Food and Bioproducts Processing 147 (2024) 230–238

Contents lists available at ScienceDirect

Food and Bioproducts Processing

journal homepage: www.elsevier.com/locate/fbp

Ethylene degradation via vacuum ultraviolet photolysis: nth-order kinetic model, energy consumption assessment, and a case study for 'Fuji' apples under retail conditions

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ARTICLE INFO

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

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 (E_{EO}), 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°C 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.

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 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 colour changes, preserve flavour and aroma, reduce pathogen susceptibility, and enhance overall quality control (Álvarez-Hernández et al., 2018). Hence, the effective management of ethylene concentrations during the storage and transportation of fruit and vegetables is crucial in preventing premature ripening and minimizing postharvest losses and waste.

Conventional technologies, including adsorption, catalytic oxidation, K_2MnO_4 oxidation, and biofilters, have been employed to regulate

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https://doi.org/10.1016/j.fbp.2024.07.006
Received 15 March 2024; Received in revised form 24 May 2024; Accepted 8 July 2024
Available online 11 July 2024

ethylene concentrations and extend the shelf-life of fruit (Álvarez-Hernández et al., 2020; 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 investigated the degradation kinetics of ethylene using VUV photolysis and assessed the efficacy of VUV photolysis in preserving the quality of apple fruit under retail conditions. By exploring the kinetic behaviour of VUV photolysis, valuable information can be

