Y. (2011). Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. *Separation and Purification Technology*, *77*(1), 26–32. https://doi.org/https://doi.org/10.1016/j.seppur.2010.11.014

Chou, M.-S., & Chang, K.-L. (2007). UV/ozone degradation of gaseous hexamethyldisilazane (HMDS). *Chemosphere*, *69*(5), 697–704. https://doi.org/https://doi.org/10.1016/j.chemosphere.2007.05.040

Da Silva, J. C. G., Alves, J. L. F., Mumbach, G. D., & Di Domenico, M. (2023). Photocatalytic degradation of ethylene in tubular microreactor coated with thin-film of TiO2: Mathematical modeling with experimental validation and geometry analysis using computational fluid dynamics simulations. *Chemical Engineering Research and Design*, *196*, 101–117. https://doi.org/https://doi.org/10.1016/j.cherd.2023.06.036

De Bruijn, J., Gómez, A. E., Melín, P., Loyola, C., Solar, V. A., & Valdés, H. (2019). Effect of doping natural zeolite with copper and zinc cations on ethylene removal and postharvest tomato fruit quality. *Chemical Engineering Transactions*, *75*, 265–270. https://doi.org/10.3303/CET1975045

de Chiara, M. L. V., Pal, S., Licciulli, A., Amodio, M. L., & Colelli, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO2/SiO2 nanocomposites: Effects on the ripening of mature green tomatoes. *Biosystems Engineering*, *132*, 61–70. https://doi.org/10.1016/j.biosystemseng.2015.02.008

Department of Agriculture, F. and F. (2022). *A PROFILE OF THE SOUTH AFRICAN APPLE MARKET VALUE CHAIN 2020*. www.dalrrd.gov.za

Du, L., Song, J., Forney, C., Palmer, L. C., Fillmore, S., & Zhang, Z. (2016). Proteome changes in banana fruit peel tissue in response to ethylene and high-temperature treatments. *Horticulture Research*, *3*. https://doi.org/10.1038/hortres.2016.12

Duca, C. (2015). *Effect of water matrix on Vacuum UV process for the removal of organic micropollutants in surface water*. The University of British Columbia.

Duque, L. F., Amador, M. V., Guzmán, M., Asensio, C., & Valenzuela, J. L. (2021). Development of a new essential oil-based technology to maintain fruit quality in tomato. *Horticulturae*, *7*(9), 303.

Emadpour, M., Ghareyazie, B., Rezaei kalaj, Y., Entesari, M., & Bouzari, N. (2015). *Effect of the Potassium Permanganate Coated Zeolite Nanoparticles on the Quality Characteristic and Shelf Life of Peach and Nectarine*.

Feiyan, C., Pehkonen, S. O., & Ray, M. B. (2002). Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. *Water Research*, *36*(17), 4203–4214. https://doi.org/https://doi.org/10.1016/S0043-1354(02)00140-9

Fonseca, J. de M., Pabón, N. Y. L., Nandi, L. G., Valencia, G. A., Moreira, R. de F. P. M., & Monteiro, A. R. (2021). Gelatin-TiO2-coated expanded polyethylene foam nets as ethylene scavengers for fruit postharvest application. *Postharvest Biology and Technology*, *180*, 111602. https://doi.org/https://doi.org/10.1016/j.postharvbio.2021.111602

Hooijberg, E. H., Miller, M., Cray, C., Buss, P., Steenkamp, G., & Goddard, A. (2018). Serum protein electrophoresis in healthy and injured southern white rhinoceros (Ceratotherium simum simum). *PLoS ONE*, *13*(7). https://doi.org/10.1371/journal.pone.0200347

Hrazdina, G., Kiss, E., Galli, Z., RosenField, C., Norelli, J. L., & Aldwinckle, H. S. (2003). DOWN REGULATION OF ETHYLENE PRODUCTION IN “ROYAL GALA” APPLES. *Acta Horticulturae*, *628*, 239–251. https://doi.org/10.17660/ActaHortic.2003.628.29

Huang, H., Huang, H., Zhang, L., Hu, P., Xu, Y., Ye, X., Liang, X., Chen, J., & Ji, M. (2014). Photooxidation of Gaseous Benzene by 185 nm VUV Irradiation. *Environmental Engineering Science*, *31*(8), 481–486. https://doi.org/10.1089/ees.2014.0100

Huang, H., Lu, H., Huang, H., Wang, L., Zhang, J., & Leung, D. Y. C. (2016). Recent development of VUV-based processes for air pollutant degradation. *Frontiers in Environmental Science*, *4*, 17.

Kader, A. A. (1985). Ethylene-induced Senescence and Physiological Disorders in Harvested Horticultural Crops. *HortScience*, *20*(1), 54–57. https://doi.org/10.21273/HORTSCI.20.1.54

Kang, I.-S., Xi, J., & Hu, H.-Y. (2018). Photolysis and photooxidation of typical gaseous VOCs by UV Irradiation: Removal performance and mechanisms. *Frontiers of Environmental Science & Engineering*, *12*, 1–14.

Keller, N., Ducamp, M.-N., Robert, D., & Keller, V. (2013). Ethylene removal and fresh product storage: a challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation. *Chemical Reviews*, *113*(7), 5029–5070.

Khedr, E., & Al-Khayri, J. (2023). Synergistic Effects of Tragacanth and Anti-ethylene Treatments on Postharvest Quality Maintenance of Mango (Mangifera indica L.). *Plants*, *12*, 1887. https://doi.org/10.3390/plants12091887

Kim, K., Chun, I.-J., Suh, J. H., & Sung, J. (2023). Relationships between sensory properties and metabolomic profiles of different apple cultivars. *Food Chemistry: X*, *18*, 100641. https://doi.org/https://doi.org/10.1016/j.fochx.2023.100641

Li, J., Sun, Q., Sun, Y., Chen, B., Wu, X., & Le, T. (2019). Improvement of banana postharvest quality using a novel soybean protein isolate/cinnamaldehyde/zinc oxide bionanocomposite coating strategy. *Scientia Horticulturae*, *258*, 108786. https://doi.org/https://doi.org/10.1016/j.scienta.2019.108786

Li, L., Ban, Z., Limwachiranon, J., & Luo, Z. (2017). Proteomic Studies on Fruit Ripening and Senescence. *Critical Reviews in Plant Sciences*, *36*(2), 116–127. https://doi.org/10.1080/07352689.2017.1355173

Li, M., Li, D., Feng, F., Zhang, S., Ma, F., & Cheng, L. (2016). Proteomic analysis reveals dynamic regulation of fruit development and sugar and acid accumulation in apple. *Journal of Experimental Botany*, *67*(17), 5145–5157. https://doi.org/10.1093/jxb/erw277

Liang, P., de Aragão, E. V. F., Giani, L., Mancini, L., Pannacci, G., Marchione, D., Vanuzzo, G., Faginas-Lago, N., Rosi, M., & Skouteris, D. (2023). OH (2Π)+ C2H4 reaction: a combined crossed molecular beam and theoretical study. *The Journal of Physical Chemistry A*, *127*(21), 4609–4623.

Lien, N., Horváth, V., Mai, D., Hitka, G., Zsom, T., & Kókai, Z. (2018). Effect of 1-MCP, ethylene absorber and ozone on melon quality during storage. *Progress in Agricultural Engineering Sciences*, *14*, 101–110. https://doi.org/10.1556/446.14.2018.S1.10

Lin, S., Miao, Y., Huang, H., Zhang, Y., Huang, L., & Cao, J. (2022). Arabinogalactan Proteins: Focus on the Role in Cellulose Synthesis and Deposition during Plant Cell Wall Biogenesis. *International Journal of Molecular Sciences*, *23*, 6578. https://doi.org/10.3390/ijms23126578

Lin, Y.-T., Weng, C.-H., Hsu, H.-J., Huang, J.-W., Srivastav, A. L., & Shiesh, C.-C. (2014). Effect of oxygen, moisture, and temperature on the photo oxidation of ethylene on N-doped TiO2 catalyst. *Separation and Purification Technology*, *134*, 117–125. https://doi.org/https://doi.org/10.1016/j.seppur.2014.07.039

Liu, A., Mulac, W. A., & Jonah, C. D. (1988). Kinetic isotope effects in the gas-phase reaction of hydroxyl radicals with ethylene in the temperature range 343-1173 K and 1-atm pressure. *The Journal of Physical Chemistry*, *92*(13), 3828–3833.

Mabusela, B., Belay, Z., Godongwana, B., & Caleb, O. (2023). Application of VUV photolysis reactor for shelf-life extension and prediction of apple fruit. *[Status: Submitted]*.

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023a). Application of vacuum ultraviolet photolysis reactor and loss of firmness prediction for stored ‘Fuji’ apples. In *Acta Horticulturae* (Issue 1382). https://doi.org/10.17660/ActaHortic.2023.1382.2

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023b). Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics and removal in mixed-fruit storage, and direct exposure to ‘Fuji’ apples during storage. *Journal of Food Science and Technology*. https://doi.org/10.1007/s13197-023-05775-3

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, & Caleb, O. J. (2022). Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of

Fruit and Vegetables Along the Value Chains: a Review. *Food and Bioprocess Technology*, *15*(1), 28–46. https://doi.org/10.1007/s11947-021-02703-1

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, Mathabe, P. M. K., & Caleb, O. J. (2021). Trends in ethylene management strategies: towards mitigating postharvest losses along the South African value chain of fresh produce – a review. *South African Journal of Plant and Soil*, *38*(5), 347–360. https://doi.org/10.1080/02571862.2021.1938260

Mahmoudkhani, F., Rezaei, M., Asili, V., Atyabi, M., Vaisman, E., Langford, C., & De Visscher, A. (2016). Benzene degradation in waste gas by photolysis and photolysis-ozonation: experiments and modeling. *Frontiers of Environmental Science & Engineering*, *10*, 1–10. https://doi.org/10.1007/s11783-016-0876-4

Marhavý, P., Kurenda, A., Siddique, S., Dénervaud Tendon, V., Zhou, F., Holbein, J., Hasan, M. S., Grundler, F. M. W., Farmer, E. E., & Geldner, N. (2019). Single-cell damage elicits regional, nematode-restricting ethylene responses in roots. *The EMBO Journal*, *38*(10), e100972. https://doi.org/https://doi.org/10.15252/embj.2018100972

Namrata Pathak. (2019). *Photocatalysis and vacuum ultraviolet light photolysis as ethylene removal techniques for potential application in fruit storage*. Technical University Berlin.

Palou, L., Crisosto, C. H., Garner, D., & Basinal, L. M. (2003). Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes. *Postharvest Biology and Technology*, *27*(3), 243–254.

Pathak, N., Caleb, O. J., Geyer, M., Herppich, W. B., Rauh, C., & Mahajan, P. V. (2017). Photocatalytic and photochemical oxidation of ethylene: Potential for storage of fresh produce—A review. *Food and Bioprocess Technology*, *10*, 982–1001.

Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2017). Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage. *Biosystems Engineering*, *159*, 33–45. https://doi.org/https://doi.org/10.1016/j.biosystemseng.2017.04.008

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. https://doi.org/https://doi.org/10.1016/j.postharvbio.2018.09.006

Potuschak, T., Lechner, E., Parmentier, Y., Yanagisawa, S., Grava, S., Koncz, C., & Genschik, P. (2003). EIN3-Dependent Regulation of Plant Ethylene Hormone Signaling by Two Arabidopsis F Box Proteins: EBF1 and EBF2. *Cell*, *115*(6), 679–689. https://doi.org/10.1016/S0092-8674(03)00968-1

Sardabi, F., Mohtadinia, J., Shavakhi, F., & Jafari, A. A. (2014). The Effects of 1-Methylcyclopropen (1-MCP) and Potassium Permanganate Coated Zeolite Nanoparticles on Shelf life Extension and Quality Loss of Golden Delicious Apples. *Journal of Food Processing and Preservation*, *38*. https://doi.org/10.1111/jfpp.12197

Schaffer, R. J., Friel, E. N., Souleyre, E. J. F., Bolitho, K., Thodey, K., Ledger, S., Bowen, J. H., Ma, J. H., Nain, B., Cohen, D., Gleave, A. P., Crowhurst, R. N., Janssen, B. J., Yao, J. L., & Newcomb, R. D. (2007). A genomics approach reveals that aroma production in apple is controlled by ethylene predominantly at the final step in each biosynthetic pathway. *Plant Physiology*, *144*(4), 1899–1912. https://doi.org/10.1104/pp.106.093765

Shenoy, S., Pathak, N., Molins, A., Toncheva, A., Schouw, T., Hemberg, A., Laoutid, F., & Mahajan, P. V. (2022). Impact of relative humidity on ethylene removal kinetics of different scavenging materials for fresh produce industry. *Postharvest Biology and Technology*, *188*, 111881. https://doi.org/https://doi.org/10.1016/j.postharvbio.2022.111881

Shi, Y., Jiang, L., Zhang, L., Kang, R., & Yu, Z. (2014). Dynamic changes in proteins during apple (Malus x domestica) fruit ripening and storage. *Horticulture Research*, *1*. https://doi.org/10.1038/hortres.2014.6

Shinga, M. H., & Fawole, O. A. (2023). Opuntia ficus indica mucilage coatings regulate cell wall softening enzymes and delay the ripening of banana fruit stored at retail conditions. *International Journal of Biological Macromolecules*, *245*, 125550. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2023.125550

Smilanick, J. L. (2003). Use of ozone in storage and packing facilities. *Washington Tree Fruit Postharvest Conference*, 1–10.

Sun, X., Li, C., Yu, B., Wang, J., & Wang, W. (2023). Removal of gaseous volatile organic compounds via vacuum ultraviolet photodegradation: Review and prospect. *Journal of Environmental Sciences*, *125*, 427–442. https://doi.org/https://doi.org/10.1016/j.jes.2022.01.020

Suttikul, T., Nuchdang, S., Rattanaphra, D., Kingkam, W., Moonsrikaew, W., Photsathain, T., & Phalakornkule, C. (2022). Plasma-assisted ethylene removal using silica gel and zeolite in AC dielectric barrier discharge. *Chemical Engineering and Processing - Process Intensification*, *179*, 109066. https://doi.org/https://doi.org/10.1016/j.cep.2022.109066

Taiti, C., Vivaldo, G., Masi, E., Giordani, E., & Nencetti, V. (2023). Postharvest monitoring and consumer choice on traditional and modern apricot cultivars. *European Food Research and Technology*, *249*. https://doi.org/10.1007/s00217-023-04311-z

Wang, J. H., & Ray, M. B. (2000). Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. *Separation and Purification Technology*, *19*(1), 11–20. https://doi.org/https://doi.org/10.1016/S1383-5866(99)00078-7

Wang, J., Yang, C., Wang, C., Han, W., & Zhu, W. (2014). Photolytic and photocatalytic degradation of micro pollutants in a tubular reactor and the reaction kinetic models. *Separation and Purification Technology*, *122*, 105–111. https://doi.org/https://doi.org/10.1016/j.seppur.2013.11.011

Wang, W., Vignani, R., Scali, M., & Cresti, M. (2006). A universal and rapid protocol for protein extraction from recalcitrant plant tissues for protomic analysis. *Electrophoresis*, *27*, 2782–2786. https://doi.org/10.1002/elps.200500722

Welty, J., Rorrer, G. L., & Foster, D. G. (2014). *Fundamentals of Momentum, Heat and Mass Transfer*. John Wiley & Sons.

