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## Control of Ethylene in the Postharvest Environment

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The beneficial and harmful effects of ethylene ( $C_2H_4$ ) on harvested horticultural products are well documented. The purpose of this presentation is to outline the technologies currently available in commercial horticulture for both the application of  $C_2H_4$  to harvested horticultural crops, and the protection of these crops from the undesirable effects of  $C_2H_4$ . The research base for this topic cuts across many areas of considerable postharvest research, including temperature effects, atmospheric modification, and regulation of  $C_2H_4$  synthesis. A complete review of any of these topics is beyond the scope of the presentation, and, in most instances, the reader is referred to recent research reports or comprehensive reviews of the specific subject.

### Postharvest application of ethylene

**History and economic importance.** The use of practices to hasten fruit ripening dates to antiquity (35), although it was not known until relatively recently that  $C_2H_4$  was the causal agent. The earliest practices employed the emanations from ripe fruit or the smoke generated from burning combustible products. The use of kerosene stoves for "sweating" or "forced curing" of citrus was a well-established commercial practice by the late 1800s. It was believed that the high temperatures and high humidities in the "sweating" rooms resulted in degreening. Sievers and True (43) demonstrated that degreening was due to some unknown gaseous product from the incomplete combustion of kerosene. Denny (15) provided convincing evidence in 1924, that  $C_2H_4$  was the effective constituent in "stove gas", and described a method for commercially degreening lemons using cylinders of compressed  $C_2H_4$  gas.

Denny's work (15) marked the beginning of the knowledgeable use of  $C_2H_4$  gas in commercial degreening and fruit ripening practices. Harvey (27) published the 1st comprehensive bulletin describing the commercial application of  $C_2H_4$  for ripening bananas, pineapples, dates, Japanese persimmons, tomatoes, hard pears, apples, and muskmelons. Interestingly, one early commercial use for  $C_2H_4$  was for blanching celery (26), a practice which has long since been discontinued.

Rosa (39) predicted that for tomatoes "the acceleration of the coloring process by low concentrations of  $C_2H_4$  is sufficiently great to make it commercially valuable. . .". These words seem especially prophetic when considering the economic importance of  $C_2H_4$  applications in postharvest horticulture today. Although it is not

possible to assign an exact monetary value for  $C_2H_4$  use, it is accurate to state that  $C_2H_4$  applications play an important role in the orderly marketing of fresh citrus (excluding limes), tomatoes, bananas, mangoes, and honeydew melons. Recent reports (20, 47, 48) indicate that these products have a value of over 1.9 billion dollars in the United States alone.

**Sources of ethylene.** There are 3 potential sources of  $C_2H_4$  for commercial use: liquids, gases, and ripening fruit. Liquid sources are  $C_2H_4$ -releasing chemicals such as (2-chloroethyl) phosphonic acid, commonly known as ethephon. This chemical is registered and widely used for preharvest applications to concentrate maturity or otherwise facilitate harvest of several horticultural crops. According to the label, the only presently registered use for postharvest application is for the degreening of lemons in Florida (49). Therefore, further discussion will be limited to the other sources of  $C_2H_4$  for postharvest use.

Ethylene gas can be generated *in situ* or purchased in compressed cylinders. The gas is generated by catalytic conversion of a flammable liquid concentrate (Ethy-Gen) to  $C_2H_4$  gas (11). This is one of the most popular commercial sources of  $C_2H_4$  gas. The other widely used source of  $C_2H_4$  gas is that purchased in compressed cylinders of either pure  $C_2H_4$  or  $C_2H_4$  diluted with an inert gas such as the product called "banana gas" (50, 3, 51).

Postharvest physiologists are aware that ripening fruit produce  $C_2H_4$ , but many commercial handlers either are unaware of or ignore this fact. If ripening room operators conscientiously monitored  $C_2H_4$  levels in these rooms, then the use of ripening fruit might be a viable commercial alternative. However, the use of ripening fruit as a source of  $C_2H_4$  generally is limited to home ripening recommendations.

**Which source to use?** The source of  $C_2H_4$  used by handlers normally is determined by the facilities for treatment, legal considerations, cost, and safety. The use of  $C_2H_4$  gas requires some type of enclosure. The cost of building special ripening facilities with precise temperature and humidity controls is well-justified when repeated ethylene applications are required.