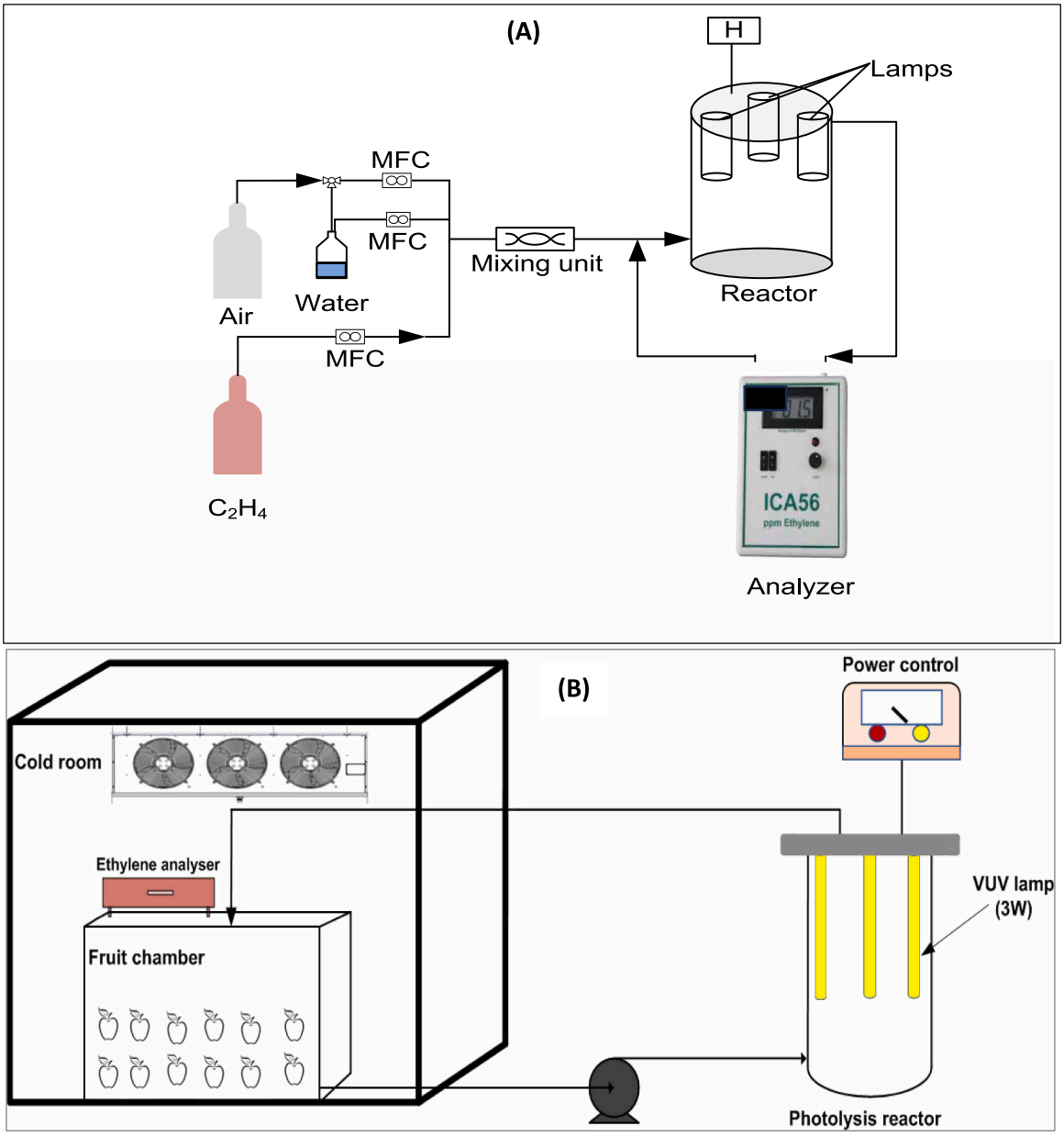

Fig. 1. **(A)** Schematic of the experimental batch reactor. MFC = Mass flow controller. **(B)** Schematic diagram of the storage experiments.

gained to advance the understanding and application of this technique in ethylene removal for enhanced postharvest management 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. This work provides the basis for upscale optimization of the performance of the VUV photolysis reactor under optimum cold storage conditions and long-term duration.

2. Materials and methods

2.1. Ethylene degradation rate

The VUV photolysis reactor consisted of three VUV lamps as shown in Fig. 1. The reactor lid was constructed from borosilicate glass and featured openings for VUV lamp fittings and a temperature and humidity sensor. The VUV lamps emit wavelengths ranging from 10 to 200 nm, this falls within the UV-C wavelength spectrum (Liu et al., 2019), which can induce autocatalytic photooxidation reactions that results in the degradation of ethylene. VUV radiation is readily absorbed by atmospheric oxygen, leading to the generation of highly reactive oxygen species and hydroxyl radicals. These reactive species facilitate the oxidation of ethylene. For UV-A and UV-B, the absorption spectrum is limited due to the band gap, and their radiation energy is insufficient to separate strong chemical bonds or induce major photochemical degradation. Out of the three UV lights, the least effective is UV-A followed by UV-B (Pathak et al., 2018; Smoleń et al., 2024). Additionally, UV-A radiation has been observed to be ineffective in degrading ethylene (Pathak et al., 2018). The desired light intensity was achieved through a combination of lamps. The radiation intensity on the reactor surface was then measured using an ultraviolet light detector. 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 analyser (Fricaval 89 S.L, Valencia, Spain). This analyser 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 was allowed to fill the reactor until the desired concentration (50 μL L^{-1}) was achieved. The VUV lamps were switched on when the ethylene concentration in the reactor was stable. Kinetics experiments were conducted by varying light intensity (0.0005, 0.0014, and 0.0021 mW m^{-2}) and humidity (20 % to 80 % RH) in the reactor. All experiments were conducted in triplicate and at ambient room temperature and atmospheric pressure.

2.2. Kinetic modelling

The photolysis oxidation reaction occurring in a batch reactor can be described by a mass balance equation, specifically an ordinary differential equation (Eqn.), 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.

$$\frac{dC_A}{dt} = r_a \tag{1}$$

The oxidation of ethylene by VUV photolysis typically involves two mechanisms: (i) the direct mechanism where the ethylene is directly decomposed by VUV radiation (Eq. 2), and (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 (Eq. 3) (Mabusela et al., 2022).

