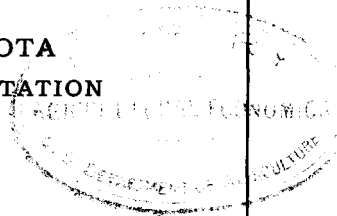


UNIVERSITY OF MINNESOTA
AGRICULTURAL EXPERIMENT STATION



ARTIFICIAL RIPENING OF FRUITS AND VEGETABLES

MAR 20 1928

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AND BOTANY

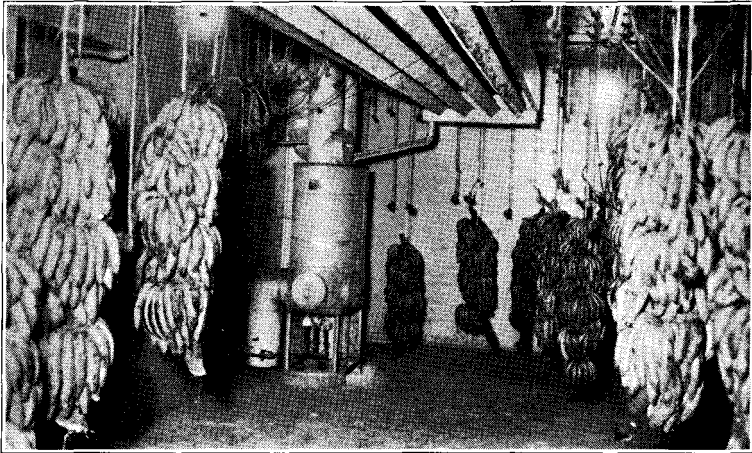


FIG. 1. BANANA ROOM EQUIPPED FOR MAINTAINING A SUITABLE TEMPERATURE AND HUMIDITY, AND GAS-TIGHT TO PREVENT THE ESCAPE OF ETHYLENE

The gas flame below the boiler heats the room and also evaporates the water in the boiler to maintain high humidity. The coils on the ceiling provide refrigeration when it is desired to stop the ripening process and hold the fruits in storage.

UNIVERSITY FARM, ST. PAUL

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ARTIFICIAL RIPENING OF FRUITS AND VEGETABLES

R. B. HARVEY

The ripening of fruits and vegetables after storage is a process that has long been in use and that has shown many commercial advantages, since it effectively lengthens the season during which fruits may be kept without canning. Fruits generally keep better if they are picked before they are mature. This is partly because the ripening process generally softens the cell wall substances and digests the starch and other constituents of the fruit, making the ripe fruit especially subject to bruising and a good medium for the growth of fungi. The cell walls of fruits that are picked green are firm, so green fruits may be shipped or stored with much less injury than ripe fruits. In ripe fruits the chemical transformations are proceeding at a high rate, while in green fruits digestion and respiration are comparatively slow. Even if the processes of respiration and digestion are slowed down by storing the fruit at temperatures near the freezing point, ripe fruits do not keep so well as green fruits. The keeping of fruits in storage in a nearly mature but firm condition is to be recommended if for no other reason than to lengthen the period of availability and to regulate the supply by removing part of the crop from the market to storage at times of over-supply.

RIPENING OF FRUITS BY ARTIFICIAL HEAT

In the past the ripening of immature fruits after a period of storage showed some disadvantages. Every one is acquainted with the excessive sourness of tomatoes picked green from the vine and ripened after a period of storage. Such fruits are at times so sour that little can be used in a salad. They are also frequently deficient in red color. Green bananas, particularly in the winter months, may be colored well but still show a deficiency of starch digestion and tannin decomposition when compared with well ripened fruits.

In the past it has been the practice to ripen bananas, tomatoes, and other fruits that must be picked green for transport and storage by subjecting them to warm temperatures. The relatively high temperature speeds up the chemical transformations and effects a ripening similar to that on the tree or vine. For green bananas of Le Gros Michel variety, 4 or 5 days may be required, depending upon the temperature used. At 80° Fahrenheit this time may be decreased, but at 60°F. ripening will be much slower than at 65° to 70°F. Generally, it has been found that ripening will be better throughout the pulp if

the temperature is not much above 65°F. At 80°F. the tendency is for the skin to ripen but not the pulp. Also, this high temperature has a tendency to shrivel the fruit. However, jobbers frequently use high temperatures when fruit is in demand because the fruit reaches a marketable color much more quickly than at 65°F. High temperature with attendant high humidity favors the development of molds and the blackening of fruits, and hastens the rotting of the fruit stalk. A blackened skin gives a bunch of bananas a poor appearance. The rotting of stalks becomes a serious matter when the decay of the fingers allows the fruits to break loose from the hand. Reynolds (41) suggests the following temperatures for the control of ripening rooms:

- 72°F. (or over) Danger of cooking
- 68°F. Fast or forced ripening
- 66°-62°F. Normal ripening
- 60°F. Slow ripening
- 58°F. Holding green bananas
- 56°F. Holding ripe bananas

There is some danger of chilling even ripe fruits at temperatures below 54°F. Green bananas may show effects of chilling at slightly higher temperatures. Incidentally, the banana will not freeze until the temperature gets to a few degrees below the freezing point, 32°F. However, badly chilled fruits that have not been frozen are liable to turn black. If only slightly chilled they may show a gray-green appearance after ripening.

In ripening tomatoes the use of high temperatures (above 80°F.) is to be avoided as far as possible, because the fruit rots badly. Usually there are enough fungus spores on the fruits to cause rotting if conditions are favorable.

It is a problem, then, with the use of heat alone, to avoid rotting discoloration, shriveling, and poor flavor at high temperature, or to avoid the long time required at low temperature. The time required to ripen the Cavendish banana by heat alone is so great as to exclude this variety from commercial use.

DISCOVERY OF THE USE OF ETHYLENE IN RIPENING

A solution of some of these difficulties of ripening fruits was discovered by the author (16, 17, 18, 19, 21, 22) in 1924. It had been known for several years that the coloration of lemons could be hastened by treating the fruits in tight rooms with the gaseous products arising from incomplete combustion. The Chinese have had a practice from ancient times of ripening hard pears by placing them in closed spaces and burning incense in the chamber. The practice was not worked out on a scientific basis, yet it was known to be effective and is still in use.

Sievers and True (45), in a study of the effects of the products of incomplete combustion on coloring lemons, found that the gases produced by kerosene stoves, the exhaust gases from automobiles, and other such gases produced in incomplete combustion hastened the production of a yellow color in the "sweating" process for ripening citrus fruits. Working on this process, Denny (4, 5, 1) experimented with the constituents of these gases and found that the unsaturated hydrocarbon gases, such as ethylene, were most effective in producing coloration. Evidently the emphasis of this application was upon the coloration of green fruits and no actual ripening or removal of excess acidity was produced in the fruit. In his patent application Denny does not use the word "ripening" nor does he indicate in his articles in the *Botanical Gazette* (5) and the *Journal of Agricultural Research* (4), that he had any knowledge of the use of ethylene as an agent for ripening fruits. In neither article is the word "ripening" used. The concentrations of ethylene gas evolved from blue-flame oil stoves used in the "sweating" process were not proper to produce actual ripening. Denny states that the concentration of ethylene should never be higher than 1-5000 for the coloration of lemons.

The effect of ethylene and other constituents of artificial and natural illuminating gas on plants had been known from the work of Crocker and Knight (3), Schonnard (44), E. M. Harvey (13), and others. The leakage of illuminating gas into greenhouses causes a whitening of leaves, and has been a cause of much litigation by greenhouse men against gas companies. A case of this nature in St. Paul started work on ethylene at the Minnesota Agricultural Experiment Station in 1924.

It occurred to the author that the whitening of leaves by ethylene is desirable in the blanching of celery. The first experiment made with ethylene included tomatoes, apples, and some other fruits, as well as celery. Positive results were obtained, and since a great amount of green celery is produced in Minnesota, the application of the ethylene treatment in the blanching of celery was immediately worked out and established on a commercial scale. The method was published in various trade journals (14, 20, 23) and by a bulletin (15) in the Minnesota Agricultural Experiment Station series. The ethylene method of blanching celery received an immediate response by the trade, and evidently is a commercial success. By taste and by chemical analysis (24, 36) treated celery was found to be higher in sugar content than untreated celery. It was found, also, that tomatoes treated with ethylene were sweeter than untreated fruits. The increase in sugar content and the removal of excess acidity seemed to offer some commercial advantages. Collaborations were established with com-

mercial jobbers and with other experiment stations. Details of the application of ethylene to ripening tomatoes were worked out by Dr. R. P. Hibbard (27) at the Michigan Agricultural College and by Dr. J. T. Rosa (43) at University Farm, Davis, California.

It became evident that the ethylene process was a boon to the fruit trade, and details of the application to a great many fruits and vegetables were worked out on material supplied by Dr. B. T. Galloway, of the Office of Foreign Seed and Plant Introduction, and Dr. F. M. Eaton, of the Bureau of Plant Industry, stationed at Sacaton, Arizona. It now appears that ethylene may be used to hasten the ripening of fruits, to remove excess acidity, to increase the sugar content, to improve the aroma, and to remove tannins and other objectionable substances.