Xiao, F., Sun, X., Li, Z., & Li, X. (2020). Theoretical Study of Radical–Molecule Reactions with Negative Activation Energies in Combustion: Hydroxyl Radical Addition to Alkenes. *ACS Omega*, *5*(22), 12777–12788.

Xie, P., Yue, S., Ding, J., Wan, Y., Li, X., Ma, J., & Wang, Z. (2018). Degradation of organic pollutants by Vacuum-Ultraviolet (VUV): Kinetic model and efficiency. *Water Research*, *133*, 69–78. https://doi.org/https://doi.org/10.1016/j.watres.2018.01.019

Xu, J., Li, C., Liu, P., He, D., Wang, J., & Zhang, Q. (2014). Photolysis of low concentration H2S under UV/VUV irradiation emitted from high frequency discharge electrodeless lamps. *Chemosphere*, *109*, 202–207. https://doi.org/https://doi.org/10.1016/j.chemosphere.2014.01.065

Yu, J., Cai, W., Chen, J., Feng, L., Jiang, Y., & Cheng, Z. (2012). Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. *Journal of Environmental Sciences*, *24*(10), 1777–1784. https://doi.org/https://doi.org/10.1016/S1001-0742(11)61021-8

Zhang, Z., Jiang, S., Wang, N., Li, M., Ji, X., Sun, S., Liu, J., Wang, D., Xu, H., Qi, S., Wu, S., Fei, Z., Feng, S., & Chen, X. (2015). Identification of differentially expressed genes associated with Apple fruit ripening and softening by suppression subtractive hybridization. *PLoS ONE*, *10*(12). https://doi.org/10.1371/journal.pone.0146061

Zheng, Q., Song, J., Campbell-Palmer, L., Thompson, K., Li, L., Walker, B., Cui, Y., & Li, X. (2013). A proteomic investigation of apple fruit during ripening and in response to ethylene treatment. *Journal of Proteomics*, *93*, 276–294. https://doi.org/https://doi.org/10.1016/j.jprot.2013.02.006

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019a). Electrospun nanofibers containing TiO 2 for the photocatalytic degradation of ethylene and delaying postharvest ripening of bananas. *Food and Bioprocess Technology*, *12*, 281–287.

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019b). Electrospun Nanofibers Containing TiO2 for the Photocatalytic Degradation of Ethylene and Delaying Postharvest Ripening of Bananas. *Food and Bioprocess Technology*, *12*(2), 281–287. https://doi.org/10.1007/s11947-018-2207-1

CHAPTER SEVEN:

MODEL DEVELOPMENT AND OPTIMISATION

Mabusela, B. P., Godongwana, B., Belay, Z. A., Mathabe, P.M.K & Caleb, O. J. (2024). Ethylene degradation via ultraviolet photolysis: Up-scaling reactor design and optimizing operating parameters. **Submitted to Food and Bioproducts Processing**

7. MODEL DEVELOPMENT AND OPTIMISATION

Abstract

This work aimed to develop a mathematical model and optimize a VUV photolysis reactor for ethylene's efficient degradation to improve the fruit's shelf life. This was achieved by investigating the photolytic degradation of ethylene through the development of mathematical mass and energy balance models to simulate ethylene concentration and temperature variation inside a photoreactor. The influence of light intensity and relative humidity (RH) on the photodegradation of ethylene was investigated to understand their impact. The results indicated that the degradation of ethylene increased with an increase in light intensity. In addition, high relative humidity favoured the degradation of ethylene. The developed mass balance model could predict the experimental concentrations with R^2 values above 0.9. Although the energy balance model underestimates the temperature inside the reactor, it accurately captures the overall trend of temperature increase, indicating the feasibility of the model. This study offers a framework for optimizing VUV photolysis reactor design and operation. It provides a sound basis for the design of large-scale reactors for possible applications in real storage environments.

Keywords: VUV photolysis, ethylene removal, postharvest storage

7.1 Introduction

Ethylene is a plant hormone that plays a crucial role in the ripening of fruits and the senescence of flowers (Basso et al., 2018). However, its accumulation can lead to premature spoilage and significant post-harvest losses in the agricultural industry. Ethylene accelerates ripening and senescence in fruits and vegetables, making its removal essential to prolong shelf life and maintaining quality. Traditional methods for ethylene removal, such as chemical scrubbers and adsorption techniques, often face limitations in efficiency and environmental impact (De Bruijn et al., 2019; Emadpour et al., 2015; Sardabi et al., 2014). Therefore, there is a growing need for innovative and sustainable approaches to effectively remove ethylene from storage environments.

Vacuum Ultraviolet (VUV) photolysis has emerged as a promising technology due to its ability to produce highly reactive hydroxyl radicals, which can effectively oxidize ethylene. VUV photolysis involves the use of high-energy photons in the VUV range (wavelengths below 200 nm) to break down ethylene molecules into less reactive and harmless by-products (Huang et al., 2016). VUV photolysis offers several advantages over conventional methods, including the potential for high efficiency (Pathak et al., 2019) and minimal chemical usage. These benefits make VUV photolysis an innovative solution to the challenges associated with ethylene removal.

The application of VUV photolysis for ethylene removal in fruit storage has been explored and has yielded satisfactory results (Mabusela et al., 2023a; Mabusela et al., 2023b; Pathak et al.; 2017; Pathak et al.; 2019). Currently, most of the work on the application of VUV photolysis is still at the laboratory scale, with commercial-scale application missing. This is due to a lack of adequate mathematical models for scale-up. Mathematical modelling is a critical tool in reactor design, enabling the optimization of operational parameters, prediction of performance under various conditions, and scaling up from laboratory to commercial applications (Da Silva et al., 2023).

According to Bagheri & Mohseni (2014), the complete modelling of the VUV process involves the simultaneous resolution of the transfer equations of mass and radiative energy (for VUV radiation). Consequently, several researchers have developed mathematical models for kinetics and radiation, which were coupled with material balances to predict the degradation rate. For instance, Chen et al. (2004) investigated the photodegradation of chloroform and carbon tetrachloride, developing a mathematical model for light, which was incorporated into the kinetic model. Mahmoudkhani et al. (2016) developed a comprehensive mechanistic model to describe the degradation of benzene gas by photolysis. The model took into account the light field model which was combined with the mass balance. Asili & De Visscher (2014) also developed a mathematical model for the photolysis of H_2S which considered material balance and flow pattern. They also developed a model for the photolysis degradation of methane and ethane, which considered the kinetics and radiation (Asili & De Visscher 2018).

While there is extensive literature on the mathematical modelling of VUV photolysis for predicting degradation efficiency, there remains a lack of mathematical models of energy balance that address temperature variation in the reactor caused by the heat emitted by the VUV lamps and chemical reactions. The temperature rise due to this heat can significantly affect the degradation efficiency. For example, Pathak et al. (2017) reported a 9% deviation between experimental and theoretical percentage removal of ethylene by VUV photolysis and attributed this deviation to the fluctuations in temperature inside the reactor. Additionally, the increase in temperature due to heat from the VUV lamp might reduce the concentration of hydroxyl radicals, which are crucial for degradation in VUV photolysis, resulting in a lower percentage removal than predicted. Thus, modelling the temperature variation in a VUV photolysis reactor is crucial for optimisation and design purposes.

The aim of this study is to develop a mathematical model for predicting ethylene concentrations and temperature profiles within the VUV reactor. By advancing the understanding of ethylene photodegradation through VUV photolysis, this study seeks to contribute to the development of more efficient and sustainable ethylene removal technology. Sensitivity analyses were conducted using different values of model parameters to determine the significance of each parameter on the degradation efficiency of ethylene.

7.2 Methods

7.2.1 Experimental apparatus

The experiments were conducted in a custom-made cylindrical photoreactor as shown in Fig. 7.1. The dimensions of the reactor are given in Table 7.1. Three VUV lamps (Dinies, Villingendorf, Germany), each with a power output of 3 W, with major radiation at 254 nm and minor radiation at 185 nm, were placed at the center of the reactor at an equal distance. The radiation intensity on the surface of the reactor was measured with a Fisherbrand Traceable Light Meter (Thermo Fisher Scientific, Waltham, MA, USA). The reactor lid was constructed from borosilicate glass and featured openings for VUV lamp fittings and a temperature and humidity sensor. The desired lamp power was achieved by manipulating the lamp combination. The moisture in the reactor was controlled by bubbling dry air through a deionized water column. A hygrometer coupled with a temperature and humidity sensor (Digital thermometer, REPTIZOO, Miami, USA) was used to measure the humidity and the temperature, respectively.

Table 7.1: Reactor dimensions and specifications for experimental setup.

Operational condition	Dimension
Reactor length (cm)	22
Reactor radius (cm)	6
VUV lamp electrical power (W)	3
Irradiation power output	Major @254 nm and minor @185 nm

The reactor was first purged with air for 20 min to remove any impurities from previous experiments. Subsequently, ethylene from an ethylene standard (100 ppm) was allowed to fill the reactor until the desired concentration (51 ppm) was achieved. The VUV lamps were switched on when the ethylene concentration in the reactor was stable.

Regular ethylene samples were collected from the reactor using an ICA 56-ethylene analyzer (Fricaval 89 S.L, Spain). This analyzer incorporated a built-in pump, which returned the gas sample to the reactor to maintain a constant gas volume.

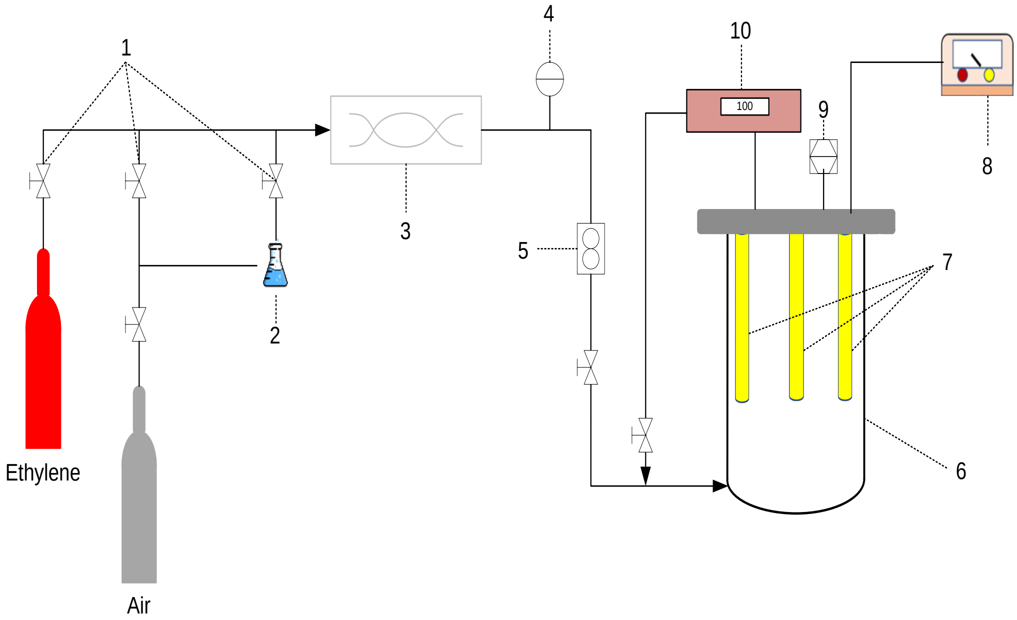


Figure 7.1: Schematic presentation of the experimental setup used for the photolytic degradation of ethylene: (1) control valves; (2) humidity device; (3) mixing unit; (4) hygrometer; (5) flow controller; (6) photolytic reactor; (7) VUV lamps; (8) power supply control; (9) thermocouple, and (10) ethylene analyser.

7.2.2 **Model development**

7.2.2.1 *Material balance*

The general mass balance equation of ethylene in the reactor is given by:

$$\frac{d(C_A V)}{dt} = F_{A0} - F_A \pm r_A V \quad (7.1)$$

Where C_A is the molar concentration of ethylene, V is the volume of the reaction mixture, F_{A0} and F_A are the inlet and outlet molar rates, respectively, and r_A represents the rate of depletion of ethylene. For a batch reactor, there is no material entering and leaving the system; hence the mass balance equation simplifies to:

$$\frac{d(C_A)}{dt} = -r_A = kC_A^n \quad (7.2)$$

7.2.2.2 Energy balance

An energy balance of the photolysis reaction in the batch reactor accounts for the heat of reaction, the radiant energy emitted by the VUV lamps, and the net rate of convective heat transfer to the surroundings as follows:

$$\rho C_p V \left(\frac{dT}{dt}\right) = \Delta H_{rxn} r_A V - hA(T - T_a) + G_{uv} \tag{7.3}$$

where C_p and ρ *are* the density and specific heat capacity of the reaction mixture, respectively; H_{rxn} is the enthalpy of reaction; *h* is the heat transfer coefficient; *A* is the heat transfer area; *T* and T_a are the reaction mixture temperature and ambient temperature, respectively; and G_{uv} is the heat flux by the VUV lamps.