$$C_2H_4 + h\nu \xrightarrow{k_1} oxidation\ products \tag{2}$$

$$C_2H_4 + \mathrm{OH} \xrightarrow{k_2} \mathrm{x}C_2H_4 + yCO_2 \tag{3}$$

Therefore, the overall photolytic degradation rate (r_a) of ethylene can be represented by the following non-elementary expression in Eq. 4 (Xie et al., 2018):

$$r_a = k_1[C_2H_4]^x + k_2[C_2H_4]^y[OH]_{ss}^z \tag{4}$$

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:

$$\frac{dC_{C_2H_4}}{dt} = -k_1[C_2H_4]^x \tag{5}$$

Eq. 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 analyse 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, assuming that the reaction orders with respect to ethylene concentration for both pathways are equal ($x = y$), Eq. (4) can be simplified and expressed as Eq. (6), which is then similar to Eq. (5):

$$\frac{dC_{C_2H_4}}{dt} = -k_{app}[C_2H_4]^n \tag{6}$$

where,

$$k_{app} = k_1 + k_2[OH]_{ss}^z \tag{7}$$

In VUV photolysis, most authors assumed 1st and 2nd order degradation kinetics (Cheng et al., 2011; 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 behaviour. Thus, Eqs. (5) and (6) can be solved to obtain ethylene concentration as a function of time. The solution to the equations is as follows:

$$C_A = \left[C_{AO}^{-n+1} - (n-1)kt\right]^{\frac{1}{-n+1}} \tag{8}$$

Eq. (8) is developed based on the following conditions of operation and assumptions: (i) 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; (ii) negligible pressure change in the reactor, meaning the volume and gas density do not change and hence the fractional-volume change (ε) is zero; and (iii) 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, USA).

2.3. 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 E_{EO} can be calculated using the following formula:

$$E_{EO} = \frac{P \times t \times 10^3}{V \times \log \frac{C_0}{C}} \quad (9)$$

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.

2.4. Case study

The storage investigation of 'Fuji' apples was conducted using 30 L chambers. Fresh 'Fuji' apples harvested at commercial maturity (total soluble solids (TSS), 12.8 % ± 0.14; titratable acidity (TA), 0.37 % ± 0.37) 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 bulk harvest was sorted for uniformly sized and non-damaged apples, and these were divided into two treatment batches. 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 and RH 80 % (± 1.0) for 28 days to mimic retail display conditions. In the treatment experiment, only the chamber was placed inside the cold room, and the air was circulated through the reactor using a pump (Mabusela et al., 2023). A detailed schematic diagram is provided is Fig. 1B.

Additionally, the optimum RH for apple storage ranges between 90 % and 95 % for long-term cold storage temperatures between 0.5 and 4°C depending on the cultivar (Hasan et al., 2024). However, under retail conditions such high RH is could often be detrimental. For example, Tu et al. (2000) assessed the impact of RH on apple quality at retail conditions. Notably, holding apples at high RH (95 %) resulted in the development of mealy texture, due to low tensile strength and enhanced cell separation. Hence, this work was conducted at 80 % RH. Fruits in the chambers connected to the VUV reactor and control were sampled at regular intervals and processed using a juice extractor (4294 J700, Braun, China). The juice obtained was used to measure pH, TSS and titratable acidity (TA). Total soluble solid was measured using a calibrated hand-held refractometer (PAL-1, ATAGO, Japan), and the results were expressed as %. Titratable acidity was obtained via titration of fruit juice with 0.33 N of sodium hydroxide (NaOH) at a pH of 8.2, using Crison Titromatic 1 S/2B (Crison Instruments, Barcelona, Spain) and the results were expressed as %. The TSS/TA was calculated using the results obtained.

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 ($p \leq 0.05$).

3. Results and discussion

3.1. Effects of light intensity

The presence of VUV lamps, which generate energetic photons, is crucial for the photodegradation of pollutants (Sun et al., 2023). In this study, the intensity was varied from 0.0005 mW m^{-2} to 0.0021 mW m^{-2} 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 Fig. 2. It is evident that at 0.0021 mW m^{-2} intensity, ethylene was degraded entirely within 16 min, and this degradation time increased to 21 min at 0.0014 mW m^{-2}, while it took 42 min to degrade ethylene at 0.0005 mW/m^2 completely. The conversion efficiency increased from 19.3 % to 94.7 % as the intensity increased from 0.0005 mW m^{-2} to 0.0021 mW m^{-2}, respectively. These results are consistent with the literature, as Xie et al. (2018) reported an increase in the percentage removal of organic pollutant from 68.7 % to 94.8 % when the light intensity was increased by a factor of 2.