GENERAL INSTRUCTIONS FOR THE USE OF ETHYLENE IN RIPENING

The action of ethylene seems to be similar in both the ripening of fruits and the blanching of celery, altho final results may be different. Whether it is used to remove green color or to remove tannins, the action of ethylene seems to be of the same general nature in each type of action. For this reason the treatment has general application to different types of plant products, and the process best suited will need only minor modifications to suit the different materials. It seems probable that ethylene, of itself, does not bring about the transformation of materials, but that it acts through the normal enzymes naturally occurring in plant tissues (37, 38, 39). Consequently, conditions for the successful use of ethylene must be such that the normal enzyme actions may occur. Ethylene aids the action of these enzymes. If the temperature of the fruit is at or near the freezing point, it may be expected that ethylene will have little or no effect, because normal cell activities are not favored by such temperatures. Some jobbers have made the mistake of applying ethylene at low temperature, altho they were instructed to have a proper temperature. Several years experience indicates that for each fruit the temperature should be at about the point which is best for normal growth of the plant from which it is derived. For blanching celery the temperature can not be run as high as for ripening tomatoes or bananas. Relatively high temperatures will greatly accelerate the action of ethylene, but generally the time required to ripen fruits by ethylene is so short that it is better to use temperatures within the range from 65° to 70°F.

In the ripening of chilled bananas it seems of some advantage to use rather high temperature and humidity. Good results have been obtained in the banana trade by the liberation of steam into the "sweat-

ing" rooms. By this treatment it is claimed that the gray-green color sometimes shown by chilled fruits is largely avoided, and a good flavor is produced. It is impossible to save fruits that are actually frozen.

The best concentration for the use of ethylene is one cubic foot of gas to 1,000 cubic feet of air space (1-1,000) in the room.

The room used for ripening fruits should be of such construction as to reduce the leakage of gas to a minimum. Cellar rooms with concrete or brick walls can be made sufficiently tight by plastering all cracks in the wall and around windows. The ceiling should be plastered. Two thicknesses of closely matched lumber with building paper between will make the ceiling fairly gas tight. It is advisable in cold climates to insulate permanent ripening rooms with cork board and cover this with matched lumber or plaster to seal the insulation. No tarred paper or any materials containing fat or wax should be used in the construction, as fatty substances absorb ethylene.

The ripening room may be heated by gas, steam, or electricity. Probably steam heat from a regular steam heating plant is most desirable, but some provision should be made for automatically controlling the temperature. There are on the market gas heaters especially constructed to provide heat and moisture for maintaining proper conditions of the air in banana ripening rooms (Fig. 1, cover page). Where steam heat or electricity is used, in dry climates, provision must be made for supplying moisture to the atmosphere.

APPLICATION OF ETHYLENE IN THE RIPENING OF COMMON FRUITS

Bananas

The time required for ripening bananas by the use of ethylene varies according to the ripeness of the fruit when it is received and depends upon the variety as well as upon the temperature used. At 65°F. for Le Gros Michel, from 42 to 48 hours are required when the fruit is very green (Fig. 2). For the Cavendish variety this time is practically doubled. Cavendish fruits may be ripened from the green condition in which they are usually taken from the tree in from 84 to 96 hours. It seems to make relatively little difference whether the fruit is taken directly from the tree or has been in transit for some time, provided the same stages of greenness are used. For fruits that are partly yellow when received, less time is required. Since the time for ripening bananas at 65°F. is relatively short in comparison with that formerly required by the "sweating" process, it is desirable to keep the temperature low rather than to attempt to hasten the process by raising it to 78° or 80°F. At these higher temperatures the humidity will be high whether moisture is supplied or not, because moisture will be

given off by the fruits. With high temperature and high humidity, molds on the fruit and stalk are much more liable to develop than at 65°F. The molds of a few fruits on the bunch will spread spores over the surface of other fruits so that they will mold during shipment or in the stores. Furthermore, at the higher temperature the rate of respiration becomes very high, and this leads to the removal of sugars from the fruits. In general, in the application of ethylene to bananas it is best to keep the rooms at about 65°F.

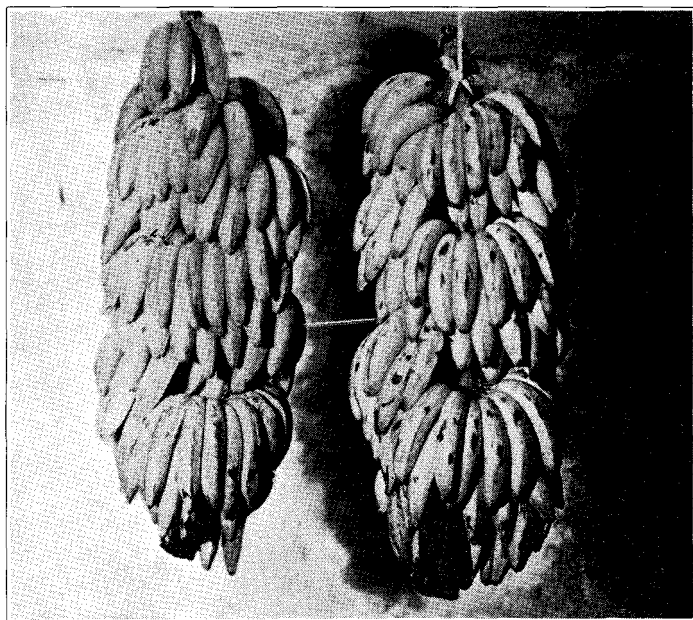


Fig. 2. Right: Bananas Treated With Ethylene (1-1,000) at 65°F. for 48 Hours

Left: Check Bunch Treated at 65°F. for 48 Hours Without Ethylene

Each bunch was picked as representative of the average color of half of a carload of bananas treated under the conditions given. The difference in color, green and yellow, is shown as dark and light.

At 65°F. it is necessary to have the relative humidity in the rooms at about 90 per cent during ripening to prevent shrinking of the fruits. After the fruit is ripe, the humidity should be decreased to 75 per cent to dry the fruit slightly. This can be accomplished by ventilation. Drying decreases the brittleness of the skin and prevents damage in handling. Men long experienced in testing the moisture content of bananas have found that those under ethylene treatment generally show less moisture shrinkage than those ripened with heat alone. This seems reasonable, because a much shorter time is required. Also, lower temperatures may be used, with a consequent decreased effect of desiccation. The ripening of bananas with ethylene gas causes the digestion

of starch to soluble sugars. This causes an increase in the osmotic concentration within the cells that should result in greater water-holding capacity. Also, ripening causes the digestion of some of the cell wall constituents, making the fruits softer in texture. The colloids produced by the ripening evidently have a greater ability to hold water and thus lead to a decreased loss of water from the fruit. It has been estimated by experienced banana jobbers that this decrease in loss of water from the use of ethylene in ripening would amount to as much as one or two pounds per bunch. Coupled with the decreased loss from rots this decreased shrinkage will more than pay the expense of the treatment.

The peel of the banana, when green, contains the green pigment, chlorophyll. During the process of ripening, the ethylene speeds up the decomposition of this pigment to colorless compounds (Fig. 3). Yellow pigments, known as carotinoids (the carotins and xanthophylls), are also present in the banana peel. They are not noticeable as long as the green pigment is present but as soon as the chlorophyll has been decomposed they become evident in the yellow color of the ripened fruit. Ethylene evidently has no effect upon the decomposition of these yellow pigments, or upon the decomposition of red pigments, known as anthocyanins. Red bananas, commonly known as horse bananas, retain their red color on ripening. It is advisable to stop the ripening of bananas by lowering the temperature in the rooms when there is still a little green left in the tip, if they are to be shipped. As the ripening process has been set off by the ethylene treatment, bananas will ripen in the stores quickly enough from this stage. It is desirable to have the fruits sufficiently firm to withstand handling in transporting them to the trade.

The flavor of fruits treated with ethylene is better than that of fruits ripened by heat alone. The decomposition of starch is greater in treated fruits with an attendant increase in sugar content. Bananas treated with ethylene taste sweeter than those ripened with heat alone (39). Also, a greater amount of banana oil is apparently produced in the fruits.

Tasting squads, including horticulturists trained in testing fruits for flavor, have agreed that the flavor of ethylene-treated fruit is superior to that of untreated fruit. Bananas treated with propylene have a little better flavor than those treated with ethylene. Three horticulturists agreed on this superiority, not knowing what treatment had been given. One horticulturist has tasted all of the bananas treated in twenty or thirty trials with ethylene and with propylene, and the checks, and has never failed to recognize those treated with ethylene and with propylene, and the check, altho the treatment



Fig. 3—Bananas Showing Differences in Color Produced by Ethylene Treatment

Right: Four bananas treated with ethylene 1-1000 for 48 hours at 65°F. Notice breaking of the peel.

Center: Four bananas showing original color. Fruits kept at low temperature.

Left: Four bananas kept at 65°F. for 48 hours without ethylene.

The use of colored illustrations in this bulletin was made possible by the generosity of The Ohio Chemical & Mfg. Co. of Cleveland, Ohio.

was not known beforehand. Green bananas contain an appreciable quantity of tannins. Some persons have difficulty in digesting bananas that are not perfectly ripe, evidently because of these tannins. During the ripening with ethylene these substances are removed, probably by oxidation. When heat alone is used, particularly a high temperature, the tannins are sometimes left in the fruits so that they are not of particularly good flavor altho the peels may show good color. It is desirable for children to have bananas thoroly ripened, and for this reason the ethylene treatment shows a considerable advantage. The change in flavor of the ripened bananas is accompanied by a change in texture, indicating a production of pectinous substances in the pulp. Evidently this change has much to do with the palatability of the fruit.

As the time for ripening is much decreased, and as a lower temperature may be used, there seems to be less rotting of fruits ripened with ethylene than of those ripened by the "sweating" process. Other than this, we have been unable to find any effect of the ethylene in either decreasing or increasing the keeping quality of the fruits.