There are many correlations in the literature that can be used to calculate heat transfer utilizing the Nusselt number. However, there is a lack of specific correlations for heat transfer in VUV photolysis reactors. The heat transfer coefficient (*h)* in Eq. (7.3) is obtained from the Nusselt number (N_u*)* by making use of the correlation by Welty et al. (2014). Although this correlation might not be ideal for a cylindrical reactor, it relies on the Reynolds number (*Re)* and Prandtl number (*Pr),* which are critical dimensionless groups in heat transfer analysis, making it a practical choice despite its limitations.

$$N_u = 0.664 Re^{0.5} Pr^{0.33} \tag{7.4}$$

where *Re* is the Raynolds number

$$Re = \frac{\rho v d}{\mu} \tag{7.5}$$

Pr is the Prandtl number

$$Pr = \frac{\mu C_p}{k} \tag{7.6}$$

And the Nusselt number is defined as:

$$N_u = \frac{hd}{k} \tag{7.7}$$

7.2.2.3 Kinetic modelling

It has been reported that the degradation of many organic compounds, including ethylene, by VUV photolysis often follows first-order kinetics (Cheng et al., 2011; Pathak et al., 2017; Pathak et al., 2019; J. H. Wang & Ray, 2000; Yu et al., 2012). The rate constant can be affected by many factors such as temperature and light intensity and can be expressed by the following relationship:

$$k = f(T, I) \tag{7.8}$$

where T is the temperature, and I is the light intensity. The relationship between the kinetic constant and temperature can be given by the Arrhenius equation as follows:

$$k = Ae^{\frac{-E_a}{RT}} \tag{7.9}$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant. The Beer-Lambert law is widely used to model UV light intensity (Duca, 2015):

$$I = I_0 e^{(-k_a C_A L)} \tag{7.10}$$

here I_o is the initial light intensity, k_a is the absorption coefficient, and L is the distance travelled by the light through the reactor. Combining Eqs. (7.9), (7.10) and (7.2) gives the mass balance equation:

$$\frac{dC_A}{dt} = -AI_0 e^{-(\frac{E_a}{RT} + k_a C_A L)} C_A \tag{7.11}$$

Substituting Eq. (7.11) into Eq. (7.3) gives the following energy balance equation:

$$\frac{dT}{dt} = \frac{1}{\rho C_p V}\left(\Delta H_{rxn} A e^{-(\frac{E_a}{RT} + k_a C_A L)} I C_A V - hA(T - T_a) - G_{uv}\right) \tag{7.12}$$

The heat of reaction (ΔH_{rxn}) represents the heat loss or generation from the reaction. Since the radical species involved in VUV photolysis reactions generally exhibit lower heats of reaction compared to reactions involving stable molecules, ΔH_{rxn} was omitted in the model. The omission of ΔH_{rxn} has also been supported by Asili (2018), who, upon calculating the heat of the reaction, reported that any temperature increase resulting from the photolysis reaction of ethylene was negligible compared to the heat transferred from the VUV lamp.

Equation (7.11) and (7.12) were solved using MATLAB. The primary goal was to identify the constants *A*, E_a and k_a by fitting experimental data. After obtaining the model parameters, another series of experiments, in which the light intensity and relative humidity were changed, were carried out to assess the model's ability to predict experimental data accurately.

7.2.2.4 *Model fit*

The fitting procedure of the mathematical model was performed with MATLAB software (The Mathworks, USA). The solver ODE45 was used to integrate the ordinary differential equation (ODE) system of equations (7.11) and (7.12), and the solver Fminsearch was utilised to carry out nonlinear least-squares regression analysis to evaluate the best-fit. Confidence in the model's accuracy and reliability is established by comparing the simulated values with the measured values using the coefficient of determination (R^2) from regression analysis. To validate the proposed model, model predictions are compared with experimental results of Mabusela et al. (2024).

7.3 Results and discussion

7.3.1 *Photolysis of ethylene*

Figure 7.2 illustrates the trend observed during the oxidation of ethylene in a photolytic reactor. Initially, the ethylene concentration remained constant while the UV light was off, indicating that the reactor had reached a steady state. When the lamps were switched on, ethylene concentration exhibited a linear decrease, reaching 5.1 ppm after 10 minutes of exposure. When the light was turned off for 10 minutes, the ethylene concentration remained stable, and when the lamps were switched on again the concentration of ethylene decreased. This demonstrated that no significant oxidation occurred in the absence of light and that the disappearance of ethylene is due to the photolysis.

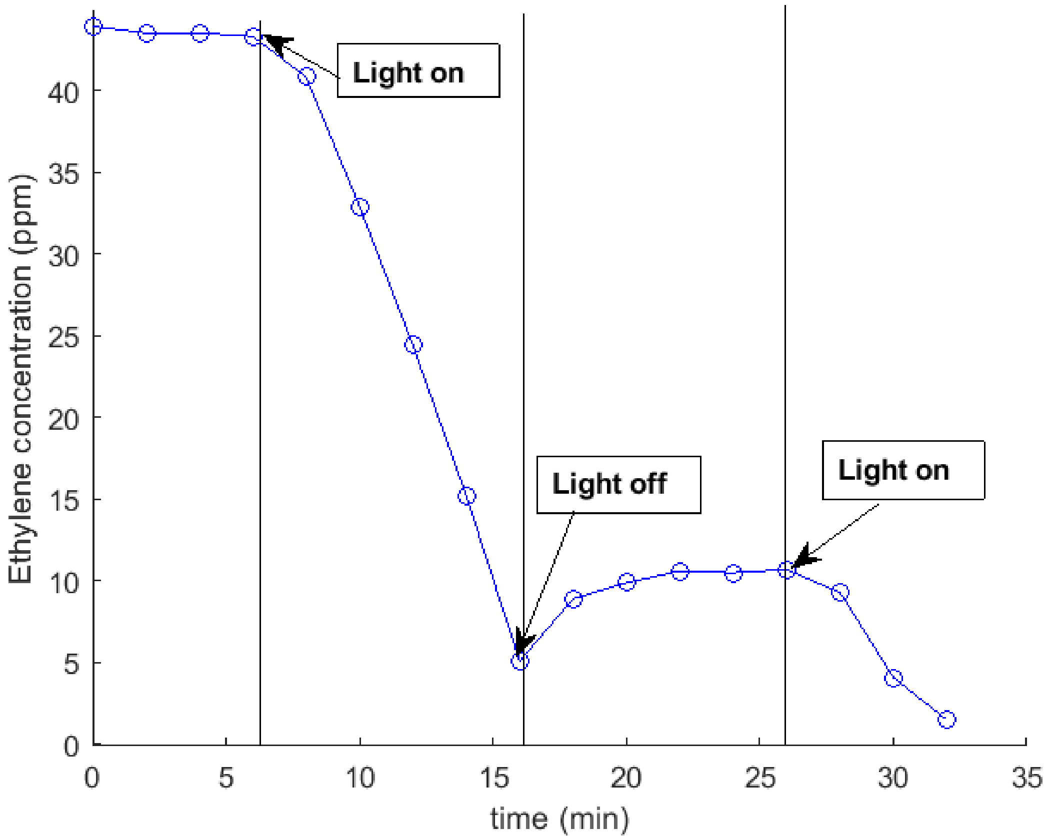


Figure 7.2: Oxidation of ethylene in a photolytic reactor

The oxidation of ethylene by VUV photolysis typically involves two mechanisms: (i) the direct mechanism where the ethylene is directly decomposed by VUV radiation, and (ii) the indirect oxidation where •OH radicals generated through VUV photolysis of another compound (usually a precursor such ausels water or oxygen) attack ethylene, leading to its oxidation (Mabusela et al., 2022).

$$C_2H_4 + hv \overset{k_1}{\rightarrow} oxidation\ products \tag{7.13}$$

$$C_2H_4 + \mathrm{OH} \overset{k_2}{\rightarrow} \mathrm{x}C_2H_4 + yCO_2 \tag{7.14}$$

Thus, the concentration of ethylene decreases upon light activation due to these photodegradation mechanisms.

7.3.2 *Model validation*

Figure 7.3 shows the experimental data and model predictions for ethylene degradation to identify the model parameters *A, E_a,* and k_a. The model parameters were found to have values of A = 2019.29 m^2/mW s, E_a = -2559.83 J/mol K, and k_a = 0.2367 ppm^{-1} m^{-1}. The model parameters were used to fit experimental data at light intensities of 5 x10^{-5} mW/m^2 and 2.1 x 10^{-4} mW/m^2 and RH of 90% to analyse the ability of the model to predict experimental data.

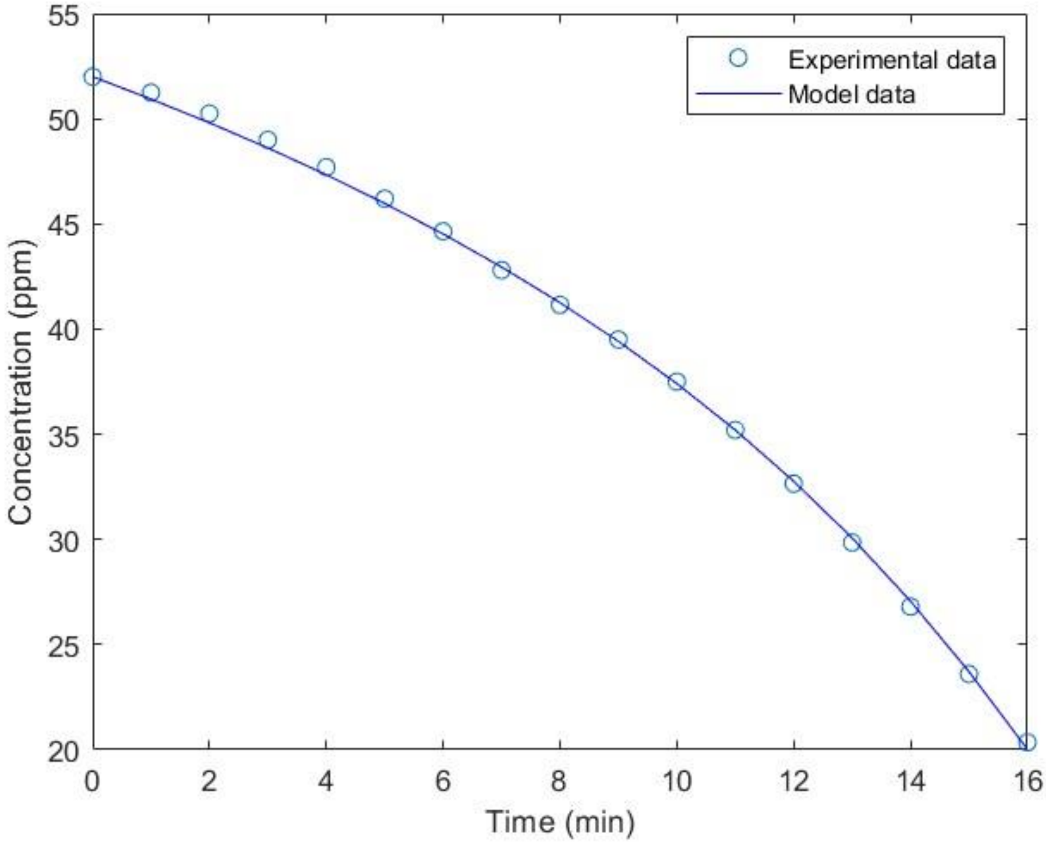


Figure 7.3: Comparison between model calculations and experimental data to find the model constants. Light intensity: 1.4 x10^{-4} mW/m^2, relative humidity: 20% and ethylene concentration: 51.2 ppm

7.3.3 *Activation Energy*

Figure 7.4 shows the plot of ln *k* vs. 1/*T*. The graph indicates that as the temperature increases, the rate of reaction increases, which is contrary to the expected result for a negative activation energy. Negative E_a values implies that the rate constant decreases as the temperature increases. In the context of VUV photolysis, this is observed because an increase in temperature decreases the concentration of hydroxyl radicals (moisture), ultimately leading to a decrease in the rate constant. A similar plot of ln *k* vs. 1/*T* for the degradation of alkenes, displaying both positive and negative activation energy regions, was also observed by Xiao et al. (2020).

The graph can be divided into two distinct regions: a low-temperature region and a high-temperature region. The presence of these two regions suggests a change in reaction mechanisms (Liang et al., 2023). The negative activation energy calculated by the model appears to lie in the low-temperature region. This indicates that if the wattage were to increase, the trend in the graph would eventually show a positive slope, resulting in negative activation energy. A negative activation energy for ethylene of -4000 J/mol in the low-temperature range has also been reported by Liu et al. (1988), which is not far from the estimated activation energy in this study. Photolysis of ethylene involves the degradation of ethylene by highly reactive radicals, and it is believed that many of the radical-molecule reactions have negative activation energies (Xiao et al., 2020).

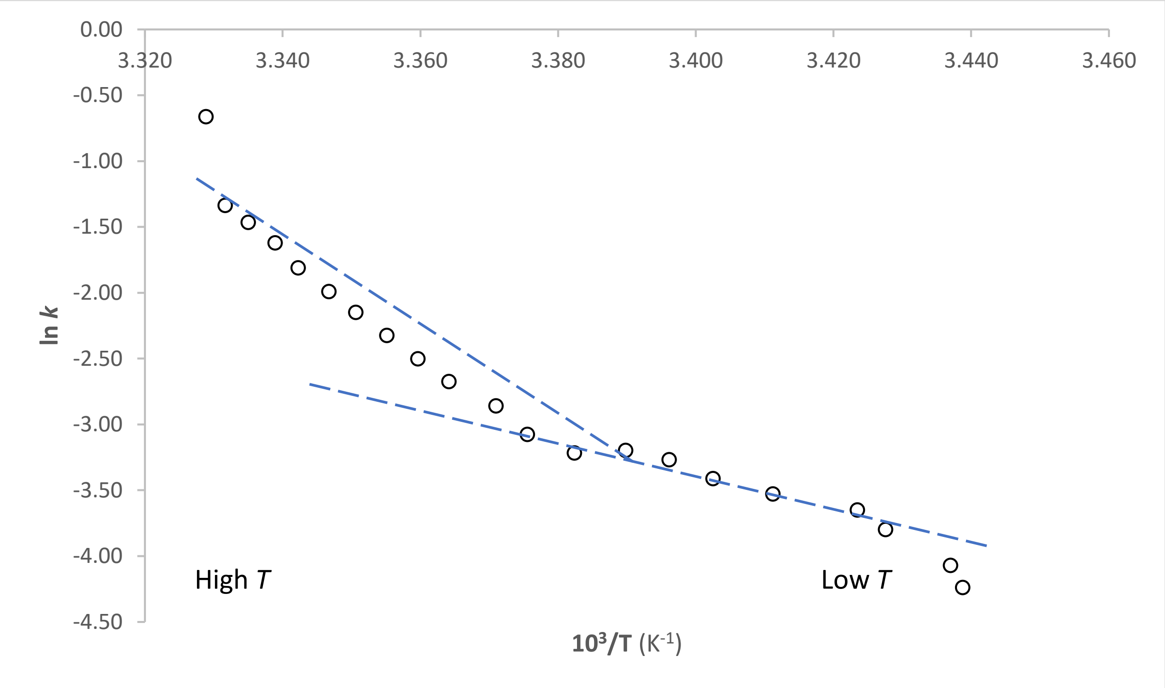


Figure 7.4: Plot of reaction rate constant as a function of temperature at 1.4 x10^{-4} mW/m^2.

7.3.4 *Effect of light intensity*

Figure 7.5 shows a comparison of model predictions and experimental data at different light intensities. The results show that the model accurately predicted the experimental data at both high and low light intensities with R^2 = 0.9269 and R^2 = 0.9372, respectively. The photolytic degradation rate of ethylene increased with an increase in light intensity. Increasing light intensity generates more photons leading to more production of radicals, which enhances the removal of ethylene.