Higher light intensity leads to the generation of more photons, resulting in enhanced ethylene removal. Since the ethylene concentration remained constant, the ethylene molecules under 0.0021 mW m^{-2} intensity received more photons compared to those under 0.0005 mW m^{-2} intensity, leading to increased ethylene conversion. Additionally, increasing intensity 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).

3.2. Effect of relative humidity

The ethylene concentration and light intensity were kept constant at 51.6 μL L^{-1} and 0.0021 mW m^{-2}, respectively. The effect of RH humidity was studied at two levels: 20 % and 80 %. The impact of RH on the removal efficiency of ethylene is presented in Fig. 3. Increasing RH from 20 % to 80 % resulted in a significant increase in the removal efficiency of ethylene, from 73 % to 95 %, respectively ($p < 0.05$). As observed in Eq. 6, moisture in the system promotes the formation of highly reactive OH radicals that readily react with ethylene leading to enhanced degradation.

Consistent with the findings of this work, 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 favourable application of VUV photolysis in the postharvest management for ethylene, as many fruits and vegetables are stored in high-humidity environments.

3.3. Kinetic analysis of ethylene

3.3.1. Effect of lamp power

A notable trend was observed: as the light intensity increased from 0.0005 mW m^{-2} to 0.0021 mW m^{-2}, the rate constant also significantly increased by 86 %. Table 1 presents the rate constants of ethylene degradation at various light intensities. This observation aligns with the well-known dependence of the rate constant in VUV photolysis on light intensity (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

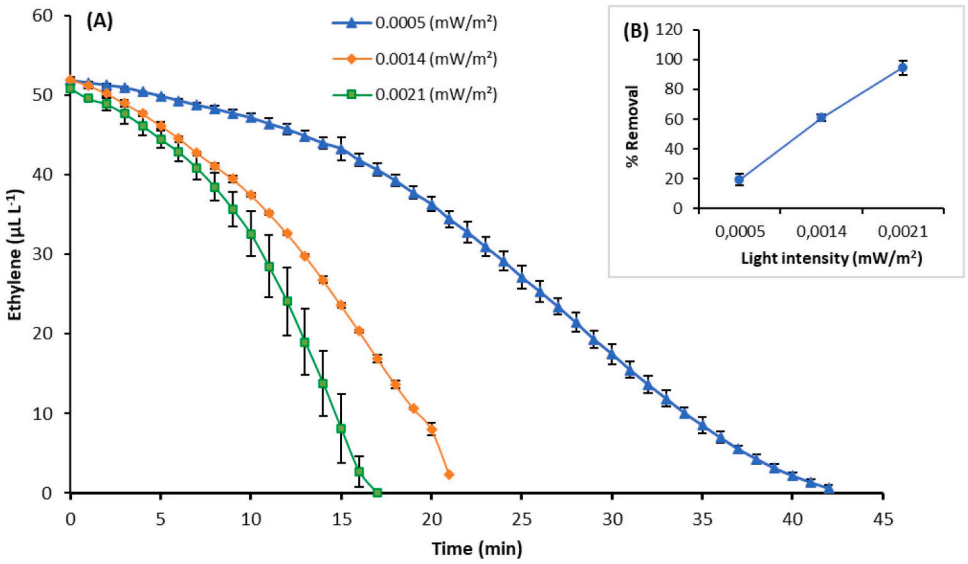

Fig. 2. Changes in ethylene concentrations and percentage removal at different lamp powers **(A)**, and percentage removal of ethylene calculated after 15 min **(B)**. Error bars indicate standard deviation from mean value ($n = 3$).

