CONTROLLING ETHYLENE FOR EXTENDED PRESERVATION OF FRESH FRUITS AND VEGETABLES

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ABSTRACT

This paper describes work conducted to enhance the quality of fresh produce delivered to troops around the world. Specifically, the program objective is to control ethylene produced by fresh fruits and vegetables (FF&V) in refrigerated containers with the use of a novel Ethylene Elimination Unit (EEU). This paper describes the analytical, experimental, and design work conducted to establish the feasibility of the EEU. Analytical modeling and process simulation were used throughout the design process as a means of predicting the performance of the system design. Reaction kinetics of the ozonolysis of ethylene were modeled using the Chemkin ® analysis platform; the results were compared to experimental data. The reaction rate results were incorporated into a process simulation to determine the effects of key design parameters on the overall performance of the system. Integrating process simulation into the design process enabled development of a prototype EEU that meets or exceeds performance and cost goals.

1. BACKGROUND

Fresh Fruits and Vegetables (FF&V) are an essential dietary supplement to standard operational rations. Mixed cases of FF&V are transported and stored in refrigerated containers. As FF&V ripen, they produce and release ethylene. Ethylene (C_2H_4) is a ripening hormone naturally produced by some produce. The accumulation of ethylene gas (C_2H_4) in the transport and storage and the accelerated decay of FF&V is a significant problem for the Military. Low levels of ethylene (less than 1 PPM) can induce fruit ripening, produce undesirable changes to flavors (bitterness), color (yellowing or browning), texture (softening), and increase susceptibility to disease (Peiser, G and Suslow, T.V, 1998). The respective sensitivities of various FF&V are listed in Table 1.

Table 1: Ethylene Sensitivity Chart

Fruits & Vegetables	*Rate of Ethylene Production*	*Level of Ethylene Sensitivity*	*Principal Reaction to Ethylene Gas*
Apples	Very High	High	Scald
Apricots	High	High	Decay
Asian Pears	High	High	Decay
Avocados	High	High	Decay
Bananas	Moderate	High	Decay
Cantaloupe	High	Moderate	Decay
Cherimoya	Very High	High	Decay
Lemons, Limes	Moderate	Moderate	Mold
Melons	Moderate	High	Decay
Nectarines	High	High	Decay
Papaya	High	High	Decay
Passion Fruit	Very High	High	Decay
Peaches	High	High	Decay
Pears	High	High	Decay
Persimmons	Moderate	High	Decay
Potatoes	Very Low	Moderate	Sprouting
Tomatoes	Moderate	High	Shrink, Decay

By controlling ethylene, the storage life of FF&V can be significantly extended. There are existing technologies that are aimed at addressing ethylene levels in FF&V transport and storage. One particular commercial-off-the-shelf (COTS) air purification equipment was tested to control the ethylene levels inside a container containing 200 pounds (five 40-pound cases) of bananas. For this test, a temperature of 55° F was maintained in two identical refrigerated containers, one retrofitted with a COTS unit and a second container without the unit. Ethylene concentrations in both these containers were monitored on a daily basis. To maintain the integrity of the atmosphere within the container, ethylene concentrations were measured through a 1-inch port in the container. This preliminary test was more

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focused on the levels of ethylene that were being produced and the COTS unit's ability to destroy it and less focused on the ripeness or quality of bananas over time. However, the containers were briefly entered once a week ensure that the bananas were not completely spoiled, particularly since the ethylene levels produced were higher than expected. The data show that the COTS unit controlled the concentration of ethylene as compared to the uncontrolled container.