Each handler also must consider the legality of  $C_2H_4$  application (25). Ethylene gas used for plant regulation such as coloration or ripening of fruit and vegetables is regarded legally as a pesticide for regulatory purposes (52). Therefore, it must be registered with the Environmental Protection Agency (EPA) and the appropriate state agencies. Containers of  $C_2H_4$  gas or  $C_2H_4$ -releasing liquids must bear EPA approved labeling, including EPA registration and establishment numbers, intended uses, ingredients statement, and appropriate precautionary labeling statements.

Because of the explosive nature of certain mixtures of  $C_2H_4$  and

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air, most insurance regulations contain very specific recommendations about fruit degreening and ripening processes (36, 4). For example, these recommendations specify the type of electrical wiring and piping to be used in ripening rooms. Other state and local fire marshal rules or building codes may apply (46). Generally, these rules all pertain to safety, but this may change. Recently, a bill was introduced in the California state legislature which would have required that tomatoes treated with  $C_2H_4$  be labeled "artificially ripened".

Safety must be a prime consideration in the technology of  $C_2H_4$  application. Ethylene gas is explosive in air at concentrations from 3.1% to 32% (31,000 to 320,000 ppm) (8). To put these values in proper perspective, the minimum explosive concentration (3.1%  $C_2H_4$  in air) exceeds the suggested  $C_2H_4$  concentrations for tomato ripening (24) and citrus degreening (56) by 200 and 6200 times, respectively. One might conclude, therefore, that it would take extreme negligence for the fruit ripening process to be dangerous. However, explosive accidents have occurred in the past. Safety during  $C_2H_4$  application is dependent upon the operator,  $C_2H_4$  source, and the method of application. The safety advantages afforded by the catalytic generator, and "banana gas" sources of  $C_2H_4$  may be negated by the operator and the method of application. Each ripening room operator should have equipment to measure  $C_2H_4$  concentrations. This is accomplished readily with an inexpensive gas detector kit and  $C_2H_4$  detector tubes obtainable from several companies that sell specialty gases.

**Methods of applying  $C_2H_4$  gas.** The methods of applying  $C_2H_4$  gas can be placed into 3 categories: shot, trickle, and flow-through. Shot methods employ the rapid injection of  $C_2H_4$  into the ripening room atmosphere. This can be accomplished by weighing the amount of  $C_2H_4$  dispensed from a cylinder, using a premeasured amount (lecture bottle), or timing the delivery of  $C_2H_4$  from a cylinder. The original system described by Denny (15) was a shot method, with the  $C_2H_4$  delivered in a premeasured container. Dispensing  $C_2H_4$  directly from large cylinders can be extremely dangerous and never should be done. Shot methods have the advantage of simplicity, but the disadvantage of requiring frequent room aerations to prevent carbon dioxide ( $CO_2$ ) buildup which necessitates recharging the room with  $C_2H_4$  following each aeration.

The "trickle" method can be defined as the slow, continuous dispensing of  $C_2H_4$  into the ripening room atmosphere. Usually, compressed  $C_2H_4$  cylinders are equipped with a regulator and flow meters to control the flow of  $C_2H_4$ . In practice, the catalytic generator also is a trickle method for introducing  $C_2H_4$ . Trickle methods are safer than the shot methods but they still may require periodic room aeration and recharging with  $C_2H_4$ .

The flow-through system is a modification of the trickle methods. In principal, the flow-through system supplies a constant, ripening-effective blend of  $C_2H_4$  and fresh outside air which passes over the product and out an exhaust port in the room. The constant air exchange prevents  $CO_2$  accumulation to inhibitory levels and eliminates the need for periodic aeration. The flow-through system has proven to be a safe and efficient method for introducing  $C_2H_4$  for citrus degreening (56) and tomato ripening (42). Sherman and Gull (42) provided detailed instructions for installing a flow-through system.

**Commodity requirements.** One of the most important requirements is that the commodity be physiologically mature (capable of continuing normal development when detached from the plant). For some commodities like citrus, legal definitions of maturity exist (57). For others, such as tomatoes, there are no legal definitions of maturity, and it is difficult to determine whether a green fruit is mature or immature based on external appearance. Other important commodity requirements include the desired  $C_2H_4$  concentration, sensitivity to  $CO_2$ , and the optimum temperature, humidity, and length of treatment. Local extension recommendations should be consulted for specific commodity information (24, 31, 56).