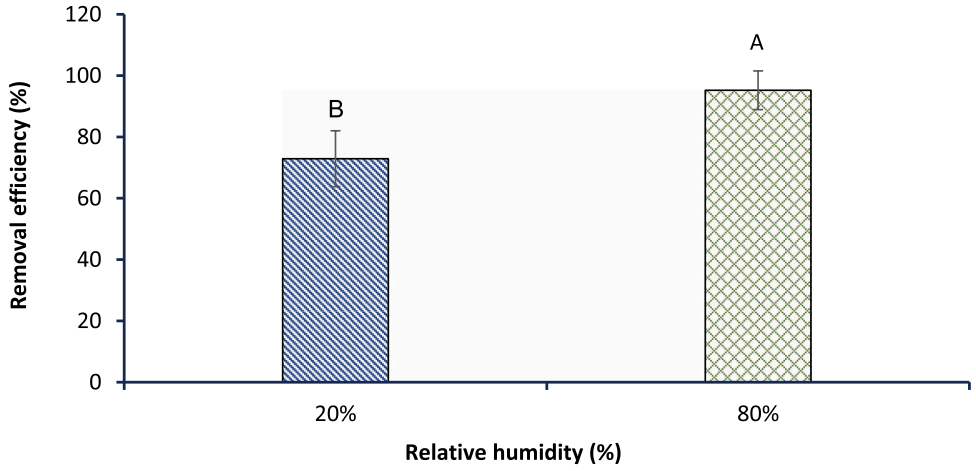

Fig. 3. Ethylene removal efficiency at two different RH (20 % and 80 %). Ethylene concentration = 51.6 µL L^{-1} and light intensity = 0.0021 mW m^{-2}. Error bars indicate standard deviation from mean value ($n = 3$), and bars with different letters are significantly different at 95 % confidence interval.

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

Intensity (mW m^{-2})	Rate constant		R^2	*RSME*
	Zero-order ($n = 0$)	Fractional order ($n = 1.17$)		
0.0005	0.497	-	98.30	0.445
0.0014	1.55	-	97.50	1.66
0.0021	-	3.627	99.55	1.69

[a] Rate constant and reaction order calculated using Eq. 8.

(HMDS), have reported similar trends.

The degradation of ethylene at intensity 0.0005 mW m^{-2} and 0.0014 mW m^{-2} 3 W followed zero-order kinetics. However, when the intensity r was further increased to 0.0021 mW m^{-2}, the reaction followed a fractional order with $n = 1.17$. To assess the accuracies of these kinetic models, Fig. 4 shows the deviation between the experimental data and mathematically predicted 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 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 intensity likely leads to the generation of additional highly reactive oxygen species, triggering chain reactions and affecting the reaction rate and mechanisms. The change in reaction mechanisms contributed to the change in reaction order.

A shift in reaction order in VUV photolysis is common due to the varied nature and types of reactive species generated under different operational conditions. For instance, the hydrogen peroxide-based oxidation of α-pinene followed only first order, however, all other reaction parameters were kept constant, with no leaching activity against the active species (Cánepa et al., 2011). In contrast, Cheng et al. (2011) observed a change in reaction order from 1st to 2nd order with an increase in the concentration of α-pinene. In the 2nd order one of the reactants is changed to the second power or two reactants changed from zero to the first power. In this work, according to reactions 2 and 3, increasing lamp power, results in increased number of photons, leading