The concentration of ethylene should be kept at one cubic foot of gas to 1,000 cubic feet of air space in the room. This concentration should never be exceeded, because an overdose is injurious. The peel will become brown with dark spots before the pulp is ripe. Ethylene will effect ripening at concentrations much lower than this maximum, but it is desirable to establish this concentration because gas will leak from the room and the concentration probably will be decreased by absorption into the fruits. This amount of gas has generally been found to be independent of the quantity of fruit in the room. Evidently a proper concentration is required to set off the ripening rather than a certain weight of gas per unit weight of fruit. One pound of ethylene will ripen at least 100,000 pounds of bananas. A large part of the gas escapes from the rooms. Only a small part of the ethylene is absorbed by the fruit, so the actual concentration in the treated fruit is exceedingly small. It is generally desirable to liberate the gas in the rooms for 5 or 10 minutes. This allows it to be distributed through the room and prevents a high concentration around the exit tube. The treatment can be applied most conveniently just before the rooms are closed for the night. The rooms remain undisturbed over night and sufficient time is allowed for the gas to set off the ripening process. In ordinary practice it is difficult to keep the rooms entirely closed during the day because the person in charge usually opens the room temporarily to take out bananas or to adjust the temperature. For Le Gros Michel bananas, only one or two treatments with gas are required. For the Cavendish variety the gas should be applied each evening. On account of the short time required for ripening, it is

desirable to treat only the quantity of fruit required for orders. Fruits should not be treated on Friday and Saturday unless they are sufficiently green to hold over until Monday.

No very thoro study has been made of the ripening of banana varieties other than Le Gros Michel and Cavendish. No doubt, however, this treatment may be applied to other banana varieties and to plantains. The Cavendish offers some advantages because it contains a small amount of fruit acids. When the fruit is ripened, these acids in combination with the sugars produce a somewhat better flavor than that of the ordinary banana. The Cavendish fruit also has a little more banana oil, making it a little better flavored. The fruits have some disadvantage in having a greater amount of dissepiment in the center, commonly called by the trade "back bone." Also, some objection to this variety has been found in the rather large, heavy bunches, which tend to break on handling. Possibly this breaking is due as much to rotting of the stalk as to excessive weight. It has been impossible to ripen Cavendish fruit successfully by heat alone. The fruits will hang in the ripening rooms for 8 days or more and the peel will turn black or rot before the pulp will ripen. However, by the use of ethylene a good color and ripening of the pulp can be produced. Ethylene treatment should make this variety usable, and it is desired by some dealers more than Le Gros Michel because of its superior flavor. The Cavendish variety is resistant to the Panama disease of the common banana, caused by a root-rot fungus, *Fusarium*. The Cavendish can be raised on soils so thoroly infested by the Panama disease that Le Gros Michel variety can not be grown. Panama disease has caused the loss of millions of dollars through the wiping out of whole plantations of Le Gros Michel bananas. It seems possible to bring in Cavendish bananas on these plantations now that the fruit can be successfully ripened. The Cavendish has been about the only banana shipped from Honolulu to the west coast of the United States. Fruits from this region are generally shipped on the deck of the vessel so they are received in a partly ripened condition.

Effect of Ethylene on Respiration of Bananas

Some data have been obtained on the effect of ethylene on the rate of respiration (40). The rate of carbon dioxide production was measured by an apparatus consisting of a glass container in which the bananas were placed, attached to suitable wash bottles to free the incoming air of carbon dioxide and to keep the air saturated with water vapor, and connected to the conductivity cell devised in this laboratory (25). The Hall and Adams (12) arrangement for the conductivity apparatus was used.

One or two bananas were usually used and the tests lasted from 5 to 15 hours. The fruits were given one or more doses of ethylene carefully measured with a micro gas burette. The usual dose was one part of ethylene to 1,000 parts of air, since this is the best concentration for ripening bananas. The ethylene was allowed to act for from 15 to 20 minutes and then the aspiration was resumed. Conductivity readings were taken every 15 to 30 minutes thereafter for one to two hours, and if a second dose of ethylene was given to the same specimen the procedure was repeated. In all cases the rate of respiration expressed in milligrams of carbon dioxide per hour was doubled or trebled within a short time and then fell to a low value. This indicates that the available carbohydrates or some other substrate used in respiration were first used up and that subsequently other enzymes came into play to replenish the reserve.

Fruits from the same bunch without ethylene showed a relatively constant respiratory rate in experiments performed simultaneously with the ethylene trials.

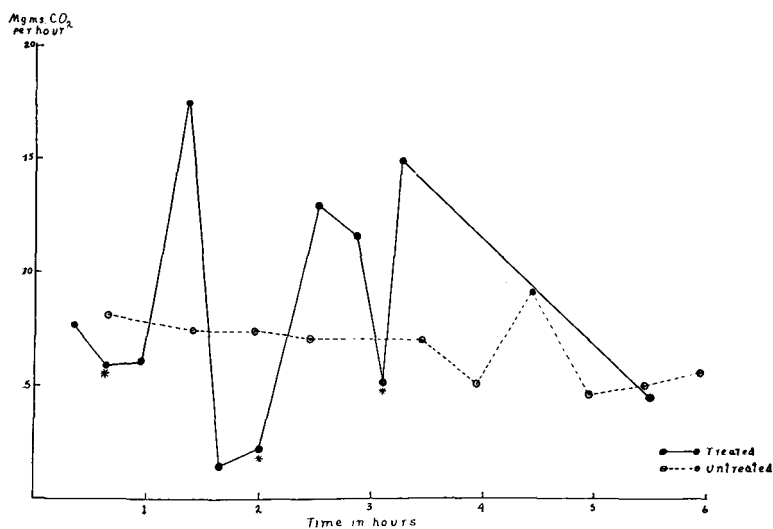


Fig. 4. Influence of Ethylene on Rate of Respiration of Bananas
Ethylene (1-1,000) administered at points marked by asterisk

Since the trend in all trials was the same, it was deemed best to show the graph of one typical ethylene-treated banana and of one check-run simultaneously to illustrate the point rather than to attempt to graph several runs on the same paper. This graph (Fig. 4) is typical of many other curves, using Le Gros Michel and Cavendish bananas.

Pineapples

Pineapples as they are received at the market are not usually given any ripening treatment, but they are generally cut at a stage of maturity that the fruit will be fairly ripe when it reaches the consumer. Frequently pineapples are sold too green because the dealer does not wish to take the loss incident to the rots produced while the fruits are ripening in storage. These fungous rots are especially destructive. Of the organisms concerned, *Thielaviopsis* is probably most destructive, altho both blue and yellow molds are found abundantly on the fruits. A large part of these rots probably could be avoided by picking the fruits in a greener condition so that they would not be bruised in transit. Green pineapples are very firm and withstand shipment well. In the past it has not been practicable to ship very green fruits because they are too sour when they reach the trade. With the use of ethylene it should now be possible to ripen fruits shipped in the green condition. When ripened with ethylene they have an excellent flavor. The aroma is increased and the excess acidity is removed, yielding a quality seldom found on the market. The greenest fruits yield the best flavor when ripened with ethylene.

Pineapples as received in the crate usually show much variation in the degree of ripeness. For this reason it is difficult to get all the fruits to the same stage of ripeness for sale. With ethylene treatment, the ripening is sufficiently rapid to allow all the fruits in a crate to ripen uniformly. The greenest fruits require 3 or 4 days at 65°F. and a gas concentration of one cubic foot of ethylene to 1,000 cubic feet of air space. The humidity should be kept rather low in the ripening rooms, much lower than for bananas. With high humidity, fungi grow over the surface of the pineapples and start rots by infecting the fruits at the "eyes" or in bruised places. This can be avoided by maintaining a low humidity. No surface sterilizing agent has been found especially effective in controlling these fungi, because the rough surface of the fruit prevents perfect surface sterilization.

In some pineapple varieties, particularly the long Chaconas, some difficulty is found in the unevenness of ripening of the top and bottom parts of the fruit. The top may be sour altho the bottom is quite ripe. With the use of ethylene this unevenness in ripening is much reduced, so that the whole fruit may be used at one time. The Chaconas variety has an excellent flavor, superior to that of the Hawaiian fruit. The Red Spanish, altho a large fruit, shows less difference in top and bottom ripening than the Chaconas. The color and flavor of the Red Spanish pineapple are improved by the use of ethylene when compared with check fruits kept at the same temperature for the same time but without ethylene. Part of this is due to an increase

in aromatic substances and part to a decrease in acidity produced by the ethylene.

The pineapple does not contain large amounts of starch, which in digestion could produce sugars, but each molecule of sucrose present is split to give two molecules of invert sugar. This increase in invert sugar together with the decrease in acidity accounts for the greater sweetness of the ethylenized fruits (38, 39).

Part of the desirability of pineapple as a fruit comes from its high content of protein-splitting enzyme, bromelin. Singers and public speakers frequently use fresh pineapples to clear the throat. The canned fruit is ineffective except for the acid it contains. If pineapples are treated with ethylene, the activity of this protein-digesting enzyme is much increased. In fact, if large quantities of raw pineapple should be eaten, some discomfort would be found in the digestion, and removal of the mucous membrane of the tongue and mouth. A stinging sensation will be felt on the tongue and even on the lips. However, in the quantity usually eaten at one time no injurious effect is observable.

The removal of acids from pineapple is evidently effected by their oxidation. It is possible to remove practically all the acid, yet this is not desirable. Fruits from which all the acids have been removed have a flat taste.

Effect of Ethylene on Enzymes of Pineapples

The effect of ethylene on the proteoclastic enzymes is to increase the protein digestion (Regeimbal and Harvey [37, 38]). Four pineapples of the same size and degree of ripeness, as judged from external appearance, were selected for treatment. The lots were given ethylene or propylene (1-1,000) once a day for four days. On the fifth day they were sampled for texture and flavor by a tasting squad. To avoid prejudiced opinions the members of the squad were not told in advance of the treatments administered, but each was required to give first an opinion of the acidity, sweetness, and aroma of the pineapples. They agreed that the ethylene-treated fruits were much superior to the untreated fruits, and that propylene produced a better flavor than ethylene.