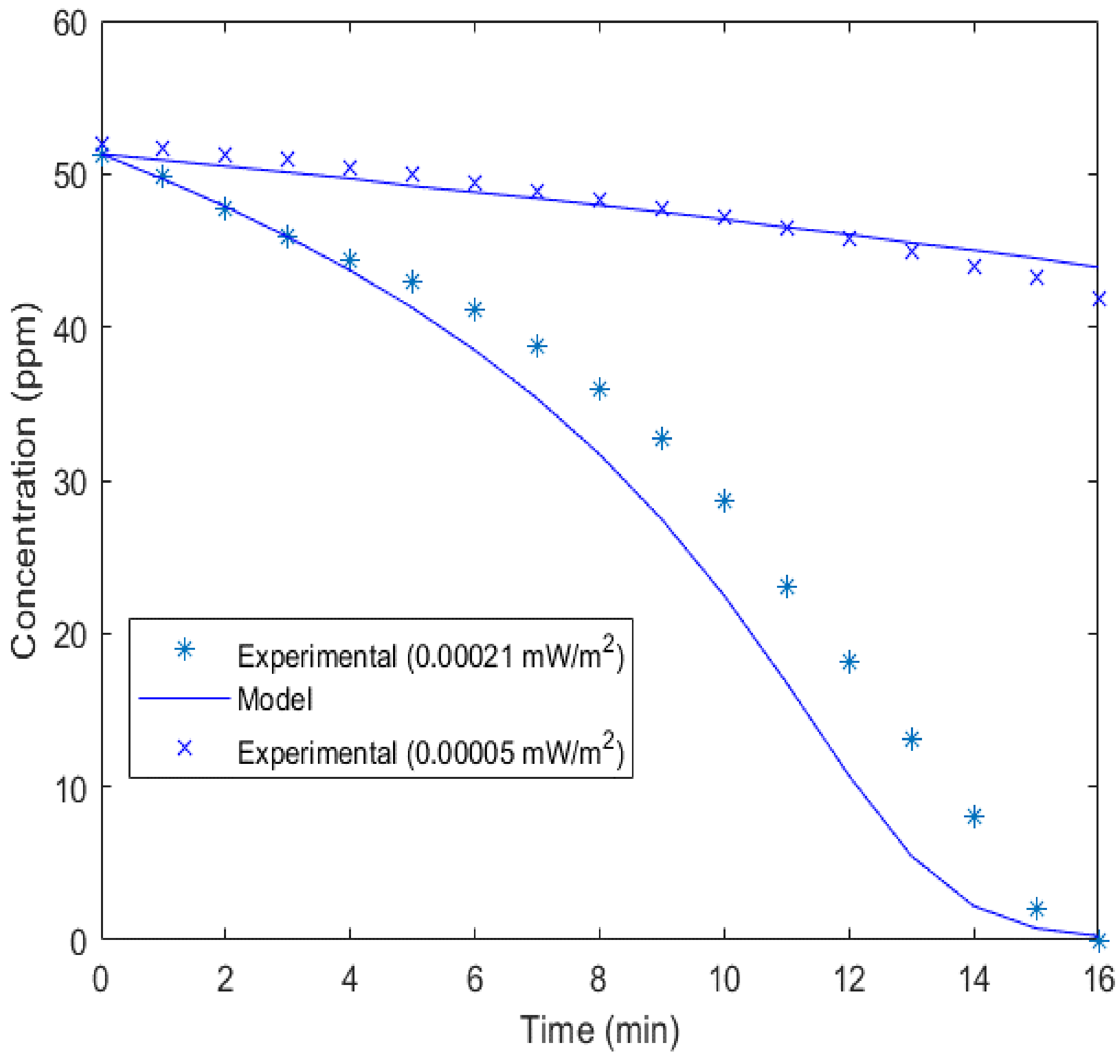


Figure 7.5: Experimental and predicted C_2H_4 concentrations as a function of light intensity, RH = 20%

7.3.5 Effect of relative humidity

The calculated model parameters were also used to predict the degradation profile at high RH (90%) with an initial ethylene concentration of 51.2 ppm and light intensity of 2.1 $\times 10^{-4}$ mW/m^2. The model fitting is depicted in Fig. 7.6. The measured conversion of ethylene agreed with the simulated conversion with R^2 = 0.9816 However, at the latter stage, the simulated conversion diverged slightly from the measured conversion. This likely arises from the increased concentration of hydroxyl radicals at high humidity, which significantly contribute to ethylene degradation. High RH promotes hydroxyl radical generation, leading to their active participation in ethylene degradation. This ultimately changes the dominant degradation mechanism, resulting in the model's inability to accurately predict the conversion.

Wang et al. (2014) observed a similar phenomenon in their model for p-chlorobenzoic acid (p-CBA) degradation via VUV photolysis. Their model also showed discrepancies with experimental data under varying operating conditions due to the influence of hydroxyl radicals and the resulting shift in reaction mechanisms. To improve the accuracy of our model, the influence of hydroxyl radicals needs to be incorporated into the kinetic model.

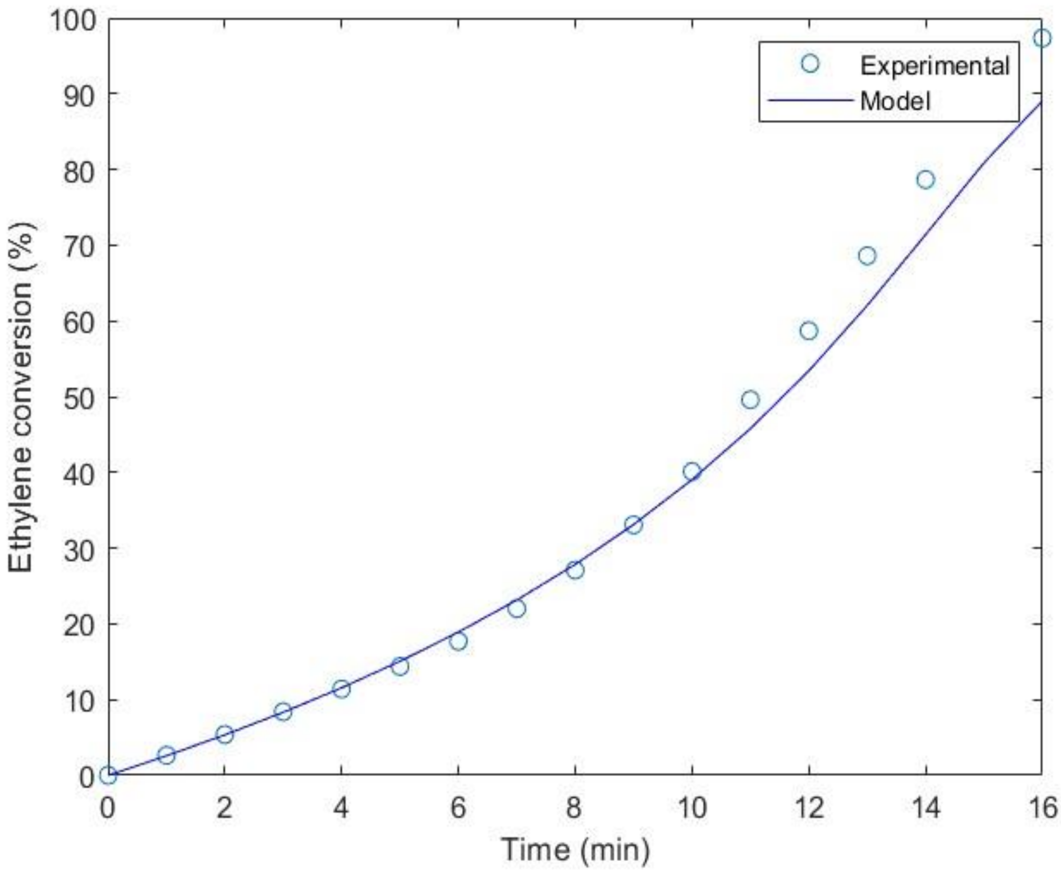


Figure 7.6: Experimental and model prediction data at high RH (90%)

7.3.6 *Sensitivity analysis*

To evaluate the degradation efficiency through sensitivity analysis, various process conditions and reactor dimensions were adjusted. The simulation results were compared across different scenarios to identify the optimum parameters.

The results of reactor optimization for ethylene degradation are shown in Fig. 7.7 and Fig. 7.8. The base case was defined with an initial ethylene concentration of 51 ppm, light-intensity

1.4 x10^{-4} mW/m^2, reactor length of 0.3 m, and temperature of 296 K. The light optimization simulation results in Fig. 7.7 clearly show that increasing light intensity leads to higher degradation rates of ethylene. As the light intensity increases, while maintaining a constant ethylene concentration, the number of photons increases, subsequently enhancing ethylene degradation via the direct degradation mechanisms. However, increasing light intensity should be done with caution since it is directly linked to operational costs. Therefore, it can be deduced that the optimum light intensity is 3.0 x10^{-4} mW/m^2 as complete degradation of ethylene is achieved in 11 minutes under this intensity.

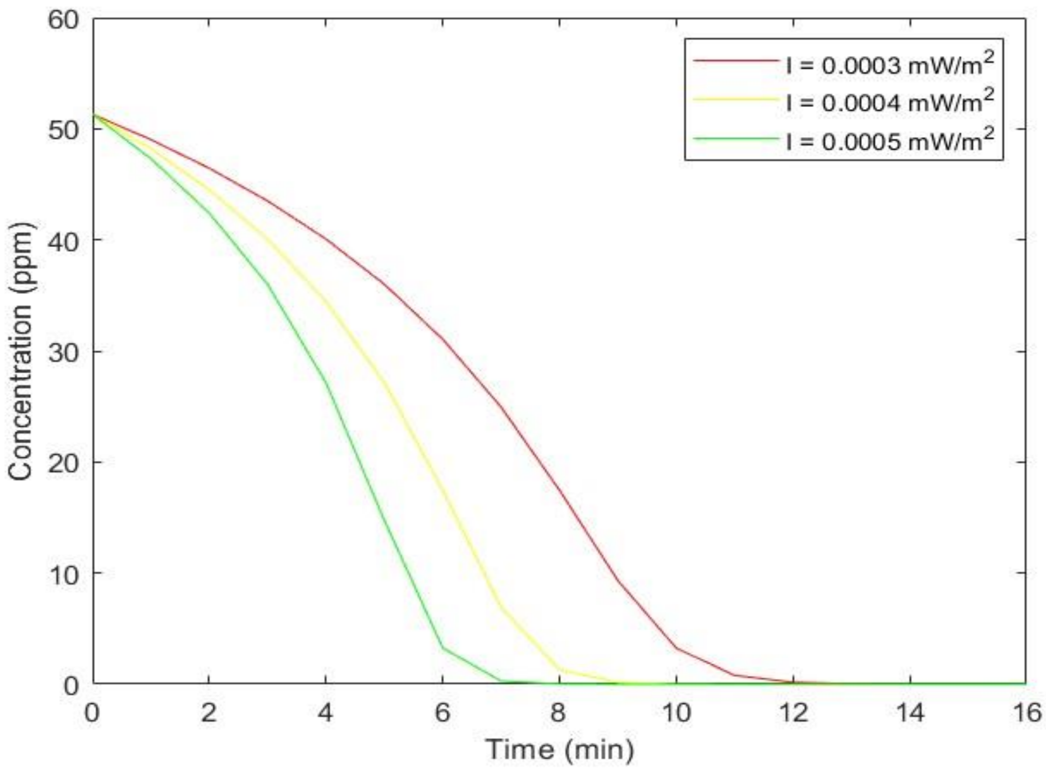


Figure 7.7: Sensitivity tests results for ethylene degradation at different light intensities

Another crucial factor in designing a VUV photolysis reactor is the reactor length. Sensitivity tests in Fig. 7.8 indicate that halving the reactor length to 0.15 m increases the degradation removal rate from 66% to 99.9% in just under 16 minutes. Decreasing the reactor length further to 0.10 m did not have any significant change in ethylene removal efficiency. In a shorter batch reactor, the intensity of VUV light per unit length may be higher, resulting in an increased removal rate. Additionally, given that reactive radicals such as OH radicals are short-lived with shelf-life of approximately 10^{-9} seconds (Pathak, 2019), shortening the reactor length promotes higher utilization of hydroxyl radicals, enhancing removal efficiency.

On the other hand, increasing the reactor length to 0.35 m and 0.5 m showed a negative impact on the removal efficiency. In longer reactors, the VUV light may not be utilized as efficiently. As the light travels further, it can be absorbed or scattered, reducing the intensity available for initiating the photolysis reactions, leading to lower degradation rate. Additionally, in longer reactors, the concentration of the short-lived radicals can drop significantly as the distance from the light source increases, resulting in less effective interaction with ethylene molecules. Therefore, according to the model, the optimum length for the reactor design is 0.15 m.

Increasing the temperature by 10 K did not positively affect the removal efficiency; instead, it reduced the removal efficiency from 66% to 41.2%. Although increasing the temperature is generally expected to accelerate the degradation rate, this was not observed in this study. This outcome is also reflected in the negative activation energy calculated. Increasing temperature reduces the moisture inside the reactor, which in turn decreases the concentration of OH radicals responsible for the indirect degradation of ethylene, thus lowering the removal rate. Asili (2018)also developed a comprehensive mathematical model for the photolysis of some selected hydrocarbons and found that higher temperatures decreased overall conversion.

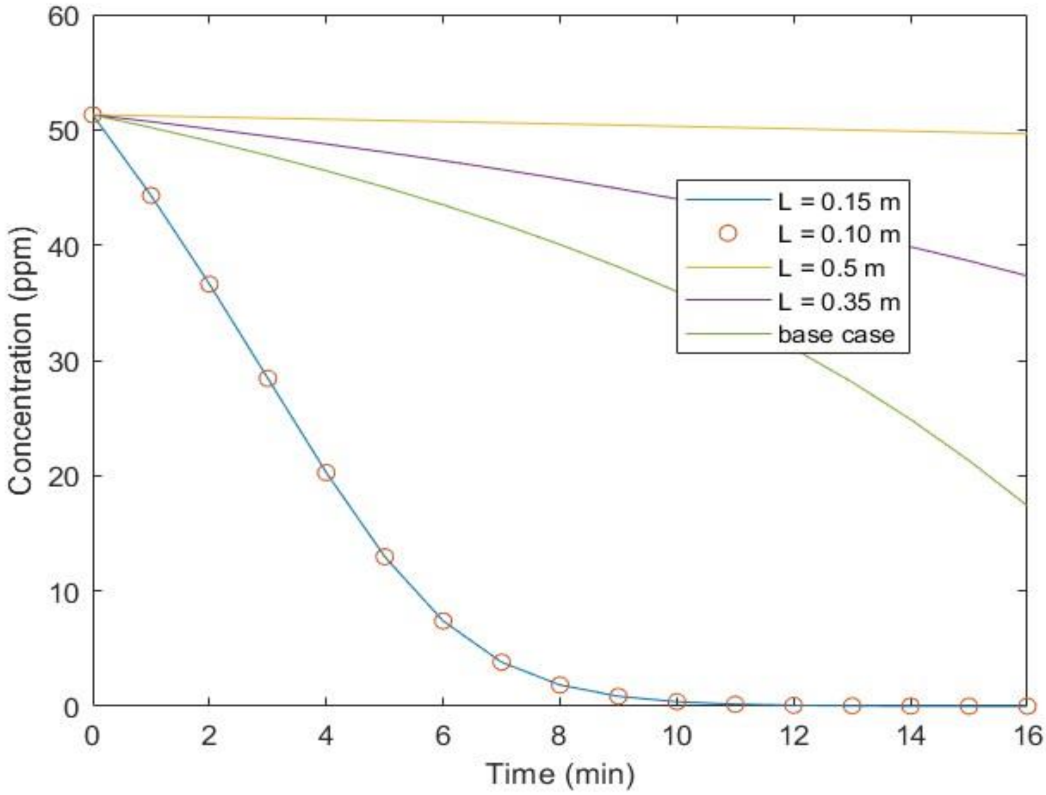


Figure 7.8: Effect of increasing reactor length on the removal efficiency of ethylene

7.3.7 *Temperature profile*

The VUV lamp in the reactor may experience significant heat losses, which can result in temperature variations within the photoreactor. Such variations can influence the degradation efficiency and the overall performance of the photoreactor. In this study, the temperature was not maintained at a constant level; instead, the temperature rise inside the photoreactor was carefully monitored to understand its impact on the process.