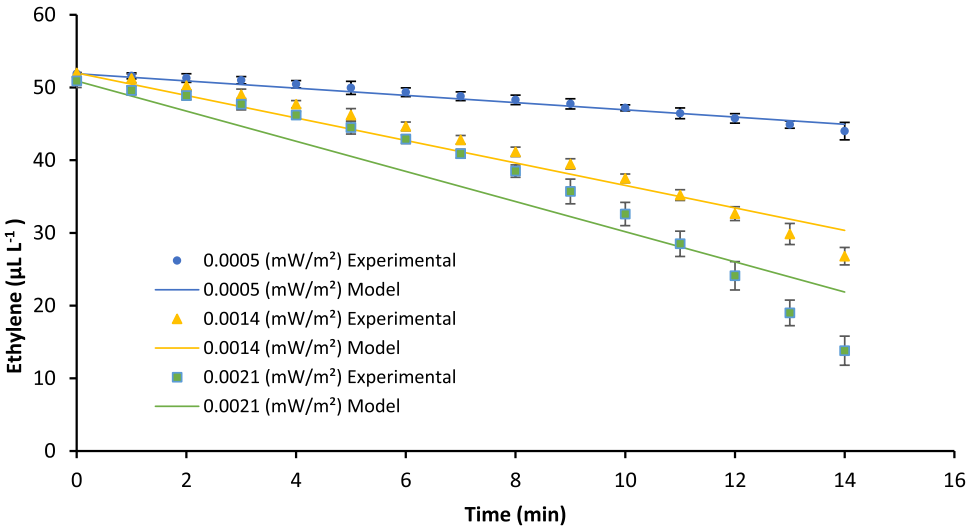

Fig. 4. Description of changes in ethylene concentrations based on experimental data and mathematical prediction of the effects of light intensity (RH = 20 %, C_0 = 51.6 µL L^{-1}). Error bars indicate standard deviation from mean value (n = 3).

to generation of more hydroxyl radicals. This, in turn, alters the ethylene degradation pathway, as evidenced by the change in reaction order.

While the kinetic model effectively characterized ethylene degradation, it is essential to acknowledge that the complexity of industrial-scale processes often necessitates more comprehensive models for reactor design. Therefore, it is recommended that future research focus on the development of comprehensive model that can capture the dynamics inherent in large-scale reactor systems.

3.3.2. *Effect of relative humidity*

The impact of increasing relative humidity (RH) to 80 % on the rate constant and reaction order is depicted in Fig. 5. Through calculations based on Eq. (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 Fig. 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 20–80 % 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 and 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.

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

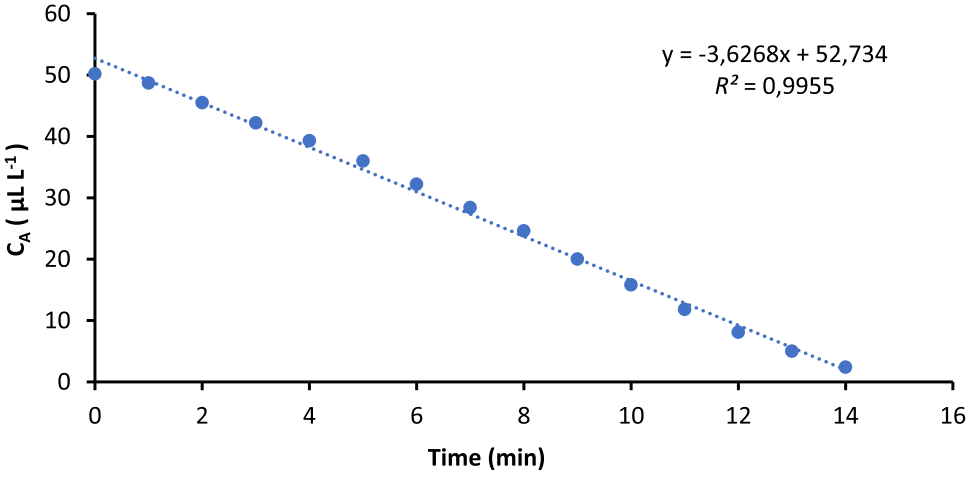

Fig. 5. Zero-order kinetic model. Experimental conditions: [C_2H_4] = 51.6 µL L^{-1}, 0.0021 mW/m^2, and RH = 80 %.

of the designed VUV photolysis reactor. Table 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 and Chang, 2007).

The VUV reactor in this study achieved the lowest E_{EO} value of 0.61 kW L^{-1} $order^{-1}$ at 9 W 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 and 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 m^{-3} $order^{-1}$, 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 thereby ultimately minimizing food waste.