## Protecting harvested products from ethylene

**History and economic importance.** Some of the earliest investigations of  $C_2H_4$  were related to its detrimental effects on plants and have been thoroughly reviewed (1). Crocker and Knight (12) re-

ported that "sleep" of carnations (failure of buds to open or premature closing of buds) was caused by 0.5 to 1 ppm  $C_2H_4$ . Examples of the adverse effects of  $C_2H_4$  on harvested horticultural products continue to appear in literature. Risse and Hatton (38) recently reported the detrimental effects of  $C_2H_4$  on harvested watermelons.

It is extremely difficult to assess the economic importance of protecting harvested horticultural products from  $C_2H_4$ . Abeles has pointed out the problems of estimating the economic losses caused by  $C_2H_4$  as a component of air pollution (1, 2). Detrimental effects of  $C_2H_4$  during the normal short-term marketing of fruit and vegetables are not well-defined and certainly are secondary to considerations regarding the maintenance of optimum temperature and humidity in the postharvest environment. However, costs to the individual shippers involved can easily run into tens of thousands of dollars when losses do occur from problems like russet spotting of lettuce or yellowing of cucumbers. Economic evaluations of long-term storage responses to  $C_2H_4$  (5, 17, 28) generally have not been reported because investigators have not wanted to speculate about extended season prices. Detrimental effects of  $C_2H_4$  may be most important for ornamental crops where estimates once placed postharvest losses at about 20% due to mishandling. However, mishandling included poor temperature management, and improper humidity, as well as exposure to  $C_2H_4$  (45). In summary, losses caused by  $C_2H_4$  are known to occur, but they are usually quantitatively undefined. A conservative estimate for the United States would be in the tens of millions of dollars annually.

**Strategies for protection.** The strategies for protecting harvested horticultural products from the detrimental effects of  $C_2H_4$  can be placed into 3 major categories: avoidance, removal, and inhibition. Although these techniques are grouped for convenience it should be remembered that they may overlap and are not mutually exclusive.

**Avoidance.** Circumvention of undesirable product exposure to  $C_2H_4$  begins with careful harvesting, grading, and packing which includes selecting the desired maturity and avoiding mechanical injury. The 2nd and probably most important step in avoidance is proper temperature management, which should include rapid cooling to the product's lowest safe temperature. This suppresses ethylene production and reduces sensitivity to ethylene (9). Chilling temperatures should be avoided when handling chilling-sensitive commodities, however, because increased  $C_2H_4$  production frequently follows chilling injury (55). Ethylene-sensitive commodities should not be transported, stored, or displayed with  $C_2H_4$ -generating commodities. Guidelines suggesting compatible product mixes have been published (33). Given the food distribution system in the United States, it is not possible to avoid undesirable exposure to product-generated  $C_2H_4$  completely, but exposure should be kept to a minimum. Placing ripe tomatoes between iceberg lettuce and cucumbers in retail produce displays may be colorful, but it completely ignores the biology of these products and constitutes unnecessary exposure of the produce to undesirable temperatures and  $C_2H_4$ .

Other management steps for avoidance include minimizing the use of internal combustion engines during product handling in enclosed spaces, and following strict sanitation practices to insure that overripe and decaying products are promptly removed.

**Removal.** Undesirable levels of  $C_2H_4$  in produce storage areas can be removed by simple ventilation with fresh air if the air is not polluted with high  $C_2H_4$  levels. Usually, one air exchange per hour is required to maintain a low  $C_2H_4$  level. Ripening room facilities located in produce distribution centers always should be vented to the outside to ensure that  $C_2H_4$  is not accidentally introduced into the storage environment of the distribution center.

$C_2H_4$  can be scrubbed from the atmosphere by trapping and/or conversion to other products when ventilation cannot be used for removal. A large number of reagents and techniques have been tested over the years (1, 7, 15), but only potassium permanganate is presently in common commercial use. To be effective,  $KMnO_4$  must be adsorbed on a suitable carrier with a large surface area. Celite, vermiculite, silica gel, alumina pellets (1), perlite (40), and expanded glass (32) have all been successfully used as carriers. A number of commercial potassium permanganate scrubbers are avail-

able in sachets, filters, blankets, and other specialized trapping devices (37, 18, 19). Ethylene is trapped most effectively when air is drawn through the scrubber. Potassium permanganate scrubbers are advantageous because they change from purple to brown as the  $\text{MnO}_4^-$  is reduced to  $\text{MnO}_2$ . The major disadvantage of permanganate scrubbers seems to be their expense (7, 40).