All the fruits of one treatment were placed together, cut into cubes, and after thoro mixing, 100-gram samples were taken for chemical analysis and 200-gram samples for enzyme study. The samples for enzyme study were immediately ground fine through a Russwin food chopper and the juice was pressed out through cheesecloth. The quantity of juice in both cases was 110 cc. out of 200 grams of material, so the juice was not more concentrated in one than in the other, as

moisture determinations showed the same total solid content in each sample.

The substrate for proteoclastic enzymes consisted of a 10 per cent suspension of repurified casein dispersed in 2×10^{-3} gram equivalent of ammonium hydroxide. This concentration of ammonium hydroxide is supposed to combine completely with the casein, forming ammonium caseinate. Other protein substrates were used, but the results were not so reliable as with casein, owing to the foaming of the solutions in the Van Slyke apparatus.

Ten cubic centimeters of the pressed juice was added to 90 cc. of the substrate, thoroly mixed, and allowed to act at about 75°F . At intervals, 10-cc. portions were removed and the proteoclastic activity was determined by the amount of amino nitrogen given off in six minutes by shaking in the Van Slyke amino nitrogen apparatus. Each point was the average of two determinations that checked very closely. As will be seen from Figure 5, altho they started at the same time, the ethylene-treated sample soon took the lead and maintained it until the close of the experiment.

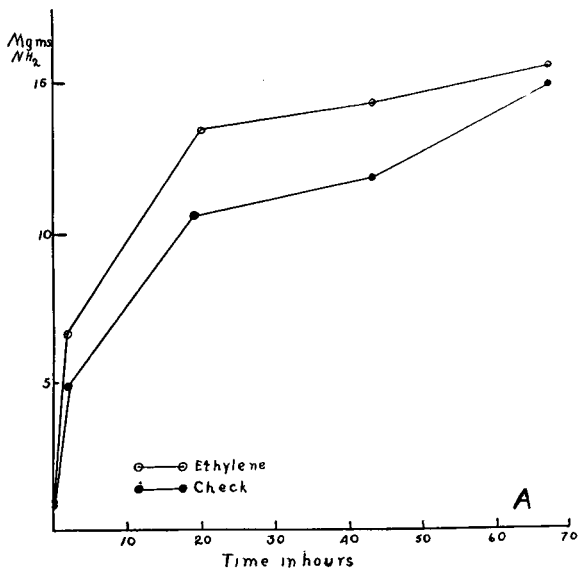


Fig. 5. Effect of Ethylene on the Proteoclastic Enzymes of Pineapples

The effect of ethylene and of propylene treatment on the inversion of sucrose in pineapples is shown in Table I. There is a decrease in total sugars but an increase in direct reducing sugars. Respiration evidently accounts for the decrease in total sugars.

TABLE I
EFFECT OF ETHYLENE AND OF PROPYLENE UPON THE SUGARS OF PINEAPPLE

	Check	Ethylene	Propylene
Total sugars, per cent	11.8	10.4	9.0
Direct reducing sugars, per cent	5.0	5.4	7.0

Dates

Dates have given some difficulty to the growers in Arizona because they will not ripen on the tree. Dates are very astringent when green, owing to the presence of tannins. The present practice in handling green dates is to put them into heated rooms for 10 or 12 days. The temperature is held at 95° to 105°F. Under this treatment the tannins disappear and there are changes in color and texture. The color changes from light greenish yellow to the dark brown of ripe dates. In the "sweating" room there is probably an inversion of the sucrose to invert sugar, resulting in a sweeter fruit.

As the dates are kept at a high temperature, soft rots are frequently the cause of heavy losses. The date crop is valuable, and the fruits are of high quality when ripened. One of the most difficult problems now facing the date growers of the southwest will be solved if the fruits can be ripened without the large losses incurred in the methods now used.

The use of ethylene hastens the ripening and the removal of tannins from dates. The time required may be very much decreased by the use of ethylene; also, the temperature need not be so high. Judging from experimental quantities, the quality of the treated fruit appears good. It will be necessary to try ethylene on commercial quantities before the application can be recommended to the trade.

As the date ripens, the browning frequently begins at one spot and extends over the whole fruit in a few hours. Fermentation processes seem to be concerned in the ripening. When the browning has extended over half the date, there is no tannin in the brown area while on the same fruit there is apparently as much in the green area as before ripening began. The removal of tannin is quickly accomplished when browning is once started. Some tannins may be oxidized to non-astringent substances. Probably, also, there is a condensation or adsorption of the tannin by colloidal carbohydrates to reduce the astringency.

Under ethylene treatment the Saily date ripens somewhat more quickly than the Deglet Noor. By proper treatment the tannin can be removed from either of these varieties within 24 hours. Whether or not sufficient invert sugar is produced in this time to make a high quality date needs to be tried on commercial quantities.

Japanese Persimmons

Japanese persimmons have an excellent flavor and appearance. They are very soft and can not be shipped when fully ripe. Fruits of non-astringent varieties may be picked sufficiently green to withstand shipment. To get the best flavor the fruits must be fully ripe. At present, no ripening of these non-astringent varieties is undertaken. Some ripening takes place in the stores. C. C. Thomas, of the Office of Foreign Seed and Plant Introduction,¹ gave the following information on ripening persimmons:

"The persimmons may, in general, be divided into two classes, one of which is astringent and the other non-astringent. The non-astringent can again be divided into two classes, one of which has yellow flesh and is always non-astringent, while the other has a dark flesh—the darkness being due to numerous small brown specks scattered through the flesh. In this group the fruits are non-astringent and have the dark flesh if seeds are present, but where seeds are not present the flesh is pure yellow and astringent. In any case the astringent varieties lose their astringency when fully mature and soft. If left on the trees after about the first of November, the fruits will begin to soften and from that time on for several weeks will be ripening a few at a time. In the softened condition they, of course, cannot be shipped to the markets. It is therefore the practice to gather them when hard and send them to the various markets, there to be sold either as hard fruits, to be ripened up by the consumer or else held by the fruit dealers and ripened up before they are sold to the consumer.

"In order to get a uniformly-ripened product that can be sold by the fruit stores directly to the consumer, various processes have been worked out to bring about the loss of the astringency and make it possible to supply these to the consumer in a condition ready to eat. For some reason or other, however, these processes have not been put into practical operation from the market standpoint and the fruits which appear on the market here in Washington and in various places in California and other sections of the country are marketed just as they come from the trees. This sort of marketing is detrimental to the sale of this fruit because persons buying it and not realizing what it is necessary to do in order to ripen the fruit attempt to eat it and find this impossible and throw it away.

"The Japanese ripen them in sake tubs in which rice beer has been stored, the fruit being placed in the tubs as soon as they have been emptied. The head of the tub is immediately replaced and made airtight; in from five to fifteen days, depending somewhat upon the temperature, they are removed and while still sound are non-astringent.

¹ Form letter of instructions from the Office of Foreign Seed and Plant Introduction.

The Bureau of Chemistry has worked on this problem and found that carbon dioxide could be used for this purpose. In their experiments they used churns and secured very good results. It has also been found that fruits immersed in warm water for twelve hours at from 85° to 105°F. will lose their astringency.

"Various types of injury also will cause the fruits to lose their astringency. This question is discussed and methods for ripening proposed by Roeding² and by Gore³." A discussion of the Japanese method of ripening persimmons is given by Fairchild (8) and by Condit (2).

Some very fine varieties of persimmons are particularly desirable on account of their size and the comparative absence of seeds. The fruits must be picked in a firm condition for shipment. When sold, altho their appearance is excellent, the fruit is disappointing on account of its astringency. By the use of ethylene all the tannins can be removed from these varieties within 50 hours. The gas should be applied in a tight room or box, holding the concentration at one part of gas to 1,000 parts of air. The ripening will be sufficiently rapid at 65°F. altho it may be hastened by raising the temperature a few degrees above this. The astringent Tsuruneko and Tamopan varieties have excellent texture and flavor after 50 hours treatment with ethylene. At 40 hours just a trace of astringency is left in the skin, but after 50 hours no tannin is left. Untreated fruits held at the same temperature but without ethylene are still very astringent after 50 hours. The flavor of the non-astringent varieties, Atago and Fujū, is much improved by ethylene. According to Lloyd (31, 32, 33, 34) the tannins of the persimmon are absorbed by colloidal carbohydrates during the natural ripening process. Evidently the ethylene treatment is able to remove astringency. Howard (28) discusses the occurrence of tannins in the persimmon.

There will be much less loss of persimmons if they are picked greener for shipment. This will result in less bruising. The expense of ripening them with ethylene at the destination is negligible.

Tomatoes

The ripening of green or partly ripe tomatoes is one of the best applications of ethylene in commercial practice. In the northern part of the United States fresh tomatoes for salads are available from the local crop for only a few weeks. For the greater part of the year the fruits are shipped in from Florida, California, Texas, and Mexico. In the late months of winter much of this fruit is very green, and altho there has been a practice of "sweating" the tomatoes, the quality is

²See 41, 42.

³See 10, 11.

often poor. The "sweated" fruits are pale in color and frequently are too acid. Sometimes as much as half the carload is lost by spoilage during ripening. If the fruits arrive free from disease, rotting is decreased. In common practice the fruit is kept at high temperature (up to 80°F.) and high humidity. By these conditions the development of fungi is favored.