3.5. Application of VUV photolysis on apple storage

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 Fig. 6. At the end of day 28, the concentration of ethylene detected in the VUV treatment was significantly lower than the control chamber ($p < 0.05$), 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 the 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.

3.5.2. Effects on quality attributes

The results indicate that the pH of control apples was 3.83 at the end of storage duration, slightly higher than that of treated apples. The pH of apples can be influenced by the amount of ethylene in storage (Table 3). Since an increase in fruit pH is associated with fruit ripening (Alonso Salinas et al., 2022), the apples in the control were riper 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. The titratable acidity of 'Fuji' apples declined by 28 % under control storage conditions, while the VUV treatment only declined by 21 % at the end of storage (Table 3). According to Caleb et al. (2016), during postharvest storage the concentration of organic acids could decrease due to their metabolism as a respiratory substrate and/or their conversion into sugars. Similarly, 1-MCP treated 'Fuji' apples maintained higher acidity levels during storage (Zhang et al., 2023). The authors observed that 1-MCP which serves as ethylene blocker, lowered the expression of some genes involved in the glycolysis pathway, up regulated other genes associated with the expression of sucrose and starch synthase, and prevented sucrose, starch, and other substrates breakdown along the metabolic pathway of glucose and fructose during fruit storage (Zhang et al., 2023). Previous studies have reported a decline in acidity during storage at ambient temperature (Ahmad et al., 2021).

Furthermore, apples under VUV treatment showed the lowest TSS content (11.9 %), while untreated apples had the highest TSS content (12.5 %) at the end of the storage period (Table 3). Similar results of increase in TSS during storage at ambient temperature as noted for untreated apples in this study has been reported in literature (Ahmad et al., 2021). The observed increment in TSS during storage as noted in the control is largely associated with the postharvest physiological ripening of the fruit, which involves the degradation of polysaccharides, such as the degradation of pectin substances into simple sugars (Al-Dairi et al., 2021). In addition, 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 and Al-Khayri, 2023). In this study, a linear increase in TSS/TA was observed during the storage period. Control apples showed the highest TSS/TA ratio, while treated apples showed the lowest ratio after the 28-day storage period. This result is consistent with previous study where untreated samples (control) without any measure that influence ethylene management or production maintained higher TSS/TA ratio (Khedr and Al-Khayri, 2023). Overall, the delayed increase in TSS in the treated apples could be associated with the effective removal of ethylene production by the VUV reactor treatment, which minimized ripening impact on the apples. The gradual increase in the TSS/TA ratio in the treated apples is attributed to the effectiveness of the VUV reactor in removing ethylene from within the chamber.

Table 2
Comparison of E_{EO} values for ethylene degradation at different intensities and RHs.

Intensity (mW m^{-2})	RH (%)	E_{EO} (kW L^{-1})
0.0005	20.0	3.423489
0.0014	20.0	1.570788
0.0021	20.0	0.752732
	80.0	0.605668

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. The study also found that the rate constant increased by 86 % with higher RH level. The developed kinetic models successfully fitted the experimental data, demonstrating a strong agreement between the model predictions and actual measurements. This confirms the accuracy and reliability of the proposed model in representing ethylene's degradation kinetics under varying conditions. Economic feasibility assessment using a figure of merit revealed favourable E_{EO} values within acceptable limits, indicating the energy efficiency of the VUV photolysis reactor.