The energy balance model of equation (7.12) was utilized to predict the temperature rise inside the reactor. This model takes into account the various energy inputs and outputs, including the heat generated by the VUV lamp, and the heat dissipated to the surroundings. By incorporating these factors, the model aims to provide a realistic simulation of the temperature dynamics within the reactor.

Figure 7.9 presents both the measured temperature profile inside the photolysis reactor and the predicted temperature profile. The comparison between these two profiles reveals that the average difference between the simulated and measured values is -3.58 K. This indicates that while the model tends to underestimate the actual temperature, it effectively captures the overall trend of temperature increase.

The slight underestimation by the model could be due to several factors, such as unaccounted heat losses or generation by the chemical reaction. Despite this discrepancy, the model's ability to mirror the upward trend in temperature rise is valuable. It suggests that the model can be a useful tool for predicting temperature behaviour in similar reactor setups, allowing for better control and optimization of the photolysis process.

The observed temperature variations within the photoreactor highlight the importance of monitoring and modeling temperature dynamics to ensure optimal reactor performance. The energy balance model, despite its minor underestimation, provides a reliable means to simulate temperature changes and can aid in the design and operation of more efficient photoreactors.

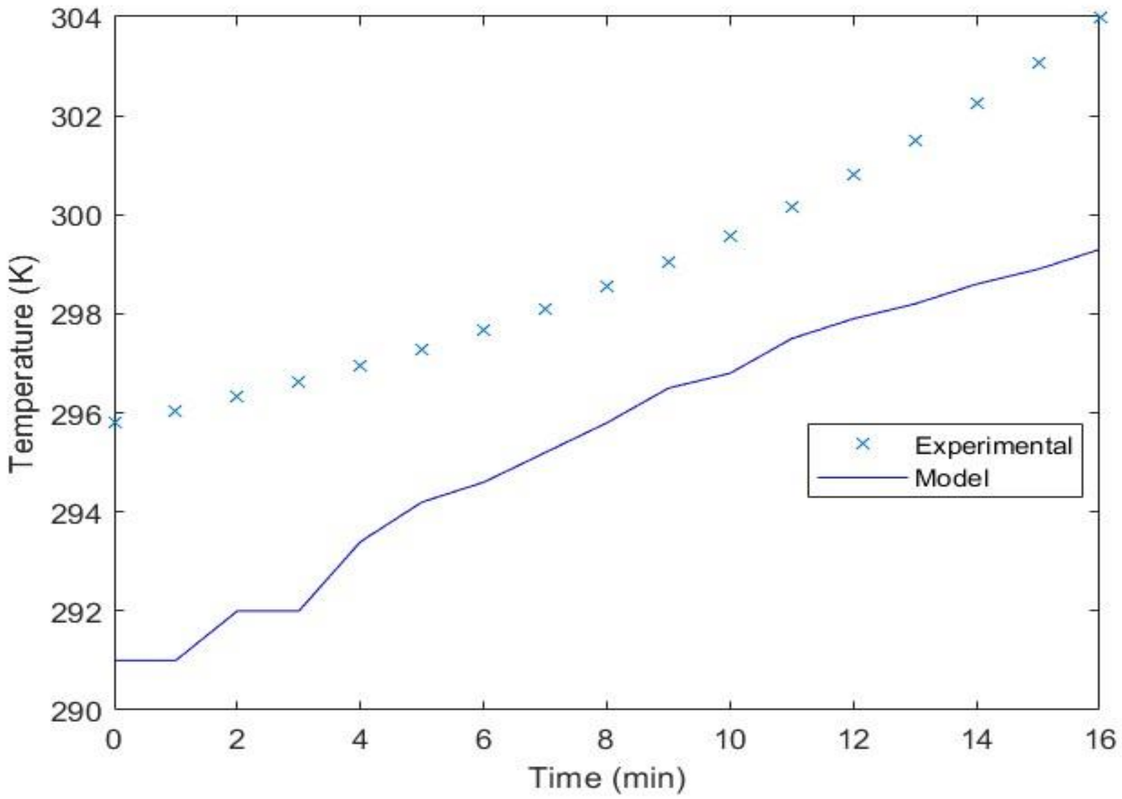


Figure 7.9: Temperature profile inside the VUV photolysis reactor

7.4 Conclusion

The photolytic degradation of ethylene was investigated. Mathematical mass balance and energy balance models were developed to simulate the ethylene concentration and temperature variation inside the photoreactor. Key parameters such as light intensity, reactor length, and temperature were systematically varied to understand their impact on ethylene degradation. Activation energy was calculated by parameter estimation using MATLAB, resulting in a value of -2559.83 J/mol. The plot of ln(k) vs. 1/T indicated a shift in the controlling mechanisms of the reaction, suggesting the presence of parallel reactions.

A mass balance model was used to simulate the concentration of ethylene under different operating conditions of light intensity and RH. The results showed that increasing light intensity enhanced degradation. Additionally, high RH favoured ethylene degradation due to the increased presence of hydroxyl radicals. The developed model was able to predict the experimental concentrations with R^2 values above 0.9.

A sensitivity analysis was performed to investigate key factors affecting the design and optimization of the VUV photolysis reactor. Light intensity and reactor length were determined to have the most significant impact on ethylene degradation. Increasing light intensity and decreasing reactor length improved removal efficiency. In contrast, increasing temperature resulted in a decrease in conversion, consistent with the negative activation energy calculated.

The energy balance model provided valuable insights into predicting temperature rise within the reactor, despite slightly underestimating the measured values. The model accurately reflected the upward trend in temperature, underscoring its potential as a tool for optimizing reactor conditions.

The developed mathematical model offers guidance for optimizing reactor design and operation to achieve efficient ethylene degradation. Further studies on the effect of other operational conditions and reactor configurations on the efficiency of ethylene removal are needed to optimize the photolysis reactor.

7.5 Summary

This chapter focused on fulfilling the thesis's main goal of developing a mathematical model to describe the degradation of ethylene within a VUV photolysis reactor. Mathematical models for mass and energy balances were created to simulate ethylene concentration and temperature variations within the reactor. Key parameters, including light intensity, reactor length, and temperature, were varied to assess their impact on ethylene degradation. The developed model offers valuable insights for optimizing the design and operation of VUV photolysis reactors, providing better control of temperature variations and enhancing ethylene degradation. This is a significant result, demonstrating the model's potential for designing more efficient VUV photolysis reactors.

References

Alexander, L., & Grierson, D. (2002). Ethylene biosynthesis and action in tomato: A model for climateric fruit ripening. *Journal of Experimental Botany*, *53*, 2039–2055. https://doi.org/10.1093/jxb/erf072

Alonso Salinas, R., Motos, J. R., Núñez-Delicado, E., Gabaldon, J., & López-Miranda, S. (2022). Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures. *Agronomy*, *12*, 616. https://doi.org/10.3390/agronomy12030616

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., Ventura-Sobrevilla, J. M., & Martínez-Hernández, G. B. (2018). Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food and Bioprocess Technology*, *11*(3), 511–525. https://doi.org/10.1007/s11947-018-2076-7

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Miranda-Molina, F. D., & Artés-Hernández, F. (2020). Postharvest quality retention of apricots by using a novel sepiolite–loaded potassium permanganate ethylene scavenger. *Postharvest Biology and Technology*, *160*, 111061. https://doi.org/https://doi.org/10.1016/j.postharvbio.2019.111061

Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R., & Anderson, W. A. (1995). UV oxidation for drinking waterfeasibility studies for addressing specific water quality issues. *Proceedings of the AWWA WQTC, New Orleans, LA*, 18811898.

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018a). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1). https://doi.org/10.1088/1755-1315/141/1/012003

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018b). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1), 012003. https://doi.org/10.1088/1755-1315/141/1/012003

Asili, V. (2018). *Mechanistic Model for Ultraviolet Degradation of Light Hydrocarbons in Waste Gas*. University of Calgary.

Asili, V., & De Visscher, A. (2018). Modelling methane and ethane photolysis in waste gas: Optimization of reaction networks. *The Canadian Journal of Chemical Engineering*, *96*(8), 1674–1683. https://doi.org/https://doi.org/10.1002/cjce.23124

Bagheri, M., & Mohseni, M. (2014). Computational fluid dynamics (CFD) modeling of VUV/UV photoreactors for water treatment. *Chemical Engineering Journal*, *256*, 51–60. https://doi.org/https://doi.org/10.1016/j.cej.2014.06.068

Basso, A., de Fátima Peralta Muniz Moreira, R., & José, H. J. (2018). Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening. *Journal of Photochemistry and Photobiology A: Chemistry*, *367*, 294–301. https://doi.org/10.1016/j.jphotochem.2018.08.027

Bu, J., Yu, Y., Aisikaer, G., & Ying, T. (2013). Postharvest UV-C irradiation inhibits the production of ethylene and the activity of cell wall-degrading enzymes during softening of tomato (Lycopersicon esculentum L.) fruit. *Postharvest Biology and Technology*, *86*, 337–345. https://doi.org/10.1016/j.postharvbio.2013.07.026

Chang, K.-L., Sekiguchi, K., Wang, Q., & Zhao, F. (2013). Removal of Ethylene and Secondary Organic Aerosols Using UV-C-254 (+) (185) (nm) with TiO2 Catalyst. *Aerosol and Air Quality Research*, *13*, 618–626. https://doi.org/10.4209/aaqr.2012.07.0195

Chen, F., Yang, Q., Pehkonen, S. O., & Ray, M. B. (2004). Modeling of Gas-Phase Photodegradation of Chloroform and Carbon Tetrachloride. *Journal of the Air & Waste Management Association*, *54*(10), 1281–1292. https://doi.org/10.1080/10473289.2004.10470991

Chen, L., Xie, X., Song, X., Luo, S., Ye, S., & Situ, W. (2021). Photocatalytic degradation of ethylene in cold storage using the nanocomposite photocatalyst MIL101(Fe)-TiO2-rGO. *Chemical Engineering Journal*, *424*, 130407. https://doi.org/https://doi.org/10.1016/j.cej.2021.130407

Cheng, Z.-W., Jiang, Y.-F., Zhang, L.-L., Chen, J.-M., & Wei, Y.-Y. (2011). Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. *Separation and Purification Technology*, *77*(1), 26–32. https://doi.org/https://doi.org/10.1016/j.seppur.2010.11.014

Chou, M.-S., & Chang, K.-L. (2007). UV/ozone degradation of gaseous hexamethyldisilazane (HMDS). *Chemosphere*, *69*(5), 697–704. https://doi.org/https://doi.org/10.1016/j.chemosphere.2007.05.040

Da Silva, J. C. G., Alves, J. L. F., Mumbach, G. D., & Di Domenico, M. (2023). Photocatalytic degradation of ethylene in tubular microreactor coated with thin-film of TiO2: Mathematical modeling with experimental validation and geometry analysis using computational fluid dynamics simulations. *Chemical Engineering Research and Design*, *196*, 101–117. https://doi.org/https://doi.org/10.1016/j.cherd.2023.06.036

De Bruijn, J., Gómez, A. E., Melín, P., Loyola, C., Solar, V. A., & Valdés, H. (2019). Effect of doping natural zeolite with copper and zinc cations on ethylene removal and postharvest tomato fruit quality. *Chemical Engineering Transactions*, *75*, 265–270. https://doi.org/10.3303/CET1975045

de Chiara, M. L. V., Pal, S., Licciulli, A., Amodio, M. L., & Colelli, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO2/SiO2 nanocomposites: Effects on the ripening of mature green tomatoes. *Biosystems Engineering*, *132*, 61–70. https://doi.org/10.1016/j.biosystemseng.2015.02.008

Department of Agriculture, F. and F. (2022). *A PROFILE OF THE SOUTH AFRICAN APPLE MARKET VALUE CHAIN 2020*. www.dalrrd.gov.za

Du, L., Song, J., Forney, C., Palmer, L. C., Fillmore, S., & Zhang, Z. (2016). Proteome changes in banana fruit peel tissue in response to ethylene and high-temperature treatments. *Horticulture Research*, *3*. https://doi.org/10.1038/hortres.2016.12

Duca, C. (2015). *Effect of water matrix on Vacuum UV process for the removal of organic micropollutants in surface water*. The University of British Columbia.

Duque, L. F., Amador, M. V., Guzmán, M., Asensio, C., & Valenzuela, J. L. (2021). Development of a new essential oil-based technology to maintain fruit quality in tomato. *Horticulturae*, *7*(9), 303.

Emadpour, M., Ghareyazie, B., Rezaei kalaj, Y., Entesari, M., & Bouzari, N. (2015). *Effect of the Potassium Permanganate Coated Zeolite Nanoparticles on the Quality Characteristic and Shelf Life of Peach and Nectarine*.