By the use of ethylene the time for ripening tomatoes can be greatly decreased and the quality of the fruit increased. Under ethylene treatment, tomatoes take on a bright red color in from 4 to 6 days from the perfectly green condition. If the fruits are partly red, less time is required. The excess acidity is removed, giving a flavor at least equal to that of tomatoes ripened on the vine. There will be some difference in the rate of ripening, depending upon the variety. Ordinarily this difference does not amount to more than 24 hours for different varieties in the same stage of maturity.

The red pigment of the tomato fruit is known as lycopin. This pigment is an isomer of the yellow pigment of carrots and many other plants, known as carotin. Lycopin exists in the red-ripe tomato fruit along with carotin and other yellow pigments, the xanthophylls. Yellow varieties of tomatoes do not have lycopin, their color is due to the yellow carotin and xanthophylls. All these pigments are present in the cells in structures known as chromoplasts. When the tomato is green, no lycopin is present. Carotins and xanthophylls are commonly present, altho their color is masked by the green pigment, chlorophyll. As the fruit ripens either on the vine or with ethylene treatment in storage, the chlorophyll is decomposed to colorless substances, probably by an enzyme that has been found by Gardner (9) to cause its decomposition. As the chlorophyll decreases in quantity, the fruits become light green in color. In ripening on the vine the red color usually develops first at the blossom end on the side of the fruit exposed to the sunlight. In ethylene treated fruits, the red color frequently appears at the stem end and rays of red color are seen spreading out from the stem scar along the dissepiments (Fig. 6). This clearly shows that the entrance of the gas into the fruit hastens ripening. Evidently there is a rather rapid synthesis of lycopin following the administration of ethylene. Fruits of the Globe family of tomato varieties are deficient in yellow pigments. These fruits are inclined to have a purplish red color. The Stone and Earliana types have relatively large amounts of yellow pigments, but when the fruits are ripe the yellow color is masked somewhat by lycopin, making the color a cardinal red. Fruits of the Globe type may be somewhat deficient in color as they are ripening, but have good color when fully ripe. With some varieties of the Stone type there may be a delay in the appearance of lycopin during the ripening



Fig. 6—Early Stages in the Ripening of Tomatoes with Ethylene

Notice the production of red color at the stem end and in the tissues above the septa. This is evidence that the ethylene enters at the stem scar and diffuses along the conducting vessels in the septa.

The use of colored illustrations in this bulletin was made possible by the generosity of The Ohio Chemical & Mfg. Co. of Cleveland, Ohio.

with ethylene so that the fruits may at first appear mostly yellow, but in a few hours this gives way to the red color, evidently owing to the synthesis of lycopin. Duggar (6, 7) found that temperature is a factor of great importance in the production of red color in the tomato. High temperatures tend to produce fruits deficient in lycopin.

It is possible to ripen very immature tomatoes by the ethylene process. Altho it is not recommended as a commercial practice, tomatoes so immature as to be only two inches in diameter can be ripened with good color and flavor in from 6 to 8 days by the use of ethylene. The larger fruits in a cluster can be held in the ripe condition until the smaller fruits are red. There is some commercial advantage in this, for fruits lacking uniformity as they are received can all be ripened at one time by the application of ethylene so that the labor of sorting is decreased.

In the early part of the local tomato season the price is relatively high. It is practical to pick fruits that are nearly mature and to ripen them with ethylene for the early market before the price decreases. Removing these early fruits from the vines will decrease the yield at the time when the local crop is at its height. At the end of the season just before the tomatoes are caught by frost, it is advisable to pick the salable fruits, store them in the green condition for a few weeks, and then ripen them with ethylene. The fruits will store better in the green condition than when ripe. It is advisable to ripen the most immature fruits first because they have not matured sufficiently to form the waxy cuticle, which prevents loss of moisture. Immature fruits have a greater tendency to shrivel than those that have matured sufficiently to have a tough, waxy cuticle. This practice should effectively spread the tomato season so that the fruits need not be dumped on the market at the height of the season.

The tomatoes may be treated in baskets or crates. The gas will penetrate sufficiently if the crates are not tightly packed. In baskets there is always plenty of air circulation to allow the gas to penetrate. The temperature should be 65° to 75°F. and the humidity should be sufficient (80 to 90 per cent) to prevent shriveling. At higher temperatures rots are likely to develop, altho 80°F. can be used on fruits free from disease or cracks.

If the concentration is increased above one part of ethylene to 1,000 parts of air, the ripening will not be so rapid and some injury may appear, causing the surface at the stem end particularly to take on a brownish yellow color.

A comparison of the time required for ripening on the vine and by ethylene was made by selecting two dozen fruits each from several varieties in a tomato patch, tagging half of the fruits left on the vine

and taking for ethylene treatment fruits of exactly the same size and maturity. All were in the white stage, just before pink begins to appear. The fruits treated with ethylene were all ripe in 4 days, when those on the vine were showing only a little pink. A comparison was made of the flavor produced by ethylene treatment and by ripening on the vine by selecting fruits from the vine of exactly the same color as those treated with ethylene. All the members of a tasting squad of six persons, including three horticulturists experienced in tasting fruits for quality, agreed on the better flavor and decreased acidity of the ethylene-treated fruits as compared with those ripened on the vine.

Hard Pears

Pears are ordinarily picked somewhat green and allowed to ripen in storage. There are no particular difficulties in ripening the Bartlett variety. Some of the hybrid varieties must be planted instead of the Bartlett in certain regions where pear blight is a serious problem. Fruits of these hybrids, while of excellent size and appearance, are too hard. Through the kindness of Dr. B. T. Galloway, of the Office of Foreign Seed and Plant Introduction, samples of these hybrids were obtained for treatment with ethylene. The fruits ripened in 4 or 5 days with good flavor, color, and texture. There was a very marked mellowing of the flesh, evidently with some digestion of the stone cells. Some very hard sand pear hybrids obtained from the Minnesota Fruit Breeding Farm were treated in like manner with ethylene. These fruits required from 6 to 8 days to become mellow. The fruits seemed somewhat lacking in flavor and they have too much stone cell tissue to compete with Bartlett pears on the market; however, the astringency was removed. These sand pear hybrids are used principally on account of their winter hardiness. Probably better varieties will not be available in Minnesota for some time. Altho the fruit may not be of much commercial importance in this state, treatment will make it more palatable.

For the blight-resistant hybrids that are inclined to be too hard, the details of the treatment must be worked out on a commercial scale to secure the best keeping and eating qualities.

For ages the Chinese have ripened the hard sand pears, native of China, by treating them in tight boxes with the fumes arising from the incomplete combustion of incense. This practice is still in vogue and has been proved to produce fruits of good flavor. Ethylene is found among the products of such incomplete combustion and may be the active agent.

Apples

A great many inquiries have been made since the introduction of the ethylene process for ripening fruits on the possibility of ripening apples with this gas for the early market. A greater part of the apple crop is ripened in storage, and properly so. There are, however, times of the year when storage apples are not available. There is great demand in late summer for apples for sauce and pies. The early varieties such as Duchess and Astrakan are frequently put on the market when entirely too sour for use. The quality of these early varieties can be much improved by ripening them with ethylene. This removes a part of the excess acidity and also part of the green color from the skin. The Duchess will show considerable reddening in 4 or 5 days, making it more marketable.

Other than in the ripening of early varieties, chemical ripening will probably not have further application to fresh apples. When green apples are intended for cider or vinegar, it will probably be advantageous to sweeten them by the use of ethylene. The removal of excessive acidity from early windfalls should give cider a better flavor. It should be remembered that starches are rather quickly digested under the ethylene treatment, so that better quality in the cider may be produced by the increase of sugars as well as by the removal of the excess fruit acids.

The ripening of apples by ethylene has not been tried on more than an experimental scale. However, fruit jobbers already equipped for ripening bananas may take advantage of this process on lots of apples received too green.

Melons

Ethylene can be used to good advantage in increasing the sweetness of muskmelons, honeydew and casaba melons. Frequently muskmelons are picked when they have reached a certain size, and the fruits may not be equally ripe. It is difficult to tell the exact stage of ripeness of a melon until it is cut. Evidently the trade demands that all muskmelons in a crate shall be of the same size. It would be desirable, where size selection is practiced, to insure the ripeness of the melons at delivery by treating them with ethylene. The public has had forced upon it so often both muskmelons and honeydew melons that were unripe that there is now much hesitation in ordering them in restaurants or on dining cars. This fetish for having all melons in a pack of exactly the same size necessitates some method of guaranteeing ripe fruits. If the housewife can hold fruits until they are ripe, there is

less objection, altho green melons never reach a proper flavor when allowed to ripen in the refrigerator.

Melons that are mature but unripe at the time of frost can be kept in storage and ripened with ethylene when needed (16). The gas penetrates into the flesh well, for in 3 or 4 days at 65°F. the flesh is sweet and of the color characteristic of the particular variety when it is ripe.

Celery

The blanching of celery by ethylene gas is a commercial process now rather extensively used. Bulletin 222, of the Minnesota Agricultural Experiment Station (15), gives complete instructions for blanching celery with ethylene.

APPLICATION OF ETHYLENE IN THE RIPENING OF TROPICAL FRUITS

Mangoes

Ordinarily mangoes are not shipped to any great extent into the north. The fruit is rather soft when ripe, and no practice for ripening it from the green condition has been initiated. To withstand shipment the fruit should be firm. Mangoes were ripened nicely in 3 or 4 days by the ethylene treatment. The fruit has a good flavor and is excellent for salads. The possibility of shipping it farther north in a firm green state should extend its range of use.

Avocadoes

Avocadoes are shipped green and are usually accepted by the trade whatever their condition on arrival. Except for the few who have visited the tropics, northerners generally do not know how avocadoes should taste. The high cost of the fruits generally precludes the use of a sufficient quantity in a salad to greatly affect the flavor whether the fruits are green or ripe.