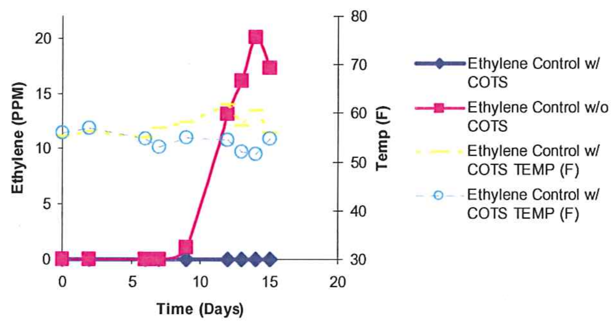

Figure 1: Comparison of actual ethylene concentrations, inside containers with and without COTS ethylene control product

These COTS systems have serious drawbacks, however. Current ethylene control technology is based on either (1) the use of ethylene adsorptive materials, which require routine regeneration or replacement, are relatively bulky and heavy, and pose a considerable environmental and cost burden, or (2) the use of existing commercial catalytic-based technologies do not meet the cost threshold for the intended Military application. The Navy has used adsorbent blankets in the past but has since determined that the logistics of stocking, using and disposing of these materials are problematic, and their use has been discontinued. The US Army Natick Soldier Research, Development, and Engineering Center (NSRDEC) has been investigating the potential for a non-consumable device that can be installed or placed in a refrigerated container that will automatically control the level of ethylene to ensure that FF&V can be stored long enough to be served to the troops.

2. INTRODUCTION

The Equipment and Energy Technology Team, Combat Feeding Directorate at NSRDEC has sponsored the development of a durable, cost effective, low maintenance, Ethylene Elimination Unit (EEU). This research and development is being carried out by Primaira, LLC as part of the DOD Small Business Innovation Research Program. The technology being developed by Primaira is based on the ozonolysis of ethylene. Ozone is a strong oxidizer, and can effectively convert ethylene to water and carbon dioxide. However, exposure of FF&V to ozone can be damaging to the produce as well. Therefore, this EEU product is a self contained system that eliminates ethylene and maintains the internal atmosphere of the container free of ozone.

3. METHODS AND RESULTS

The design process was initiated by modeling the kinetics of ozonolysis. Process simulation was subsequently used to understand the effect of key system parameters on EEU performance. Using this modeling work, a system was designed and tested to meet the Army's requirements for space, cost, power consumption and performance.

3.1. Chemical Kinetics Modeling

Chemical kinetics studies were performed by Reaction Design using the CHEMKIN® gas-phase kinetics modeling platform. These studies predicted the concentrations of ozone, ethylene, and their intermediaries in a homogenous closed reactor. These studies predicted the rate of ethylene destruction in a dry and humid air at 40°F and at 70°F with varying initial ozone and ethylene concentrations. The case where temperature was 40°F simulated a refrigerated atmosphere. This study also identified any potentially hazardous chemical intermediaries produced.

The results of the chemical kinetics modeling work are plotted in Figure 2. It shows ethylene concentration as a function of time for varying conditions of ozone concentrations, temperature and humidity. The figure illustrates the strong effect of ozone concentration on the rate of ethylene decomposition. Temperature and relative humidity have a much smaller effect on the decomposition of ethylene via ozonolysis.

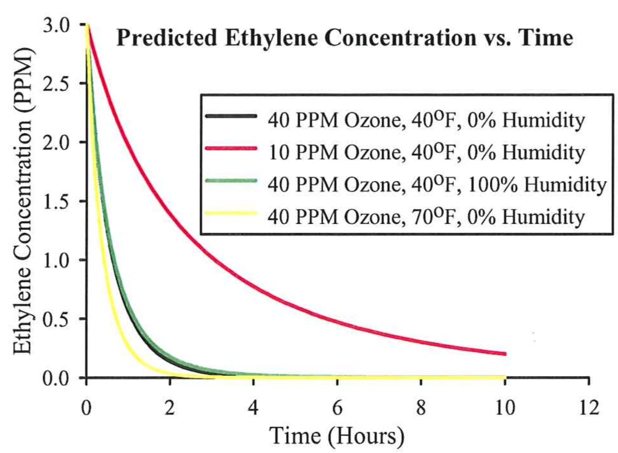

Figure 2: Theoretical ethylene concentration vs. time for different ozone concentrations, temperature, and humidity

To verify these results, experimental work was performed under conditions similar to those modeled. In these experiments, the parameters were an initial ozone concentration of 40 PPM and an initial ethylene concentration of 10 PPM in a room temperature chamber. Ozone was generated within a sealed container using ultraviolet bulbs. Ozone concentration was monitored via a Thermo Fisher Scientific ozone analyzer. Once the ozone concentration within the container reached 40 PPM, a slip stream of 1000 PPM ethylene in air was bled into the system until a final concentration of 10 PPM ethylene was obtained. Ethylene concentrations were monitored using a Varian CP 3800 gas chromatograph (GC).