Feiyan, C., Pehkonen, S. O., & Ray, M. B. (2002). Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. *Water Research*, *36*(17), 4203–4214. https://doi.org/https://doi.org/10.1016/S0043-1354(02)00140-9

Fonseca, J. de M., Pabón, N. Y. L., Nandi, L. G., Valencia, G. A., Moreira, R. de F. P. M., & Monteiro, A. R. (2021). Gelatin-TiO2-coated expanded polyethylene foam nets as ethylene scavengers for fruit postharvest application. *Postharvest Biology and Technology*, *180*, 111602. https://doi.org/https://doi.org/10.1016/j.postharvbio.2021.111602

Hooijberg, E. H., Miller, M., Cray, C., Buss, P., Steenkamp, G., & Goddard, A. (2018). Serum protein electrophoresis in healthy and injured southern white rhinoceros (Ceratotherium simum simum). *PLoS ONE*, *13*(7). https://doi.org/10.1371/journal.pone.0200347

Hrazdina, G., Kiss, E., Galli, Z., RosenField, C., Norelli, J. L., & Aldwinckle, H. S. (2003). DOWN REGULATION OF ETHYLENE PRODUCTION IN “ROYAL GALA” APPLES. *Acta Horticulturae*, *628*, 239–251. https://doi.org/10.17660/ActaHortic.2003.628.29

Huang, H., Huang, H., Zhang, L., Hu, P., Xu, Y., Ye, X., Liang, X., Chen, J., & Ji, M. (2014). Photooxidation of Gaseous Benzene by 185 nm VUV Irradiation. *Environmental Engineering Science*, *31*(8), 481–486. https://doi.org/10.1089/ees.2014.0100

Huang, H., Lu, H., Huang, H., Wang, L., Zhang, J., & Leung, D. Y. C. (2016). Recent development of VUV-based processes for air pollutant degradation. *Frontiers in Environmental Science*, *4*, 17.

Kader, A. A. (1985). Ethylene-induced Senescence and Physiological Disorders in Harvested Horticultural Crops. *HortScience*, *20*(1), 54–57. https://doi.org/10.21273/HORTSCI.20.1.54

Kang, I.-S., Xi, J., & Hu, H.-Y. (2018). Photolysis and photooxidation of typical gaseous VOCs by UV Irradiation: Removal performance and mechanisms. *Frontiers of Environmental Science & Engineering*, *12*, 1–14.

Keller, N., Ducamp, M.-N., Robert, D., & Keller, V. (2013). Ethylene removal and fresh product storage: a challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation. *Chemical Reviews*, *113*(7), 5029–5070.

Khedr, E., & Al-Khayri, J. (2023). Synergistic Effects of Tragacanth and Anti-ethylene Treatments on Postharvest Quality Maintenance of Mango (Mangifera indica L.). *Plants*, *12*, 1887. https://doi.org/10.3390/plants12091887

Kim, K., Chun, I.-J., Suh, J. H., & Sung, J. (2023). Relationships between sensory properties and metabolomic profiles of different apple cultivars. *Food Chemistry: X*, *18*, 100641. https://doi.org/https://doi.org/10.1016/j.fochx.2023.100641

Li, J., Sun, Q., Sun, Y., Chen, B., Wu, X., & Le, T. (2019). Improvement of banana postharvest quality using a novel soybean protein isolate/cinnamaldehyde/zinc oxide bionanocomposite coating strategy. *Scientia Horticulturae*, *258*, 108786. https://doi.org/https://doi.org/10.1016/j.scienta.2019.108786

Li, L., Ban, Z., Limwachiranon, J., & Luo, Z. (2017). Proteomic Studies on Fruit Ripening and Senescence. *Critical Reviews in Plant Sciences*, *36*(2), 116–127. https://doi.org/10.1080/07352689.2017.1355173

Li, M., Li, D., Feng, F., Zhang, S., Ma, F., & Cheng, L. (2016). Proteomic analysis reveals dynamic regulation of fruit development and sugar and acid accumulation in apple. *Journal of Experimental Botany*, *67*(17), 5145–5157. https://doi.org/10.1093/jxb/erw277

Liang, P., de Aragão, E. V. F., Giani, L., Mancini, L., Pannacci, G., Marchione, D., Vanuzzo, G., Faginas-Lago, N., Rosi, M., & Skouteris, D. (2023). OH (2Π)+ C2H4 reaction: a combined crossed molecular beam and theoretical study. *The Journal of Physical Chemistry A*, *127*(21), 4609–4623.

Lien, N., Horváth, V., Mai, D., Hitka, G., Zsom, T., & Kókai, Z. (2018). Effect of 1-MCP, ethylene absorber and ozone on melon quality during storage. *Progress in Agricultural Engineering Sciences*, *14*, 101–110. https://doi.org/10.1556/446.14.2018.S1.10

Lin, S., Miao, Y., Huang, H., Zhang, Y., Huang, L., & Cao, J. (2022). Arabinogalactan Proteins: Focus on the Role in Cellulose Synthesis and Deposition during Plant Cell Wall Biogenesis. *International Journal of Molecular Sciences*, *23*, 6578. https://doi.org/10.3390/ijms23126578

Lin, Y.-T., Weng, C.-H., Hsu, H.-J., Huang, J.-W., Srivastav, A. L., & Shiesh, C.-C. (2014). Effect of oxygen, moisture, and temperature on the photo oxidation of ethylene on N-doped TiO2 catalyst. *Separation and Purification Technology*, *134*, 117–125. https://doi.org/https://doi.org/10.1016/j.seppur.2014.07.039

Liu, A., Mulac, W. A., & Jonah, C. D. (1988). Kinetic isotope effects in the gas-phase reaction of hydroxyl radicals with ethylene in the temperature range 343-1173 K and 1-atm pressure. *The Journal of Physical Chemistry*, *92*(13), 3828–3833.

Mabusela, B., Belay, Z., Godongwana, B., & Caleb, O. (2023). Application of VUV photolysis reactor for shelf-life extension and prediction of apple fruit. *[Status: Submitted]*.

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023a). Application of vacuum ultraviolet photolysis reactor and loss of firmness prediction for stored ‘Fuji’ apples. In *Acta Horticulturae* (Issue 1382). https://doi.org/10.17660/ActaHortic.2023.1382.2

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023b). Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics and removal in mixed-fruit storage, and direct exposure to ‘Fuji’ apples during storage. *Journal of Food Science and Technology*. https://doi.org/10.1007/s13197-023-05775-3

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, & Caleb, O. J. (2022). Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of

Fruit and Vegetables Along the Value Chains: a Review. *Food and Bioprocess Technology*, *15*(1), 28–46. https://doi.org/10.1007/s11947-021-02703-1

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, Mathabe, P. M. K., & Caleb, O. J. (2021). Trends in ethylene management strategies: towards mitigating postharvest losses along the South African value chain of fresh produce – a review. *South African Journal of Plant and Soil*, *38*(5), 347–360. https://doi.org/10.1080/02571862.2021.1938260

Mahmoudkhani, F., Rezaei, M., Asili, V., Atyabi, M., Vaisman, E., Langford, C., & De Visscher, A. (2016). Benzene degradation in waste gas by photolysis and photolysis-ozonation: experiments and modeling. *Frontiers of Environmental Science & Engineering*, *10*, 1–10. https://doi.org/10.1007/s11783-016-0876-4

Marhavý, P., Kurenda, A., Siddique, S., Dénervaud Tendon, V., Zhou, F., Holbein, J., Hasan, M. S., Grundler, F. M. W., Farmer, E. E., & Geldner, N. (2019). Single-cell damage elicits regional, nematode-restricting ethylene responses in roots. *The EMBO Journal*, *38*(10), e100972. https://doi.org/https://doi.org/10.15252/embj.2018100972

Namrata Pathak. (2019). *Photocatalysis and vacuum ultraviolet light photolysis as ethylene removal techniques for potential application in fruit storage*. Technical University Berlin.

Palou, L., Crisosto, C. H., Garner, D., & Basinal, L. M. (2003). Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes. *Postharvest Biology and Technology*, *27*(3), 243–254.

Pathak, N., Caleb, O. J., Geyer, M., Herppich, W. B., Rauh, C., & Mahajan, P. V. (2017). Photocatalytic and photochemical oxidation of ethylene: Potential for storage of fresh produce—A review. *Food and Bioprocess Technology*, *10*, 982–1001.

Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2017). Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage. *Biosystems Engineering*, *159*, 33–45. https://doi.org/https://doi.org/10.1016/j.biosystemseng.2017.04.008

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. https://doi.org/https://doi.org/10.1016/j.postharvbio.2018.09.006

Potuschak, T., Lechner, E., Parmentier, Y., Yanagisawa, S., Grava, S., Koncz, C., & Genschik, P. (2003). EIN3-Dependent Regulation of Plant Ethylene Hormone Signaling by Two Arabidopsis F Box Proteins: EBF1 and EBF2. *Cell*, *115*(6), 679–689. https://doi.org/10.1016/S0092-8674(03)00968-1

Sardabi, F., Mohtadinia, J., Shavakhi, F., & Jafari, A. A. (2014). The Effects of 1-Methylcyclopropen (1-MCP) and Potassium Permanganate Coated Zeolite Nanoparticles on Shelf life Extension and Quality Loss of Golden Delicious Apples. *Journal of Food Processing and Preservation*, *38*. https://doi.org/10.1111/jfpp.12197

Schaffer, R. J., Friel, E. N., Souleyre, E. J. F., Bolitho, K., Thodey, K., Ledger, S., Bowen, J. H., Ma, J. H., Nain, B., Cohen, D., Gleave, A. P., Crowhurst, R. N., Janssen, B. J., Yao, J. L., & Newcomb, R. D. (2007). A genomics approach reveals that aroma production in apple is controlled by ethylene predominantly at the final step in each biosynthetic pathway. *Plant Physiology*, *144*(4), 1899–1912. https://doi.org/10.1104/pp.106.093765

Shenoy, S., Pathak, N., Molins, A., Toncheva, A., Schouw, T., Hemberg, A., Laoutid, F., & Mahajan, P. V. (2022). Impact of relative humidity on ethylene removal kinetics of different scavenging materials for fresh produce industry. *Postharvest Biology and Technology*, *188*, 111881. https://doi.org/https://doi.org/10.1016/j.postharvbio.2022.111881

Shi, Y., Jiang, L., Zhang, L., Kang, R., & Yu, Z. (2014). Dynamic changes in proteins during apple (Malus x domestica) fruit ripening and storage. *Horticulture Research*, *1*. https://doi.org/10.1038/hortres.2014.6

Shinga, M. H., & Fawole, O. A. (2023). Opuntia ficus indica mucilage coatings regulate cell wall softening enzymes and delay the ripening of banana fruit stored at retail conditions. *International Journal of Biological Macromolecules*, *245*, 125550. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2023.125550

Smilanick, J. L. (2003). Use of ozone in storage and packing facilities. *Washington Tree Fruit Postharvest Conference*, 1–10.

Sun, X., Li, C., Yu, B., Wang, J., & Wang, W. (2023). Removal of gaseous volatile organic compounds via vacuum ultraviolet photodegradation: Review and prospect. *Journal of Environmental Sciences*, *125*, 427–442. https://doi.org/https://doi.org/10.1016/j.jes.2022.01.020

Suttikul, T., Nuchdang, S., Rattanaphra, D., Kingkam, W., Moonsrikaew, W., Photsathain, T., & Phalakornkule, C. (2022). Plasma-assisted ethylene removal using silica gel and zeolite in AC dielectric barrier discharge. *Chemical Engineering and Processing - Process Intensification*, *179*, 109066. https://doi.org/https://doi.org/10.1016/j.cep.2022.109066

Taiti, C., Vivaldo, G., Masi, E., Giordani, E., & Nencetti, V. (2023). Postharvest monitoring and consumer choice on traditional and modern apricot cultivars. *European Food Research and Technology*, *249*. https://doi.org/10.1007/s00217-023-04311-z

Wang, J. H., & Ray, M. B. (2000). Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. *Separation and Purification Technology*, *19*(1), 11–20. https://doi.org/https://doi.org/10.1016/S1383-5866(99)00078-7

Wang, J., Yang, C., Wang, C., Han, W., & Zhu, W. (2014). Photolytic and photocatalytic degradation of micro pollutants in a tubular reactor and the reaction kinetic models. *Separation and Purification Technology*, *122*, 105–111. https://doi.org/https://doi.org/10.1016/j.seppur.2013.11.011

Wang, W., Vignani, R., Scali, M., & Cresti, M. (2006). A universal and rapid protocol for protein extraction from recalcitrant plant tissues for protomic analysis. *Electrophoresis*, *27*, 2782–2786. https://doi.org/10.1002/elps.200500722

Welty, J., Rorrer, G. L., & Foster, D. G. (2014). *Fundamentals of Momentum, Heat and Mass Transfer*. John Wiley & Sons.

Xiao, F., Sun, X., Li, Z., & Li, X. (2020). Theoretical Study of Radical–Molecule Reactions with Negative Activation Energies in Combustion: Hydroxyl Radical Addition to Alkenes. *ACS Omega*, *5*(22), 12777–12788.

Xie, P., Yue, S., Ding, J., Wan, Y., Li, X., Ma, J., & Wang, Z. (2018). Degradation of organic pollutants by Vacuum-Ultraviolet (VUV): Kinetic model and efficiency. *Water Research*, *133*, 69–78. https://doi.org/https://doi.org/10.1016/j.watres.2018.01.019

Xu, J., Li, C., Liu, P., He, D., Wang, J., & Zhang, Q. (2014). Photolysis of low concentration H2S under UV/VUV irradiation emitted from high frequency discharge electrodeless lamps. *Chemosphere*, *109*, 202–207. https://doi.org/https://doi.org/10.1016/j.chemosphere.2014.01.065

Yu, J., Cai, W., Chen, J., Feng, L., Jiang, Y., & Cheng, Z. (2012). Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. *Journal of Environmental Sciences*, *24*(10), 1777–1784. https://doi.org/https://doi.org/10.1016/S1001-0742(11)61021-8

Zhang, Z., Jiang, S., Wang, N., Li, M., Ji, X., Sun, S., Liu, J., Wang, D., Xu, H., Qi, S., Wu, S., Fei, Z., Feng, S., & Chen, X. (2015). Identification of differentially expressed genes associated with Apple fruit ripening and softening by suppression subtractive hybridization. *PLoS ONE*, *10*(12). https://doi.org/10.1371/journal.pone.0146061

Zheng, Q., Song, J., Campbell-Palmer, L., Thompson, K., Li, L., Walker, B., Cui, Y., & Li, X. (2013). A proteomic investigation of apple fruit during ripening and in response to ethylene treatment. *Journal of Proteomics*, *93*, 276–294. https://doi.org/https://doi.org/10.1016/j.jprot.2013.02.006

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019a). Electrospun nanofibers containing TiO 2 for the photocatalytic degradation of ethylene and delaying postharvest ripening of bananas. *Food and Bioprocess Technology*, *12*, 281–287.

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019b). Electrospun Nanofibers Containing TiO2 for the Photocatalytic Degradation of Ethylene and Delaying Postharvest Ripening of Bananas. *Food and Bioprocess Technology*, *12*(2), 281–287. https://doi.org/10.1007/s11947-018-2207-1

CHAPTER EIGHT:

GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES

8. GENERAL CONCLUSIONS AND FUTURE PERSPECTIVES

8.1 Conclusion

According to Aprilliani et al. (2018b), accumulated ethylene in fruit storage can affect the postharvest life of both climacteric and non-climacteric fruit by inducing various physiological processes including undesirable ripening of fruits. Ethylene can accumulate at any point in the supply chain, and a concentration of 0.1 $\mu L\ L^{-1}$ is often cited as the threshold level for physiological activity for fruit and vegetables (Kader, 1985). Hence, reducing ethylene concentration during postharvest can have a beneficial impact and subsequently result in an extension in shelf-life and a reduction in the deleterious effects associated with accelerated ripening.