When ripened properly, the avocado has a nutty flavor and a buttery consistency which make it an excellent constituent of salads. The flavor blends remarkably well with mayonnaise dressing. It is good, also, mixed with tart fruits.

Avocadoes received in the green condition were ripened to good flavor in 2 or 3 days under conditions recommended for bananas. The ripe fruits are soft and do not withstand bruising. No particular difference was found in the conditions or time for ripening the Baldwin or the Pollock variety. The proper stage for best flavor can be judged by a slight browning of the skin.

Papayas

Papayas have never been available in cool climates on account of the difficulties of shipping. They are much prized in the tropics as a breakfast fruit and are used much as is the muskmelon. The flesh is sweet and buttery when ripe.

By the use of ethylene, papayas picked sufficiently green to withstand shipment were ripened after shipment from Florida to St. Paul. The flavor produced was as good as that of fruits ripened in the tropics.

Custard Apples

Custard apples can be grown in California and Florida. They have such an excellent flavor that they should be used in salads or as fresh fruit. The very soft texture of the ripe fruit has excluded it from shipment from the tropics. When green the fruit is firm and has the flavor of turpentine. When treated with ethylene for 2 or 3 days, this flavor was replaced by the deliciously aromatic flavor of the fruit ripened in the tropics. Evidently there is a remarkable series of chemical changes in the aromatic substances of the fruit during ripening.

Jujubes

C. O. Thomas, of the Office of Foreign Seed and Plant Introduction, gives the following instructions in regard to the ripening of jujubes:

"No commercial method has been developed for ripening fruits of the jujubes. Naturally, they ripen on the trees during the months of September and October and in some sections this begins in August, small brown spots appearing here and there on the green fruits and gradually increasing in size until they cover the entire fruit, thus giving it the characteristic brown color. This process requires several days, depending somewhat upon the weather conditions, and soon after the fruits have become entirely colored the loss of water causes them to begin to shrivel up. They can be shipped better while green, and if the fruit is to become of commercial importance in this country it would be desirable to have a process for ripening them—possibly after they have been shipped to the point of consumption. At least the time between the time when they have become fully colored and when they are to be consumed should be reduced to a very few days if they are to reach the consumer in the best condition."

Through the Office of Foreign Seed and Plant Introduction the author was given samples of the green fruits for ripening with ethylene. They were given the usual dose of ethylene, 1-1,000, at 70°F. The treated fruits turned brown and lost the acetaldehyde-like flavor of the green fruits. Simultaneously, there was a softening of the pulp

and the appearance of relatively large amounts of sugar, making a very pleasantly flavored product with an appearance somewhat like the prune but with a flavor more like that of the date. It will be necessary to work out the details of a commercial practice for ripening jujubes in this manner, but the indications from experimental trials are promising.

RELATIVE EFFECTIVENESS AND TOXICITY OF ETHYLENE, PROPYLENE, AMYLENE, AND ESTERS IN THE RIPENING OF FRUITS

For the use of farmers and small truck growers it would be of some advantage to have a substance for ripening fruits and vegetables that is in the liquid or solid state or that could be held at pressures less than the 1,300 to 1,500 pounds per square inch required for ethylene. Acetylene generated from calcium carbide is exceedingly convenient, but this gas has a disagreeable odor and produces a noticeable flavor in fruits treated with it. Besides, acetylene is toxic to the fruit and may cause headaches in those who handle it. Having in mind the physical properties of compounds related to ethylene, a number of these were tested (26) for their effectiveness in ripening fruits. Green bananas were treated in closed chambers at known temperatures and concentrations of the substances. The fruits were taken from the same hands in the bunch for the comparative trials.

In every case propylene was found to cause ripening somewhat quicker than ethylene and to give better flavor in bananas, honeydew melons, and other fruits. The better flavor seems to be due partly to an increase in the ester content of the fruits. Since propylene produces a more rapid change, it may be expected that fruits treated with it will be sweeter after the lapse of 48 hours than those treated with ethylene. Tasting squads made up of horticulturists and others experienced in the tasting of fruits for quality were used. Unknown to each other, the members of the squad checked on the desirability of the flavors produced by propylene as compared with those produced by ethylene. In ripening hard pears, propylene (1-1,000) seemed to give quicker ripening and better flavor than ethylene. The chief difficulty in the use of propylene is that it is not now commercially available. The more extensive use of propylene will probably make more of this gas available for commercial treatments.

Ethylene oxide, methylene chloride, ethyl chloride, ethylene chloride, propylene chloride, and amylene are desirable on account of their physical property of being liquid at ordinary temperatures at comparatively low pressure, but they were found not as effective as ethylene in ripening fruits, and they all show greater toxicity, shown by the blackening

or browning of the peel. Amylene, as it is available commercially, has an objectionable odor and produces objectionable flavors in the fruit.

The esters—amyl acetate, ethyl acetate, and methyl acetate—produce browning and blackening of the peel without ripening the fruit. Amyl acetate seems more toxic than methyl or ethyl acetate. The vapor of amyl alcohol was not particularly toxic. Acetaldehyde produced a brown color similar to that of fruits ripened without gas.

It was thought possible that some of these esters might serve as solvents for ethylene and thus might be used to obtain a solution of ethylene that would not require high pressure to maintain the liquid state, but none show sufficient ethylene solubility to be of any value for the commercial application of ethylene. Ethylene is not sufficiently soluble in acetone, water, or ether to use solutions in these solvents for the treatment of fruits in quantity.

The bromine compounds related to ethylene and propylene are unsuitable for the treatment of bananas on account of the bromine flavor that they produce. Propylene bromide, ethylene bromide, propylene bromhydrin, and ethylene bromhydrin, at equivalent molecular concentrations corresponding to the concentrations of ethylene in use, produced no ripening of the pulp but strong blackening of the peel. With propylene bromhydrin the pulp also becomes black. Ethylene chlorhydrin and propylene chlorhydrin produce some ripening but not as effectively as ethylene. With propylene chlorhydrin there is considerable black spotting of the banana peel. Directly beneath the spots the pulp is mushy, while the center of the pulp is not ripened. Ethylene chlorhydrin seems somewhat less toxic than the propylene compound but produces some blackening and only slow ripening. In bananas partly ripened with ethylene chlorhydrin, the pulp has a slightly salty, chlorine-like taste, followed in a few minutes by a slight burning sensation on the palate. This flavor is at least as objectionable as that produced by acetylene.

ETHYLENE IN THE TREATED PRODUCT

The concentration of ethylene used in blanching or in ripening is so low as to make its presence ascertainable only by the most delicate of tests. A carload of from 315 to 335 bunches of bananas averaging from 55 to 60 pounds per bunch will weigh about 20,000 pounds. If this carload of fruit is placed in a room 8x10x20 (1,600 cubic feet) the dose given should be about 1.5 cubic feet. A second dose of the same size should be liberated twenty-four hours after the first. This treatment would require a total of 3 cubic feet of gas for the ripening. If none of this gas escaped from the room and if all of it was absorbed by the fruit, the 3 cubic feet, weighing 0.2335 pound, would be con-

tained in 20,000 pounds of bananas. This is at the rate of one pound of ethylene for about 100,000 pounds of bunch fruit. But only part of the bunch is sold as fruit, and the banana peel is not eaten. Provided there is no change in the ethylene after it enters the fruit, the concentration (one pound of ethylene in 100,000 pounds of bananas) would be so low as to make chemical estimation impossible. However, there is good reason to believe that ethylene is oxidized to ethyl alcohol and finally to carbon dioxide and water in the fruit in much the same manner as in the animal body (35). It would hardly be possible to demonstrate the oxidation of such extremely low concentrations of ethylene as are used for ripening fruits. This oxidation no doubt would remove a large part of the ethylene, probably all of it, by the time the fruit reaches the consumer.

The ethylene liberated into a room full of fruit may be dissipated by leakage or it may be absorbed by the fruit. The time for absorption differs with the variety of fruit and with the ease of entry through the skin. The skin of the banana contains openings called stomata through which diffuses the ethylene as well as the oxygen used in respiration and the carbon dioxide produced in respiration. Similar openings are found in the tomato peel. If these openings are closed by wilting and loss of turgidity or by low temperature, it is desirable to open them. This can be accomplished by warming the fruit and by high humidity of the atmosphere in the room.

The ethylene also penetrates along the tract of the vascular bundles of the fruit. This is clearly shown in Figure 6. In fact, in tomatoes this penetration through the stem end and along the vascular bundles may exceed the penetration through the skin.

DIFFUSION OF THE GAS INTO CRATES

Ethylene has a molecular weight of 28.04, giving it almost the same specific gravity as air and almost the same rate of diffusion. If the specific gravity of air is taken as 1.000, the specific gravity of ethylene is 0.978. It may be seen from this that the gas will have practically no tendency to accumulate at either floor or ceiling as it is being liberated from the tank.

The ethylene will penetrate sufficiently into bananas altho they are hung as closely together as possible. Tomatoes in bushel baskets can not be packed tightly and no special provision need be made for the diffusion of the gas. If tomatoes are in crates, it is best to pile the crates loosely to allow some air circulation. Celery in crates should not be packed tightly. The gas penetrates well even into large crates.

Ethylene is soluble in water, 12.8 cc. per 100 cc. of water at 65° F. (18.3°C.). It may be expected that the gas will go into solution in

water on the floor or walls of the room and into fruit that contains a high percentage of water. The gas is also soluble in oils that are known to be present in the banana peel, and in waxes and other fatty substances.

EFFECT OF ETHYLENE ON ANIMALS

No effect of being in the treating rooms has become apparent in the three years during which the author has applied ethylene in commercial practice. There is no complaint of any symptoms by men who use the gas. In fact, it is probable that the average man who smokes tobacco in any form gets much more ethylene from his tobacco (30) than he would get from the use of ethylene for ripening fruits. Also, tobacco smoke contains pyridine, carbon monoxide, and acetylene, which are far more injurious (46, 29) than ethylene itself.