The ethylene concentration was measured over time within the sealed container and compared to the computational data shown above. These data are shown in Figure 3. As can be seen the experimental and theoretical data match fairly closely.

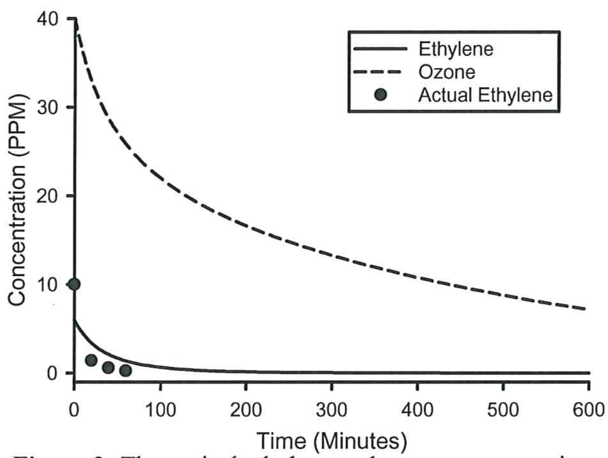

Figure 3: Theoretical ethylene and ozone concentrations along with actual ethylene measurements.

3.2. Description of Ethylene Elimination Unit

The EEU technology consists of an 8" diameter galvanized duct containing two reaction sections. In the first reaction section, ozone is generated, and ethylene is destroyed. In the second reaction section, ozone is converted back to molecular oxygen. A fan at the exit of the system draws the ethylene-laden air from the refrigerated container into the system then exhausts the air with approximately 50% less ethylene. The fan is sized to achieve 6 air changes per hour through the EEU. The overall system volume is 0.2 cu. ft. or 0.1% of the total volume of the MTRCS shipping container.

3.3. Process Simulation Data

The ethylene concentration within a shipping container can be modeled based on several key parameters, such as the volume of the container, volume of the payload, ethylene production rate by FF&V, the flow rate into the EEU, and the amount of ethylene destroyed in one pass through the EEU. This simulation is accomplished by performing a mass balance for the air volume of the shipping container, which contains one source of ethylene generation (the FF&V) and one sink for ethylene destruction (the EEU).

To validate the process simulation model at nearly full scale, experimental work was performed using a Polar King refrigerated trailer. The dimensions of the trailer were approximately 8 ft. long x 6 ft. wide x 7 ft. tall. Ethylene was pumped into the trailer at a known rate and the ethylene accumulation was measured within the trailer. The above experiment was subsequently repeated with the EEU operating, which allowed for the determination of the corresponding ethylene generation rate. With the measurements of ethylene concentration as a function of time in the container, the rate of ethylene destruction over time was calculated.

The rate at which ethylene was introduced was selected to result in a steady state value of ethylene concentration within the trailer that can be measured repeatably with the GC under conditions of the EEU operating or not operating. Process simulation was then used to predict the rate of buildup of ethylene within the trailer.

The results of this experiment and the prediction of the process simulation model are shown in Figure 4. The process simulation data closely matches the actual measured ethylene concentration with the EEU operational.