Although significant research has been conducted on developing effective technology for ethylene removal during postharvest storage, the conventional methods have coherent drawbacks that limit their commercialization, such as producing secondary waste and not being effective for continuous removal during prolonged storage. This study proposed the application of a VUV photolysis reactor for ethylene removal and preservation of fruits.

The objectives of this study are described in Chapter 1, and the overall conclusions are briefly summarised below:

- **To investigate the effectiveness of the VUV photolysis reactor in removing ethylene during the storage of apples**. The efficacy of the VUV photolysis reactor was investigated at two temperatures: room temperature (20 – 25 ℃) and 15 ℃ for 6 and 28 days, respectively. In the first experiment, the removal efficiency of the VUV photolysis reactor was compared to the removal efficiency of the commercially used technique $KMnO_4$. The removal efficiency for VUV photolysis and $KMnO_4$ was 86.9% and 25% respectively, indicating that the proposed system outperformed the commercially used KMnO4 by threefold. In the second experiment, the concentration of ethylene detected in the VUV treatment was significantly lower than that in the control chamber ($p < 0.05$), measuring 2.5 $\mu L\ L^{-1}$ and 138 $\mu L\ L^{-1}$, respectively. Therefore, it can be concluded that the VUV photolysis reactor was effective in maintaining low levels of ethylene in the storage.

- **To examine the impact of the VUV photolysis reactor on the physiological changes that occur during the storage of apples**. Apples stored in chambers linked to the VUV photolysis reactor exhibited superior quality parameters compared to those in the control group throughout the postharvest storage period. A predictive model for apple firmness was formulated, revealing that employing the VUV reactor for ethylene removal during fruit storage could potentially prolong the shelf-life of apples by an impressive 46 days, as assessed through firmness measurements.

- **To investigate the ability of the VUV photolysis reactor to suppress enzymes and proteins responsible for early ripening**. The proteomic analysis revealed a total of 17 proteins in VUV-treated apples compared to 44 proteins in the control group. Significant differences in protein expression were observed between the control and treated apples during postharvest storage. Proteins associated with firmness loss were upregulated in untreated apples. This study sheds light on the VUV photolysis reactor's impact on suppressing enzymes and proteins related to early ripening, further establishing its potential for enhancing postharvest storage practices.

- **To formulate a mathematical kinetic model to describe the process of ethylene degradation facilitated by a VUV photolysis reactor**. Two experiments were conducted to scrutinize the kinetics of ethylene removal. In the first experiment, a first-order kinetic model was assumed, and the data exhibited a good fit with the model. However, given that VUV photolysis generates different radicals under varying conditions, which influence reaction mechanisms, a second experiment adopted an n-th-order kinetic model to account for these changing mechanisms. This model revealed that light intensity and relative humidity significantly impacted the reaction rate and order. At low lamp power, ethylene degradation followed zero-order kinetics. However, as lamp power increased, the reaction order shifted to a fractional order of 1.71, indicating a more complex degradation process with higher-order dependencies. The study also explored the effects of increased relative humidity (RH) to 80% on reaction kinetics, revealing an 86% increase in the rate constant at higher RH, accompanied by a decrease in the reaction order from 1.17 to 0, indicative of a shift in degradation mechanisms. The developed kinetic models exhibited a robust agreement with experimental data, demonstrating the efficacy of the models in predicting ethylene degradation. Furthermore, an economic feasibility assessment, utilizing a figure of merit, unveiled favorable E_{EO} values within acceptable limits, affirming the energy efficiency of the VUV photolysis reactor.

8.2 Future perspectives

- **Extended storage studies at real storage conditions:** Future research should encompass long-term storage studies under real storage conditions to comprehensively evaluate the effectiveness of VUV photolysis in preserving fruit quality over extended periods. This extended analysis could delve into additional fruit quality attributes such as the production of volatile organic compounds (VOCs) and microbial spoilage. By doing so, a more thorough understanding of the reactor's impact on postharvest life, considering diverse factors, can be obtained.

- **Application to different fruit types:** This study focused on apples as the model fruit. However, it is widely acknowledged that various fruits exhibit distinct rates of ethylene production and varying sensitivities. Future research should explore the applicability of VUV photolysis across a diverse range of fruit types. Understanding how different fruits produce and respond to ethylene, and the effectiveness of VUV treatment on each can contribute to the development of tailored postharvest management strategies.

- **Proteomic analysis:** An expansion of proteomic analysis is recommended to identify and understand the specific enzymes and proteins influenced by VUV photolysis. This in-depth exploration can offer valuable insights into the molecular mechanisms governing the delayed ripening process. Such knowledge could pave the way for targeted interventions, contributing to more effective strategies for preserving fruit quality.

- **Kinetic model refinement:** The study identified an increase in reactor temperature during operation. Future research should delve into exploring more intricate kinetic models that account for additional factors, particularly temperature variations. This approach aims to enhance the precision of the model, providing a more accurate representation of the ethylene degradation process across diverse conditions.

- **Economic viability studies:** Future research should involve a comprehensive exploration of economic viability with a specific focus on scalability and practical implementation. Assessing the feasibility of integrating VUV photolysis technology into existing postharvest storage facilities will be crucial. This research can provide valuable insights into the economic benefits on a larger scale, contributing to the practicality and widespread adoption of this innovative technology.

- **Developing mathematical models for scaling up:** Research on the development of intricate mathematical models tailored for scaling up the application of VUV photolysis technology is needed. These models should account for various factors influencing scalability, such as the light model and velocity profile model. A comprehensive understanding of the scaling-up process is crucial for ensuring the seamless integration of VUV photolysis into larger postharvest storage facilities, providing valuable insights into the economic viability and practical implementation of this innovative technology on a broader scale.

BIBLIOGRAPHY

Alexander, L., & Grierson, D. (2002). Ethylene biosynthesis and action in tomato: A model for climateric fruit ripening. *Journal of Experimental Botany*, *53*, 2039–2055. https://doi.org/10.1093/jxb/erf072

Alonso Salinas, R., Motos, J. R., Núñez-Delicado, E., Gabaldon, J., & López-Miranda, S. (2022). Combined Effect of Potassium Permanganate and Ultraviolet Light as Ethylene Scavengers on Post-Harvest Quality of Peach at Optimal and Stressful Temperatures. *Agronomy*, *12*, 616. https://doi.org/10.3390/agronomy12030616

Álvarez-Hernández, M. H., Artés-Hernández, F., Ávalos-Belmontes, F., Castillo-Campohermoso, M. A., Contreras-Esquivel, J. C., Ventura-Sobrevilla, J. M., & Martínez-Hernández, G. B. (2018). Current Scenario of Adsorbent Materials Used in Ethylene Scavenging Systems to Extend Fruit and Vegetable Postharvest Life. *Food and Bioprocess Technology*, *11*(3), 511–525. https://doi.org/10.1007/s11947-018-2076-7

Álvarez-Hernández, M. H., Martínez-Hernández, G. B., Avalos-Belmontes, F., Miranda-Molina, F. D., & Artés-Hernández, F. (2020). Postharvest quality retention of apricots by using a novel sepiolite–loaded potassium permanganate ethylene scavenger. *Postharvest Biology and Technology*, *160*, 111061. https://doi.org/https://doi.org/10.1016/j.postharvbio.2019.111061

Andrews, S. A., Huck, P. M., Chute, A. J., Bolton, J. R., & Anderson, W. A. (1995). UV oxidation for drinking waterfeasibility studies for addressing specific water quality issues. *Proceedings of the AWWA WQTC, New Orleans, LA*, 18811898.

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018a). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1). https://doi.org/10.1088/1755-1315/141/1/012003

Aprilliani, F., Warsiki, E., & Iskandar, A. (2018b). Kinetic studies of potassium permanganate adsorption by activated carbon and its ability as ethylene oxidation material. *IOP Conference Series: Earth and Environmental Science*, *141*(1), 012003. https://doi.org/10.1088/1755-1315/141/1/012003

Asili, V. (2018). *Mechanistic Model for Ultraviolet Degradation of Light Hydrocarbons in Waste Gas*. University of Calgary.

Asili, V., & De Visscher, A. (2018). Modelling methane and ethane photolysis in waste gas: Optimization of reaction networks. *The Canadian Journal of Chemical Engineering*, *96*(8), 1674–1683. https://doi.org/https://doi.org/10.1002/cjce.23124

Bagheri, M., & Mohseni, M. (2014). Computational fluid dynamics (CFD) modeling of VUV/UV photoreactors for water treatment. *Chemical Engineering Journal*, *256*, 51–60. https://doi.org/https://doi.org/10.1016/j.cej.2014.06.068

Basso, A., de Fátima Peralta Muniz Moreira, R., & José, H. J. (2018). Effect of operational conditions on photocatalytic ethylene degradation applied to control tomato ripening. *Journal of Photochemistry and Photobiology A: Chemistry*, *367*, 294–301. https://doi.org/10.1016/j.jphotochem.2018.08.027

Bu, J., Yu, Y., Aisikaer, G., & Ying, T. (2013). Postharvest UV-C irradiation inhibits the production of ethylene and the activity of cell wall-degrading enzymes during softening of tomato (Lycopersicon esculentum L.) fruit. *Postharvest Biology and Technology*, *86*, 337–345. https://doi.org/10.1016/j.postharvbio.2013.07.026

Chang, K.-L., Sekiguchi, K., Wang, Q., & Zhao, F. (2013). Removal of Ethylene and Secondary Organic Aerosols Using UV-C-254 (+) (185) (nm) with TiO2 Catalyst. *Aerosol and Air Quality Research*, *13*, 618–626. https://doi.org/10.4209/aaqr.2012.07.0195

Chen, F., Yang, Q., Pehkonen, S. O., & Ray, M. B. (2004). Modeling of Gas-Phase Photodegradation of Chloroform and Carbon Tetrachloride. *Journal of the Air & Waste Management Association*, *54*(10), 1281–1292. https://doi.org/10.1080/10473289.2004.10470991

Chen, L., Xie, X., Song, X., Luo, S., Ye, S., & Situ, W. (2021). Photocatalytic degradation of ethylene in cold storage using the nanocomposite photocatalyst MIL101(Fe)-TiO2-rGO. *Chemical Engineering Journal*, *424*, 130407. https://doi.org/https://doi.org/10.1016/j.cej.2021.130407

Cheng, Z.-W., Jiang, Y.-F., Zhang, L.-L., Chen, J.-M., & Wei, Y.-Y. (2011). Conversion characteristics and kinetic analysis of gaseous α-pinene degraded by a VUV light in various reaction media. *Separation and Purification Technology*, *77*(1), 26–32. https://doi.org/https://doi.org/10.1016/j.seppur.2010.11.014

Chou, M.-S., & Chang, K.-L. (2007). UV/ozone degradation of gaseous hexamethyldisilazane (HMDS). *Chemosphere*, *69*(5), 697–704. https://doi.org/https://doi.org/10.1016/j.chemosphere.2007.05.040

Da Silva, J. C. G., Alves, J. L. F., Mumbach, G. D., & Di Domenico, M. (2023). Photocatalytic degradation of ethylene in tubular microreactor coated with thin-film of TiO2: Mathematical modeling with experimental validation and geometry analysis using computational fluid dynamics simulations. *Chemical Engineering Research and Design*, *196*, 101–117. https://doi.org/https://doi.org/10.1016/j.cherd.2023.06.036

De Bruijn, J., Gómez, A. E., Melín, P., Loyola, C., Solar, V. A., & Valdés, H. (2019). Effect of doping natural zeolite with copper and zinc cations on ethylene removal and postharvest tomato fruit quality. *Chemical Engineering Transactions*, *75*, 265–270. https://doi.org/10.3303/CET1975045

de Chiara, M. L. V., Pal, S., Licciulli, A., Amodio, M. L., & Colelli, G. (2015). Photocatalytic degradation of ethylene on mesoporous TiO2/SiO2 nanocomposites: Effects on the ripening of mature green tomatoes. *Biosystems Engineering*, *132*, 61–70. https://doi.org/10.1016/j.biosystemseng.2015.02.008

Department of Agriculture, F. and F. (2022). *A PROFILE OF THE SOUTH AFRICAN APPLE MARKET VALUE CHAIN 2020*. www.dalrrd.gov.za

Du, L., Song, J., Forney, C., Palmer, L. C., Fillmore, S., & Zhang, Z. (2016). Proteome changes in banana fruit peel tissue in response to ethylene and high-temperature treatments. *Horticulture Research*, *3*. https://doi.org/10.1038/hortres.2016.12

Duca, C. (2015). *Effect of water matrix on Vacuum UV process for the removal of organic micropollutants in surface water*. The University of British Columbia.

Duque, L. F., Amador, M. V., Guzmán, M., Asensio, C., & Valenzuela, J. L. (2021). Development of a new essential oil-based technology to maintain fruit quality in tomato. *Horticulturae*, *7*(9), 303.

Emadpour, M., Ghareyazie, B., Rezaei kalaj, Y., Entesari, M., & Bouzari, N. (2015). *Effect of the Potassium Permanganate Coated Zeolite Nanoparticles on the Quality Characteristic and Shelf Life of Peach and Nectarine*.

Feiyan, C., Pehkonen, S. O., & Ray, M. B. (2002). Kinetics and mechanisms of UV-photodegradation of chlorinated organics in the gas phase. *Water Research*, *36*(17), 4203–4214. https://doi.org/https://doi.org/10.1016/S0043-1354(02)00140-9

Fonseca, J. de M., Pabón, N. Y. L., Nandi, L. G., Valencia, G. A., Moreira, R. de F. P. M., & Monteiro, A. R. (2021). Gelatin-TiO2-coated expanded polyethylene foam nets as ethylene scavengers for fruit postharvest application. *Postharvest Biology and Technology*, *180*, 111602. https://doi.org/https://doi.org/10.1016/j.postharvbio.2021.111602

Hooijberg, E. H., Miller, M., Cray, C., Buss, P., Steenkamp, G., & Goddard, A. (2018). Serum protein electrophoresis in healthy and injured southern white rhinoceros (Ceratotherium simum simum). *PLoS ONE*, *13*(7). https://doi.org/10.1371/journal.pone.0200347

Hrazdina, G., Kiss, E., Galli, Z., RosenField, C., Norelli, J. L., & Aldwinckle, H. S. (2003). DOWN REGULATION OF ETHYLENE PRODUCTION IN “ROYAL GALA” APPLES. *Acta Horticulturae*, *628*, 239–251. https://doi.org/10.17660/ActaHortic.2003.628.29

Huang, H., Huang, H., Zhang, L., Hu, P., Xu, Y., Ye, X., Liang, X., Chen, J., & Ji, M. (2014). Photooxidation of Gaseous Benzene by 185 nm VUV Irradiation. *Environmental Engineering Science*, *31*(8), 481–486. https://doi.org/10.1089/ees.2014.0100

Huang, H., Lu, H., Huang, H., Wang, L., Zhang, J., & Leung, D. Y. C. (2016). Recent development of VUV-based processes for air pollutant degradation. *Frontiers in Environmental Science*, *4*, 17.