To test the effects of continuous inhalation of ethylene in low concentrations, five guinea pigs were put into a gas-tight incubator of 2.25 cubic feet capacity and given ethylene in a concentration of about one part per one thousand parts of air. The concentration was sufficient to ripen in 48 hours green bananas that were placed in the same cages. The air-ethylene mixture was forced at constant low pressure through the incubator at the rate of about 5 cubic feet per hour. As a check, five guinea pigs were placed in the same type of incubator and received 5 cubic feet per hour of air alone. The air was measured by two Sargent wet test meters and the ethylene by regulating a low pressure expansion valve to deliver a nearly constant number of bubbles per minute. The guinea pigs were fed the same ration of oats, water, and lettuce. At the end of 4 weeks the guinea pigs in ethylene (1-1,000) had gained an average of 34.8 per cent of their weight while the checks had gained an average of 35.9 per cent of their weight. Evidently there was no significant effect on the gain in weight due to the inhalation of ethylene. On autopsy, no lesions of any organs were detected by members of the Division of Veterinary Medicine, University of Minnesota, who had been using guinea pigs from this lot for several months. Special examinations of the lungs and respiratory passages were made for evidences of congestion or irritation produced by the ethylene, but no such effects were visible.

A similar lot of ten guinea pigs was divided into two groups of five pigs each. One of these lots was used as a check. The other lot was allowed to drink only water that had been saturated with ethylene at one atmosphere pressure. Both lots received the same food. The check lot in 4 weeks gained an average of 46.5 per cent of their weight while the lot receiving only ethylene saturated water gained an average of 54.2 per cent of their weight. There was evidently no deleterious

effect on the growth of these guinea pigs, altho they received many times as much ethylene as they would get in food treated with ethylene. The ethylene was given in the water instead of in the food because it might be oxidized in the food and thus be lost. Also, food treated with ethylene would probably contain more sugars and other digestible substances than untreated food and for this reason errors would be introduced that would not occur if ethylene was given in the water only. It might be thought that the greater gain in weight (8 per cent) of the guinea pigs receiving ethylene is significant, but with such a small lot this conclusion is not reliable. This experiment is being repeated with larger lots to find whether there is actually a growth stimulation, since this might be produced by the effect of ethylene in stimulating enzyme action in the alimentary tract, leading to better digestion in the same manner that digestion in plant tissues is stimulated by ethylene.

SUMMARY OF PRACTICAL SUGGESTIONS FOR THE APPLICATION OF ETHYLENE

Ethylene gas can be bought from chemical, dental, and hospital supply companies, in cylinders containing 13 or 25 cubic feet of gas.⁵ The 25-cubic-foot size contains sufficient gas to ripen five or more carloads of fruit. The cost of sufficient gas to ripen a carload of fruit is less than a dollar. The gas costs about \$5.00 for 25 cubic feet, but usually a deposit must be made for the use of the cylinder. The total weight of gas and cylinder of this size is about 15 pounds.

The ethylene gas is under high pressure (up to 1,300 pounds per square inch) in the steel cylinder. In handling the cylinders care must be used not to drop them. The tanks should be kept away from stoves or boilers and should not be allowed to lie in hot sunshine. Lights and fires should be kept away from them to avoid the ignition of gas which may leak from unclosed valves. The tanks should not be placed in closets or small rooms. In a small space an explosive concentration of gas in the air may be reached in case the valve is not closed.

Since the pressure on a full cylinder of ethylene is so high, a special expansion valve must be used for the measurement of the dose of gas required. This valve should be attached to the cylinder securely with a lead gasket to prevent leaks between the expansion valve and the cylinder. After attaching the expansion valve, see that the thumb-screw on it is turned in the direction of "close" until the pressure of the spring is released. Then the valve on the cylinder should be completely opened. Examine carefully for a possible escape of gas around

⁵ Information in regard to sources of ethylene, measuring gauges, and other equipment will be given upon request.

the lead gasket. Always use the valve on the tank as the shut-off valve. Do not use the expansion valve to stop the flow of gas.

A constant low pressure expansion valve discharging through a very small orifice is the most convenient means of measuring the gas, for at a constant low pressure a uniform number of cubic feet of ethylene will flow through the orifice per minute. A watch may then be used to time the flow in liberating a required volume of gas. The number of cubic feet of ethylene delivered per minute is stated on the dial face. The valve should be especially calibrated for ethylene gas. The total outlay for equipment, including gas, cylinder, and measuring gauge, should be not more than \$30. If the volume of sales does not warrant such an expenditure, it is not economical to undertake the use of ethylene. The equipment will last for many years, with reasonable care.

To determine the dose of ethylene required for a certain room, measure its height, length, and breadth in feet and multiply these together to obtain the number of cubic feet of air contained in the room. Thus a room 8 feet high, 20 feet long, and 12 feet wide contains ($8 \times 20 \times 12 = 1,920$) 1,920 cubic feet. Since only one cubic foot of ethylene should be liberated for 1,000 cubic feet of air space, divide the number of cubic feet of air space by 1,000 to obtain the number of cubic feet of ethylene to be liberated at each dose. ($1,920 \div 1,000 = 1.92$ cubic feet.) To liberate a dose of 1.92 cubic feet of ethylene into the room at a rate of 0.2 cubic foot per minute will require ($1.92 \div 0.2 = 9.6$ minutes) 9 minutes, 36 seconds. Open the valve on the tank and screw in the thumbscrew on the expansion valve until the pointer on the gauge stands constant at the point marked to deliver 0.2 cubic foot per minute. As soon as the pointer reaches this mark, note the exact second on the watch. Allow the gas to flow for the exact time necessary to release the required dose as determined beforehand (9 minutes, 36 seconds for 1.92 cubic feet). Then quickly close the valve on the cylinder and wait until the pointer on the expansion valve returns to zero, then unscrew the thumbscrew until the pressure of the spring is released.

It is not necessary to take into account the quantity of fruit in the room. It evidently is necessary to obtain an ethylene concentration at one part per 1,000 parts of air space in the room. As much gas is required, then, for obtaining the proper concentration for a small quantity of fruit as for a roomful. If the room were absolutely gas tight, it should not be necessary to restore the concentration for a small lot of fruit as soon as for a roomful, but in practice it is generally found desirable to restore the concentration each evening. When the dose of gas has been liberated, it should not be allowed to escape by opening

doors. It is best to air out the room and restore the concentration if the room is opened for more than a second or two.

During the liberation of the gas from the tank, neither fire, open lights, cigarettes, cigars, or pipes should be allowed in the room. Incandescent electric lights are safe if the switches are of the non-sparking type. Actually, the danger in handling ethylene is about the same as in allowing a very small jet on a gas stove to run unlighted for the same length of time. The concentration of ethylene used for ripening fruits is so low that within a minute or two after closing the valve, fires may be relighted with safety. The least concentration of ethylene in air that will explode (3 per cent = 30 parts per 1,000) is thirty times as great as the greatest concentration required to ripen fruits (0.1 per cent = 1 part per 1,000).

A concentration of gas greater than one cubic foot of ethylene to 1,000 cubic feet of air space will not ripen fruits as rapidly as the proper concentration. If the concentration is as high as one to 500, tomatoes will show a brownish yellow color at the stem end, and bananas will show browning of the skin before the pulp is ripe. The gas has been found to penetrate through the wrappings of tomatoes, and through boxes of fruit that are not packed too tightly to allow free air circulation.

The room may be heated by oil stove, gas, steam, or electricity. The best installation is one that allows a wide adjustment of heating to take care of the heat requirements of summer and winter conditions. A convenient gas heater is shown in Figure 7. A wood or a coal fire is not desirable, as it can not be adjusted properly and is too inconstant. A controlled radiator attached to the steam line is fairly satisfactory but may show too wide variation in temperature unless the steam pressure is very constant. If steam is available, a very compact radiator and ventilator, as shown in Figure 8, may be installed. An electric fan is used to force the air over a compact radiator. The temperature can be controlled automatically by changing the speed of the fan through an electric temperature controller. The use of automatically controlled temperatures is highly desirable. It makes possible a uniform ripening, which can be adjusted according to the desire of the operator. With uniform conditions ripening can be depended upon, so that the demands of the trade can be fulfilled on time. For banana rooms it is desirable to ventilate and lower the temperature and humidity after the fruit has been ripened. This can be accomplished by a system of air ducts and inlet valves installed with the heating unit.

The following fruits and vegetables have been ripened in large lots in commercial practice by several hundred fruit jobbers for more than

a year: Bananas of all kinds, tomatoes, celery, pineapples, cantaloupes, oranges, limes, lemons, and grapefruits.

Experiments on small lots, but not yet on a commercial scale, have demonstrated the use of ethylene to be of value for the following fruits and vegetables: Dates, jujubes, persimmons, pears, mangoes, pomegranates, peppers, alligator pears, honeydew melons, apples, plums, papayas, chayotes, chiermoya or custard apples, plantains, endive, chicory, and rhubarb.

According to the results of experimental trials, the following products probably can not be treated successfully with ethylene: Watermelons, cauliflower, asparagus, or any fruits or vegetables that contain little carbohydrate reserves or that have a thick, impenetrable rind.