Heated catalyst ethylene scrubbers were successfully used during the 1983–1984 storage season in commercial controlled atmosphere apple storages to maintain ethylene concentrations below 2 ppm in New York State, and below 1 ppm in England (Blanpied, personal communication). Another technology for  $\text{C}_2\text{H}_4$  removal, which seems promising but has yet to be commercially developed, is the use of UV light (41). Also, there is a potential for biological removal of  $\text{C}_2\text{H}_4$ . Abeles (2) discussed the role of soil bacteria as a sink for atmospheric  $\text{C}_2\text{H}_4$ . Perhaps the  $\text{C}_2\text{H}_4$ -consuming *Mycobacteria* that have been isolated from soils (14) could be genetically engineered to perform satisfactorily in horticultural applications.

**Inhibition.** Controlled atmospheres (CA) have been used widely for many years for the long-term storage of apples (13) and, to a limited extent, for other commodities, such as pears (44) and cabbage (22). CA systems require special refrigerated, gas-tight structures (16, 29) which allow for precise temperature control and maintenance of the storage atmosphere (primarily reduced  $\text{O}_2$  and elevated  $\text{CO}_2$ ). CA storage has multiple effects on the physiology of the commodity (30, 44), but the retardation of ripening is at least partially attributable to the low  $\text{O}_2$  atmosphere, slowing  $\text{C}_2\text{H}_4$  synthesis and action, and the elevated  $\text{CO}_2$  inhibiting  $\text{C}_2\text{H}_4$  action. Very low levels of  $\text{O}_2$  (17) and  $\text{C}_2\text{H}_4$  scrubbing (5, 7) may enhance the storability of products in CA. The use of CA essentially has been limited to long-term stationary storages, but at least one company, now out of business, incorporated CA capability into modern transport containers (21). Modified atmospheres (a less precise type of CA) have been used for many years on several commodities during transport.

Low pressure storage (LPS) seems to offer potential for prolonging the useful life of horticultural commodities (10, 34). LPS effectively reduces  $\text{O}_2$  levels and, in this respect, is similar to CA storage. Storage at subatmospheric pressures also increases the diffusivity of volatile gases, however, including  $\text{C}_2\text{H}_4$ , from the internal atmosphere of the commodity (10). Commercial applications of LPS systems have not been widespread to date. Grumman Allied Industries developed the Dormavac System for hypobaric transportation of perishables (23), but this met with only limited commercial success and was discontinued.

Chemical treatments could be used to protect horticultural products by inhibiting  $\text{C}_2\text{H}_4$  synthesis and/or action. Yang and Hoffman (58) reviewed many of the known inhibitors of  $\text{C}_2\text{H}_4$  biosynthesis. Some inhibitors appear to have commercial potential for regulating fruit ripening (6, 54), but their use on food products must be preceded by FDA and EPA approvals. Many ornamental horticultural crops can be protected from the detrimental effects of  $\text{C}_2\text{H}_4$  by treatment with the anionic complex silver thiosulphate (STS). Veen (53) recently reviewed some of the uses for STS in commercial horticulture.

Methods outlined here for removal of  $\text{C}_2\text{H}_4$  and inhibition of  $\text{C}_2\text{H}_4$  synthesis and/or action should not be regarded as panaceas for solving  $\text{C}_2\text{H}_4$ -related problems in commercial horticulture. The best defenses for protecting harvested horticultural products from the detrimental effects of  $\text{C}_2\text{H}_4$  are the steps outlined under avoidance. When the shelf life of products can be extended further by the methods of  $\text{C}_2\text{H}_4$  removal or inhibition of its action, then their use may be advantageous. The long term storage of apples in controlled atmospheres with  $\text{C}_2\text{H}_4$  scrubbing is a good example of post-harvest practices which employ avoidance, removal, and inhibition methods for protection from  $\text{C}_2\text{H}_4$  (7, 17).

## Summary

Control of  $\text{C}_2\text{H}_4$  in the postharvest environment is of great importance in commercial horticulture. Application of  $\text{C}_2\text{H}_4$  facilitates the orderly marketing of citrus, tomatoes, bananas, mangoes, and honeydew melons. Safe and efficient application methods have been developed and are readily available for commercial use. Detrimental

effects of  $\text{C}_2\text{H}_4$  on harvested horticultural products largely can be avoided by careful management of the postharvest environment, but this management is not always practical in commercial situations. Technologies exist for removing  $\text{C}_2\text{H}_4$  or inhibiting  $\text{C}_2\text{H}_4$  action, but there is still considerable room for improvement during the storage and handling of most commodities.

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