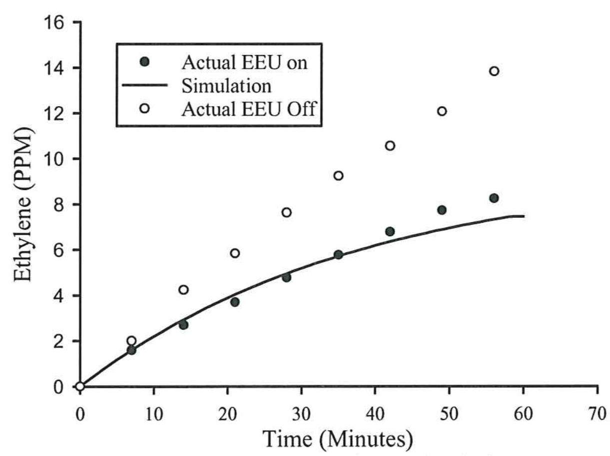

Figure 4: Comparison of experimental ethylene concetration and theoretical ethylene concentration within a shipping container

This test was conducted at ethylene generation rates that are over 200 times the expected generation rates from FF&V. The utility of the experiment is to help refine the process model being used. Using this model, the performance of an EEU operating in a full-scale refrigerated container containing a mix of fresh fruits and vegetables can be predicted. One reason to continue the design effort utilizing process simulation is that a full load of FF&V in a refrigerated container constitutes over a ton of produce. Process simulation is relied on in order to minimize the amount of produce that needs to be purchased and disposed of for a full-scale test of the EEU in the actual environment.

With the knowledge that the process simulation data closely matches experimental data, modeling the ethylene concentration within a Multi-Temperature Refrigerated Container System (MTRCS) shipping container was the next step. The key parameters to the process simulation model for a full scale refrigerated container are shown in Table 2. It was assumed that 80% of the trailer volume was filled with payload, that 25% of the payload was FF&V and that half of the FF&V was ethylene producing. The rate of production of ethylene is based on data from Skog and Chu (Skog and Chu 2001). The rate at which the EEU destroys ethylene is based on experimental findings from the EEU.

Table 2: Key process simulation parameters

Trailer Volume (cu. ft.)	820
FF&V Payload (kg)	1200
Ethylene Production Rate (μL/kg/hr)	0.5
%Ethylene Destroyed per pass through the EEU	50%
EEU air changeover rate (air changes/hr)	6

The theoretical ethylene concentration with and without the EEU technology is shown in Figure 5. These simulations show that the EEU should be able to maintain steady state ethylene concentration below 0.1PPM.

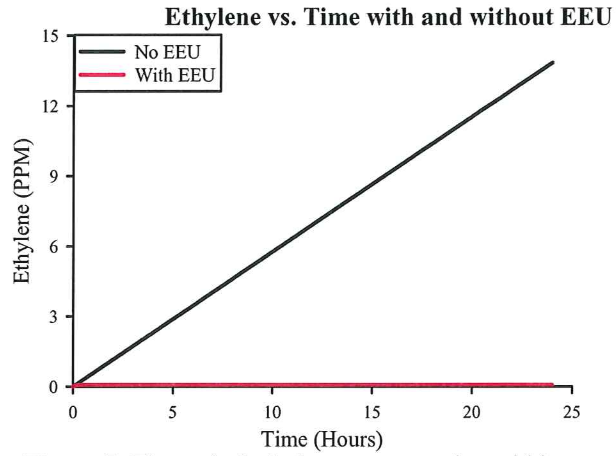

Figure 5: Theoretical ethylene concentration within a MTRCS with and without EEU technology

4. CONCLUSION

This work demonstrates the power and value of process simulation and in the cost effective development of new products. In addition, this ongoing work documents the high level of performance of the EEU, and its ability to meet the goals for maintaining ethylene concentration below a critical threshold in order to extend the shelf life of fresh fruits and vegetables.

5. REFERENCES

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P. 1, Column 2, line 6, typo, "he" should be "the".
P. 3, Column 1, Figure 3 text, typo, "concetration" should be "concentration."
P. 3, Paragraph under Figure 3, line 2, "times" is repeated. ("200 times times).
P. 3, Under Conclusion, check first sentence. Should "in" be deleted? Reads awkwardly.