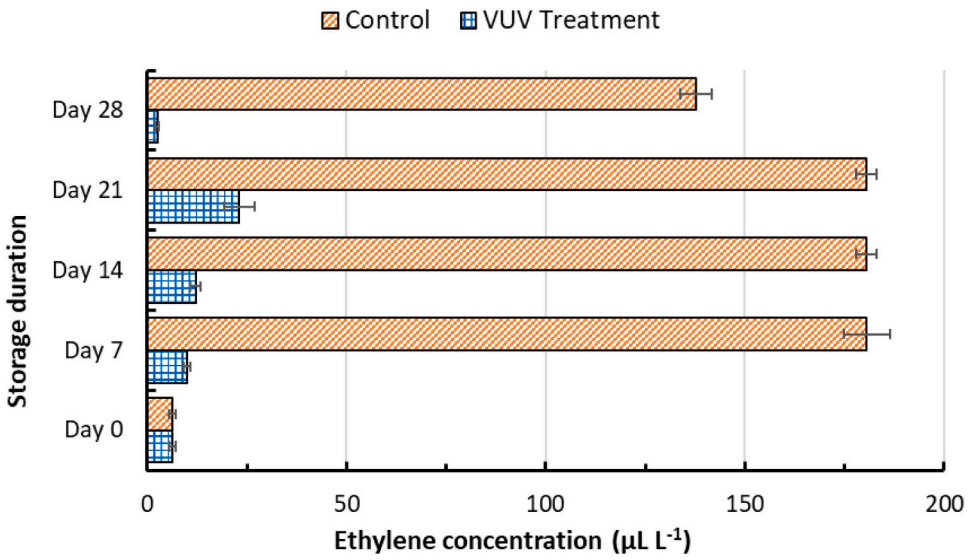

Fig. 6. Changes in ethylene concentration inside the storage chambers containing 'Fuji' apples stored at 15 °C for 28 d. Error bars indicate standard deviation from mean value ($n = 3$).

Table 3
Changes in chemical attributes of 'Fuji' apple fruit under different storages at 15°C for 28 days.

Storage days	TSS (%)		TTA (g 100 mL^{-1})		TSS/TA		pH	
	Control	Treatment	Control	Treatment	Control	Treatment	Control	Treatment
0	12.8 ± 0.14 A	12.8 ± 0.14 A	0.37 ± 0.01 A	0.37 ± 0.01 A	34.59 ± 1.15E	34.59 ± 1.15E	3.57 ± 0.05 C	3.57 ± 0.05 C
7	12.6 ± 0.14 A	12.7 ± 0.78 A	0.36 ± 0.08AB	0.41 ± 0.02 A	35.29 ± 0.15E	31.33 ± 0.75 F	3.53 ± 0.02 C	3.53 ± 0.01 C
14	12.5 ± 0.65AB	12.2 ± 0.57AB	0.35 ± 0.06 A	0.31 ± 0.04B	35.67 ± 1.05E	39.84 ± 0.45D	3.82 ± 0.01 A	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 ± 0.04 A	3.74 ± 0.02B
28	12.5 ± 0.46AB	11.9 ± 0.17 C	0.25 ± 0.01 C	0.29 ± 0.004B	49.14 ± 1.45 A	40.61 ± 0.33 C	3.88 ± 0.01 A	3.73 ± 0.00B

Mean (n = 3) values presented with the standard deviation. Different upper-case letters indicate significant differences at $p < 0.05$.

Additionally, storage application experiments confirmed the VUV reactor's capability to maintain lower ethylene levels, and effectively maintain the fruit quality attributes during the storage period compared to the control. Furthermore, this study emphasizes the importance of considering various environmental/process parameters when designing and interpreting VUV photolysis performance. Specifically, the utilization of ultrasonic humidifier in larger storage units could be incorporated inside the storage to control RH to enhance ethylene removal. Furthermore, research is needed to simulate the VUV reactor performance under pilot/commercial scale at optimum cold conditions and extended long term storage durations.

CRediT authorship contribution statement

Buntu Godongwana: Writing – review & editing, Validation, Supervision, Software, Methodology. **Bongolwethu P. Mabusela:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Oluwafemi James Caleb:** Writing – review & editing, Validation, Project administration, Funding acquisition, Conceptualization. **Zinash A. Belay:** Writing – review & editing, Visualization, Supervision, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is based upon research supported wholly/in part by the National Research Foundation (NRF) of South Africa (Grant Nos. 137990 and 146360) awarded to Dr Caleb. The authors would like to appreciate the support received from Agricultural Research Council (ARC) – Infruitec-Nietvoorbij, South Africa for providing the research platform.

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