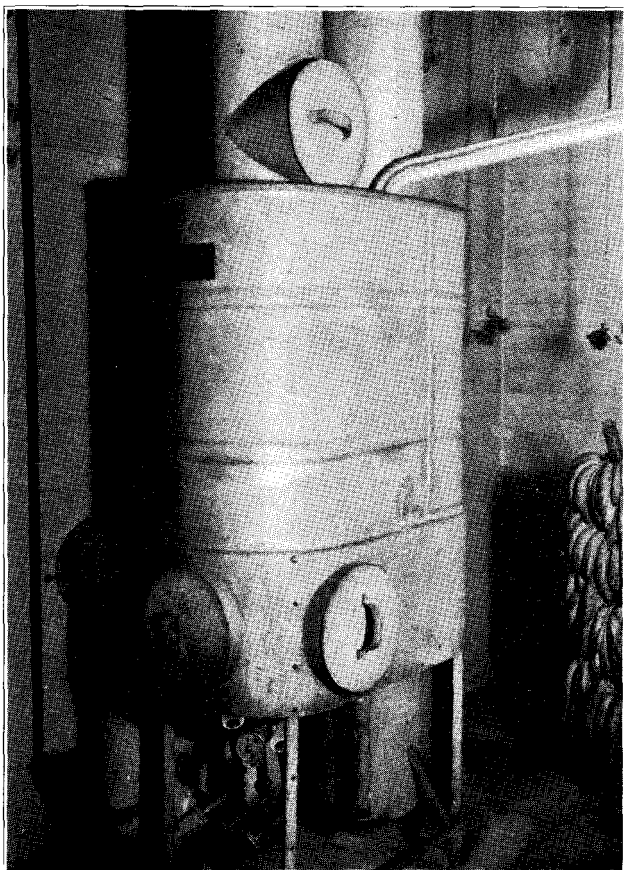


Fig. 7. Gas Heater, Ventilator, and Humidifier

The heat produced by the flame causes the air circulation in the room and also evaporates water to maintain a proper humidity.

Ethylene treatment should be tried on any plant product from which it is desired to remove chlorophyll, organic acids, tannins, or other bitter substances. It may be of use in cases in which it is desirable to increase sugar content by the hydrolysis of starch or other carbohydrates. Ethylene hastens the action of the hydrolytic and oxidizing enzymes.

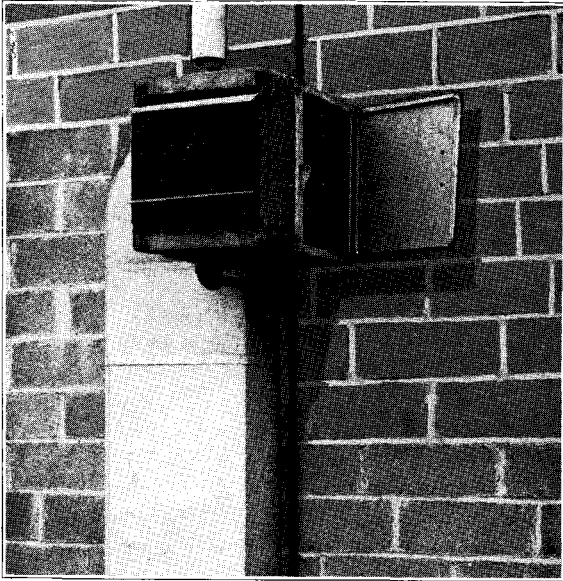


Fig. 8. Automatically Controlled Radiator of Compact Design

A fan behind the radiator is used for ventilation and to insure air circulation. The electric thermo switch may be used to control the temperature by changing the speed of the fan.

LITERATURE CITED

1. Chase, E. M. Correction concerning use of ethylene gas. *Calif. Citrograph* 9:118. 1924.
2. Condit, I. J. The kaki or oriental persimmon. *Calif. Expt. Sta. Bull.* 316, p. 257. 1919.
3. Crocker, William, and Knight, L. I. Effect of illuminating gas and ethylene upon flowering carnations. *Bot. Gaz.* 46:259-276. 1908.
4. Denny, F. E. Hastening the coloration of lemons. *J. Agr. Res.* 27:757-771. 1924.
5. ———. Effect of ethylene upon respiration of lemons. *Bot. Gaz.* 77:322-329. 1924.
6. Duggar, B. M. Lycopersicin, the red pigment of tomato, and the effects of conditions upon its development. *Wash. Univ. Studies* 1:22-45. 1913.
7. ———. Conditions affecting the development of lycopin in the tomato. *Abs. Science n. s.* 37:378. 1913. *Abs. Expt. Sta. Rec.* 29:132. 1913.
8. Fairchild, D. The Japanese method of ripening persimmons. *Abs. Expt. Sta. Rec.* 17:618. 1905-06.

9. Gardner, W. A. Abstracts of papers. Proc. Am. Soc. Plant Physiologists, Philadelphia. 1927.
10. Gore, H. C. Large scale experiments on processing. Notes on the preparation of dried persimmons. U. S. Dept. Agr. Bur. Chem. Bull. 155. 1912.
11. ————. Experiments on the processing of persimmons to render them nonastringent. U. S. Dept. Agr. Bur. Chem. Bull. 141. 1911.
12. Hall, R. E., and Adams, L. H. Application of the thermionic amplifier to conductivity measurements. J. Am. Chem. Soc. 41:1515-1525. 1919.
13. Harvey, E. M. Some effects of ethylene on the metabolism of plants. Bot. Gaz. 60:193-214. 1915.
14. Harvey, R. B. A new method of blanching celery. Minn. Horticulturist 53:41. 1925.
15. ————. Blanching celery. Minn. Agr. Expt. Sta. Bull. 222. 1925.
16. ————. Ripening with ethylene gas. Canadian Horticulturist 49:136. 1926.
17. ————. The ripening of fruits by ethylene gas. Minn. Horticulturist 54:140. 1926.
18. ————. The use of ethylene as a ripener of fruits and vegetables. Agr. Leaders Digest 7:31. 1926.
19. ————. Solving the problem of ripening tropical fruits in the north. Chicago Packer 48:16. 1926.
20. ————. Results of commercial application of ethylene for blanching celery. Market Growers Journal 38:237. 1926.
21. ————. The use of ethylene gas in ripening fruits and vegetables. The Blue Anchor 4:3. 1927.
22. ————. Chemical ripening of fruits and vegetables. Chem. Bull. 14:101, 125, 126. 1927.
23. ————. Treatment of green celery with ethylene. Am. Produce Grower 2:20, 27, 28. 1927.
24. ———— and Regeimbal, L. O. Physiology of blanching celery. Proc. Am. Assn. Adv. Sci., Washington. 1924.
25. ————. A conductivity cell for continuous measurements of respiratory rate. Plant Physiol. 1:205-206. 1926.
26. ————. Relative effectiveness and toxicity of ethylene, propylene, amy-lene, esters, and similar compounds in the ripening of fruits. Proc. Am. Soc. Plant Physiologists. Abstracts of papers. Philadelphia. 1926.
27. Hibbard, R. P. Personal communication. Nov. 30, 1925.
28. Howard, B. J. Tannin cells of persimmons. Bull. Torrey Bot. Club 33:567-576. 1906.
29. Knight, L. I., and Crocker, Wm. Toxicity of smoke. Bot. Gaz. 55:337-371. 1913.
30. Lewes, V. B. The action of heat upon ethylene. Proc. Roy. Soc. London 55:90-107. 1894.
31. Lloyd, F. E. The behavior of tannin in persimmons with some notes on ripening. Plant World 14:1-14. 1911.
32. ————. Carbon dioxide at high pressure and the artificial ripening of persimmons. Science, n. s. 34:924-928. 1911; Expt. Sta. Rec. 26:327. 1912.
33. ————. The tannin-colloid complexes in the fruit of the persimmon. Biochem. Bull. 1:7. 1911.

34. Lloyd, F. E. The induction of non-astringency in persimmons at supra-normal pressures of carbon dioxide. *Science*, n. s. **37**:228-232. 1913; *Abs. Expt. Sta. Rec.* **29**:264. 1913.
35. Luckhardt, H. B., and Carter, J. B. The physiologic effect of ethylene. *J. Am. Med. Assn.* **80**:765-770. 1923.
36. Regeimbal, L. O., and Harvey, R. B. Carbohydrate changes in celery under ethylene treatment. *Proc. Am. Assn. Adv. Sci. Kansas City.* 1925.
37. ————. The effect of ethylene on the enzymes of pineapple. *Proc. Am. Soc. Plant Physiologists. Abstracts of papers. Philadelphia.* 1926.
38. ————. The effect of ethylene on the enzymes of pineapple. *J. Am. Chem. Soc.* **49**:1117. 1927.
39. Regeimbal, L. O., Vacha, G. A., and Harvey, R. B. The effect of ethylene on the respiration of bananas during ripening. *Proc. Am. Soc. Plant Physiologists. Abstracts of papers. Philadelphia.* 1926.
40. Reynolds, P. K. *The Banana.* p. 101. Cambridge, Mass. 1927.
41. Roeding, G. C. Green persimmons made marketable. *Calif. Fruit Grower* **36**:45. 1907; *Abs. Expt. Sta. Rec.* **19**:743. 1907-08.
42. Roeding, G. W. Unpuckering persimmons. *Pacific Rural Press*, p. 333. Nov. 23, 1907.
43. Rosa, J. T. Ripening tomatoes. *Proc. Am. Soc. Hort. Sci.* **22**:315-322. 1925.
44. Schonard, F. Effect of illuminating gas on trees. pp. 1-48. Dept. Public Works, Yonkers, N. Y. 1903.
45. Sievers, A. F., and True, R. H. A preliminary study of the forced curing of lemons as practiced in California. *U. S. Dept. Agr. Bur. Plant Indust. Bull.* 232, p. 1-38. 1912.
46. Smith, J. L., and Hoskins, H. P. An experiment on the effect of inhalation of ethylene. *J. Hyg.* **1**:123-124. 1901.