Kader, A. A. (1985). Ethylene-induced Senescence and Physiological Disorders in Harvested Horticultural Crops. *HortScience*, *20*(1), 54–57. https://doi.org/10.21273/HORTSCI.20.1.54

Kang, I.-S., Xi, J., & Hu, H.-Y. (2018). Photolysis and photooxidation of typical gaseous VOCs by UV Irradiation: Removal performance and mechanisms. *Frontiers of Environmental Science & Engineering*, *12*, 1–14.

Keller, N., Ducamp, M.-N., Robert, D., & Keller, V. (2013). Ethylene removal and fresh product storage: a challenge at the frontiers of chemistry. Toward an approach by photocatalytic oxidation. *Chemical Reviews*, *113*(7), 5029–5070.

Khedr, E., & Al-Khayri, J. (2023). Synergistic Effects of Tragacanth and Anti-ethylene Treatments on Postharvest Quality Maintenance of Mango (Mangifera indica L.). *Plants*, *12*, 1887. https://doi.org/10.3390/plants12091887

Kim, K., Chun, I.-J., Suh, J. H., & Sung, J. (2023). Relationships between sensory properties and metabolomic profiles of different apple cultivars. *Food Chemistry: X*, *18*, 100641. https://doi.org/https://doi.org/10.1016/j.fochx.2023.100641

Li, J., Sun, Q., Sun, Y., Chen, B., Wu, X., & Le, T. (2019). Improvement of banana postharvest quality using a novel soybean protein isolate/cinnamaldehyde/zinc oxide bionanocomposite coating strategy. *Scientia Horticulturae*, *258*, 108786. https://doi.org/https://doi.org/10.1016/j.scienta.2019.108786

Li, L., Ban, Z., Limwachiranon, J., & Luo, Z. (2017). Proteomic Studies on Fruit Ripening and Senescence. *Critical Reviews in Plant Sciences*, *36*(2), 116–127. https://doi.org/10.1080/07352689.2017.1355173

Li, M., Li, D., Feng, F., Zhang, S., Ma, F., & Cheng, L. (2016). Proteomic analysis reveals dynamic regulation of fruit development and sugar and acid accumulation in apple. *Journal of Experimental Botany*, *67*(17), 5145–5157. https://doi.org/10.1093/jxb/erw277

Liang, P., de Aragão, E. V. F., Giani, L., Mancini, L., Pannacci, G., Marchione, D., Vanuzzo, G., Faginas-Lago, N., Rosi, M., & Skouteris, D. (2023). OH (2Π)+ C2H4 reaction: a combined crossed molecular beam and theoretical study. *The Journal of Physical Chemistry A*, *127*(21), 4609–4623.

Lien, N., Horváth, V., Mai, D., Hitka, G., Zsom, T., & Kókai, Z. (2018). Effect of 1-MCP, ethylene absorber and ozone on melon quality during storage. *Progress in Agricultural Engineering Sciences*, *14*, 101–110. https://doi.org/10.1556/446.14.2018.S1.10

Lin, S., Miao, Y., Huang, H., Zhang, Y., Huang, L., & Cao, J. (2022). Arabinogalactan Proteins: Focus on the Role in Cellulose Synthesis and Deposition during Plant Cell Wall Biogenesis. *International Journal of Molecular Sciences*, *23*, 6578. https://doi.org/10.3390/ijms23126578

Lin, Y.-T., Weng, C.-H., Hsu, H.-J., Huang, J.-W., Srivastav, A. L., & Shiesh, C.-C. (2014). Effect of oxygen, moisture, and temperature on the photo oxidation of ethylene on N-doped TiO2 catalyst. *Separation and Purification Technology*, *134*, 117–125. https://doi.org/https://doi.org/10.1016/j.seppur.2014.07.039

Liu, A., Mulac, W. A., & Jonah, C. D. (1988). Kinetic isotope effects in the gas-phase reaction of hydroxyl radicals with ethylene in the temperature range 343-1173 K and 1-atm pressure. *The Journal of Physical Chemistry*, *92*(13), 3828–3833.

Mabusela, B., Belay, Z., Godongwana, B., & Caleb, O. (2023). Application of VUV photolysis reactor for shelf-life extension and prediction of apple fruit. *[Status: Submitted]*.

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023a). Application of vacuum ultraviolet photolysis reactor and loss of firmness prediction for stored ‘Fuji’ apples. In *Acta Horticulturae* (Issue 1382). https://doi.org/10.17660/ActaHortic.2023.1382.2

Mabusela, B. P., Belay, Z. A., Godongwana, B., & Caleb, O. J. (2023b). Impact of vacuum ultraviolet (VUV) photolysis on ethylene degradation kinetics and removal in mixed-fruit storage, and direct exposure to ‘Fuji’ apples during storage. *Journal of Food Science and Technology*. https://doi.org/10.1007/s13197-023-05775-3

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, & Caleb, O. J. (2022). Advances in Vacuum Ultraviolet Photolysis in the Postharvest Management of

Fruit and Vegetables Along the Value Chains: a Review. *Food and Bioprocess Technology*, *15*(1), 28–46. https://doi.org/10.1007/s11947-021-02703-1

Mabusela, B. P., Belay, Z. A., Godongwana, B., Pathak, N., Mahajan, P. V, Mathabe, P. M. K., & Caleb, O. J. (2021). Trends in ethylene management strategies: towards mitigating postharvest losses along the South African value chain of fresh produce – a review. *South African Journal of Plant and Soil*, *38*(5), 347–360. https://doi.org/10.1080/02571862.2021.1938260

Mahmoudkhani, F., Rezaei, M., Asili, V., Atyabi, M., Vaisman, E., Langford, C., & De Visscher, A. (2016). Benzene degradation in waste gas by photolysis and photolysis-ozonation: experiments and modeling. *Frontiers of Environmental Science & Engineering*, *10*, 1–10. https://doi.org/10.1007/s11783-016-0876-4

Marhavý, P., Kurenda, A., Siddique, S., Dénervaud Tendon, V., Zhou, F., Holbein, J., Hasan, M. S., Grundler, F. M. W., Farmer, E. E., & Geldner, N. (2019). Single-cell damage elicits regional, nematode-restricting ethylene responses in roots. *The EMBO Journal*, *38*(10), e100972. https://doi.org/https://doi.org/10.15252/embj.2018100972

Namrata Pathak. (2019). *Photocatalysis and vacuum ultraviolet light photolysis as ethylene removal techniques for potential application in fruit storage*. Technical University Berlin.

Palou, L., Crisosto, C. H., Garner, D., & Basinal, L. M. (2003). Effect of continuous exposure to exogenous ethylene during cold storage on postharvest decay development and quality attributes of stone fruits and table grapes. *Postharvest Biology and Technology*, *27*(3), 243–254.

Pathak, N., Caleb, O. J., Geyer, M., Herppich, W. B., Rauh, C., & Mahajan, P. V. (2017). Photocatalytic and photochemical oxidation of ethylene: Potential for storage of fresh produce—A review. *Food and Bioprocess Technology*, *10*, 982–1001.

Pathak, N., Caleb, O. J., Rauh, C., & Mahajan, P. V. (2017). Effect of process variables on ethylene removal by vacuum ultraviolet radiation: Application in fresh produce storage. *Biosystems Engineering*, *159*, 33–45. https://doi.org/https://doi.org/10.1016/j.biosystemseng.2017.04.008

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. https://doi.org/https://doi.org/10.1016/j.postharvbio.2018.09.006

Potuschak, T., Lechner, E., Parmentier, Y., Yanagisawa, S., Grava, S., Koncz, C., & Genschik, P. (2003). EIN3-Dependent Regulation of Plant Ethylene Hormone Signaling by Two Arabidopsis F Box Proteins: EBF1 and EBF2. *Cell*, *115*(6), 679–689. https://doi.org/10.1016/S0092-8674(03)00968-1

Sardabi, F., Mohtadinia, J., Shavakhi, F., & Jafari, A. A. (2014). The Effects of 1-Methylcyclopropen (1-MCP) and Potassium Permanganate Coated Zeolite Nanoparticles on Shelf life Extension and Quality Loss of Golden Delicious Apples. *Journal of Food Processing and Preservation*, *38*. https://doi.org/10.1111/jfpp.12197

Schaffer, R. J., Friel, E. N., Souleyre, E. J. F., Bolitho, K., Thodey, K., Ledger, S., Bowen, J. H., Ma, J. H., Nain, B., Cohen, D., Gleave, A. P., Crowhurst, R. N., Janssen, B. J., Yao, J. L., & Newcomb, R. D. (2007). A genomics approach reveals that aroma production in apple is controlled by ethylene predominantly at the final step in each biosynthetic pathway. *Plant Physiology*, *144*(4), 1899–1912. https://doi.org/10.1104/pp.106.093765

Shenoy, S., Pathak, N., Molins, A., Toncheva, A., Schouw, T., Hemberg, A., Laoutid, F., & Mahajan, P. V. (2022). Impact of relative humidity on ethylene removal kinetics of different scavenging materials for fresh produce industry. *Postharvest Biology and Technology*, *188*, 111881. https://doi.org/https://doi.org/10.1016/j.postharvbio.2022.111881

Shi, Y., Jiang, L., Zhang, L., Kang, R., & Yu, Z. (2014). Dynamic changes in proteins during apple (Malus x domestica) fruit ripening and storage. *Horticulture Research*, *1*. https://doi.org/10.1038/hortres.2014.6

Shinga, M. H., & Fawole, O. A. (2023). Opuntia ficus indica mucilage coatings regulate cell wall softening enzymes and delay the ripening of banana fruit stored at retail conditions. *International Journal of Biological Macromolecules*, *245*, 125550. https://doi.org/https://doi.org/10.1016/j.ijbiomac.2023.125550

Smilanick, J. L. (2003). Use of ozone in storage and packing facilities. *Washington Tree Fruit Postharvest Conference*, 1–10.

Sun, X., Li, C., Yu, B., Wang, J., & Wang, W. (2023). Removal of gaseous volatile organic compounds via vacuum ultraviolet photodegradation: Review and prospect. *Journal of Environmental Sciences*, *125*, 427–442. https://doi.org/https://doi.org/10.1016/j.jes.2022.01.020

Suttikul, T., Nuchdang, S., Rattanaphra, D., Kingkam, W., Moonsrikaew, W., Photsathain, T., & Phalakornkule, C. (2022). Plasma-assisted ethylene removal using silica gel and zeolite in AC dielectric barrier discharge. *Chemical Engineering and Processing - Process Intensification*, *179*, 109066. https://doi.org/https://doi.org/10.1016/j.cep.2022.109066

Taiti, C., Vivaldo, G., Masi, E., Giordani, E., & Nencetti, V. (2023). Postharvest monitoring and consumer choice on traditional and modern apricot cultivars. *European Food Research and Technology*, *249*. https://doi.org/10.1007/s00217-023-04311-z

Wang, J. H., & Ray, M. B. (2000). Application of ultraviolet photooxidation to remove organic pollutants in the gas phase. *Separation and Purification Technology*, *19*(1), 11–20. https://doi.org/https://doi.org/10.1016/S1383-5866(99)00078-7

Wang, J., Yang, C., Wang, C., Han, W., & Zhu, W. (2014). Photolytic and photocatalytic degradation of micro pollutants in a tubular reactor and the reaction kinetic models. *Separation and Purification Technology*, *122*, 105–111. https://doi.org/https://doi.org/10.1016/j.seppur.2013.11.011

Wang, W., Vignani, R., Scali, M., & Cresti, M. (2006). A universal and rapid protocol for protein extraction from recalcitrant plant tissues for protomic analysis. *Electrophoresis*, *27*, 2782–2786. https://doi.org/10.1002/elps.200500722

Welty, J., Rorrer, G. L., & Foster, D. G. (2014). *Fundamentals of Momentum, Heat and Mass Transfer*. John Wiley & Sons.

Xiao, F., Sun, X., Li, Z., & Li, X. (2020). Theoretical Study of Radical–Molecule Reactions with Negative Activation Energies in Combustion: Hydroxyl Radical Addition to Alkenes. *ACS Omega*, *5*(22), 12777–12788.

Xie, P., Yue, S., Ding, J., Wan, Y., Li, X., Ma, J., & Wang, Z. (2018). Degradation of organic pollutants by Vacuum-Ultraviolet (VUV): Kinetic model and efficiency. *Water Research*, *133*, 69–78. https://doi.org/https://doi.org/10.1016/j.watres.2018.01.019

Xu, J., Li, C., Liu, P., He, D., Wang, J., & Zhang, Q. (2014). Photolysis of low concentration H2S under UV/VUV irradiation emitted from high frequency discharge electrodeless lamps. *Chemosphere*, *109*, 202–207. https://doi.org/https://doi.org/10.1016/j.chemosphere.2014.01.065

Yu, J., Cai, W., Chen, J., Feng, L., Jiang, Y., & Cheng, Z. (2012). Conversion characteristics and mechanism analysis of gaseous dichloromethane degraded by a VUV light in different reaction media. *Journal of Environmental Sciences*, *24*(10), 1777–1784. https://doi.org/https://doi.org/10.1016/S1001-0742(11)61021-8

Zhang, Z., Jiang, S., Wang, N., Li, M., Ji, X., Sun, S., Liu, J., Wang, D., Xu, H., Qi, S., Wu, S., Fei, Z., Feng, S., & Chen, X. (2015). Identification of differentially expressed genes associated with Apple fruit ripening and softening by suppression subtractive hybridization. *PLoS ONE*, *10*(12). https://doi.org/10.1371/journal.pone.0146061

Zheng, Q., Song, J., Campbell-Palmer, L., Thompson, K., Li, L., Walker, B., Cui, Y., & Li, X. (2013). A proteomic investigation of apple fruit during ripening and in response to ethylene treatment. *Journal of Proteomics*, *93*, 276–294. https://doi.org/https://doi.org/10.1016/j.jprot.2013.02.006

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019a). Electrospun nanofibers containing TiO 2 for the photocatalytic degradation of ethylene and delaying postharvest ripening of bananas. *Food and Bioprocess Technology*, *12*, 281–287.

Zhu, Z., Zhang, Y., Shang, Y., & Wen, Y. (2019b). Electrospun Nanofibers Containing TiO2 for the Photocatalytic Degradation of Ethylene and Delaying Postharvest Ripening of Bananas. *Food and Bioprocess Technology*, *12*(2), 281–287. https://doi.org/10.1007/s11947-018-2207-1