Use of Calcium Carbide for Artificial Ripening of Fruits -Its Application and Hazards

Uttam K. Bhattarai and Kshitij Shrestha
E-mail : ukbhattarai21@hotmail.com

Abstract

A review of different articles related to artificial ripening was done. Focus was given on the hazards and applications of calcium carbide for artificial ripening, being a very common practice in Nepalese Market. Litterateurs showed many hazardous aspects of carbide use and also standard procedures of safety handling aspects. But being banned by regulation, due to its hazardous aspects and lack of proper handling methods among users, it was concluded that the use of calcium carbide is to be strictly monitored and controlled.

Keywords:

Acetylene, artificial ripening, calcium carbide, climacteric and non-climacteric fruits, ethylene

1. Introduction:

Nepal has its huge potential for the production of different agricultural produces such as cereal grains including millets, legumes, fruits and vegetables, spices & condiments, among others due to its varying topography and accordingly different climatic conditions. The location of Nepal favours in producing many of the agricultural produces that are produced in all, tropical, subtropical and temperate types of climate.

As emphasised by the Agricultural Perspective Plan (APP) sufficient thrust was given for the production of High Value Crops (HVC) including fruit and vegetable products in the 9th five-year plan. Similarly, emphasis has been given in the 10th plan for the production of horticultural products. The latest statistics of Nepal shows that 511,397 MT of fruits and 1,890,100 MT of vegetables were produced in the country in the fiscal year 2003/04.The production figures of different types of fruits for the year 2003/04 is as given in the Table 1 below:

Table No -1

Production figures of different types of fruits for the year 2003/04

Fruits	**Production**
Citrus	148010 MT
Winter (Deciduous)	94988 MT
Summer (Tropical)	268399 MT

(MOAC, 2003/2004)

Citrus fruits of importance that constitute the above figures are orange, sweet orange, lime, lemon and others. Similarly, winter (deciduous) fruits comprises mainly of apple, pear, walnut, peach, plum, apricot, persimmon, pomegranate, and others. In the same way, in the order of highest production figures, tropical (summer) fruits are mango, banana, guava, litchi papaya, areca nut, jackfruit, pineapple and coconut.

The above figures indicate that fruit production of the country has sufficient role in contributing to the national Gross Domestic Product (GDP). Therefore, its production, handling and marketing i.e. from the farm to table continuum, is very important.

Some fruits are harvested only after they are ripened in the orchard and some can be harvested after they are fully matured before ripening, to facilitate for the handling and marketing of such products. The latter types of fruits before placing on the market are to be ripened. For this, artificial ripening, especially by the use of calcium carbide is being practiced in Nepal. To this end, different articles have been published in different media for and against the use of such chemicals and have created some confusion among the consumers. Therefore, this article attempts to inform the consumers whether the use of such chemical is harmful or not, how to use such ripened fruits without violating the safety norms and how to identify such fruits on the market.

2. Fruit Ripening

Ripening is a dramatic event in the life of a fruit - it transforms a physiologically mature but inedible plant organ into a visually attractive olfactory and taste sensation. Ripening marks the completion of development of a fruit and the commencement of senescence, and it is normally an irreversible event.

Ripening is the result of complex changes, many of them probably occurring independently of one another. Major changes are - seed maturation, colour changes, abscission, changes in respiration rate, changes in rate of ethylene production, changes in tissue permeability, softening, changes in carbohydrate composition, organic acid changes, protein changes, production of flavour volatiles, development of wax on skin etc (Prat, 1975).

2.1 Physiology of Respiration

A major metabolic process taking place in harvested produce or in any living plant product is respiration. Respiration can be described as the oxidative breakdown of the more complex materials normally present in cells, such as starch, sugars and organic acids, into simpler molecules such as carbon dioxide and water, with the concurrent production of energy and other molecules which can be used by the cell for synthetic reactions.

Respiration Reaction:

$$C_6H_{12}0_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{Energy}$$

Respiration rate of produce is an excellent indicator of metabolic activity of the tissue and thus is a useful guide to the potential storage life of the produce. If the respiration rate of a fruit or vegetable is measured- as either oxygen consumed or carbon dioxide evolved- during the course of its development, maturation, ripening and senescent periods, a characteristic respiratory pattern is obtained. Respiration rate per unit weight is highest for the immature fruit or vegetable and then steadily declines with age (Baile, 1964). Fruits can be divided into different groups according to their respiratory pattern (or ripening pattern).

2.2 Fruits and Ripening Patterns

Some fruits are harvested when they are fully matured and ripened in the orchard. Such fruits if harvested early cannot be ripened so as to get full taste of the produce. But, some fruits, if harvested in fully matured condition, can be ripened after harvesting without disturbing the quality. Fruits are living and respire continuously and this act is responsible in showing such characters as mentioned above. According to the respiration pattern fruits are classified into two categories as mentioned below:

2.2.1. Climacteric pattern

The rate of respiration, prior to start of ripening decreases to minimum (pre-climacteric minima) and as ripening starts, the rate of respiration increases to maximum and then falls steadily, such type of phenomenon is termed as climacteric pattern of respiration and the fruit showing such activity are climacteric fruits. It comprises most deciduous tree fruit species (apples, pears, apricots, peaches), many tropical and sub-tropical fruits (banana, guava, avocado, mango) and some fruit vegetables such as tomato.

2.2.2. Non-climacteric pattern

The growth and development of fruits is accompanied by a decline in rate of respiration. This decline is continuous throughout ripening whether it is pre or post harvest stage and continuous throughout senescence. This is non- climacteric pattern and fruits showing such activities are Non-climacteric fruits such as lemons, orange, grape, cherry, pineapple, strawberry etc.

2.3 Role of Ethylene in Ripening

Ethylene's role as a potent plant growth regulator affecting many phases of plant growth and development was established only in the last 50 years, but its effect has been known for centuries. Ethylene plays a role in the post harvest life of many horticultural crops often deleterious, speeding senescence and reducing shelf life and beneficial improving the quality of the product by promoting faster, more uniform ripening before retail distribution.

Climacteric and non-climacteric fruits may be further differentiated by their response to applied ethylene and by their pattern of ethylene production during ripening. It has been clearly established that all fruit produces minute quantities of ethylene during development. However, coincident with ripening, climacteric fruits produce much larger amounts of ethylene than non-climacteric fruits. This difference between the two classes of fruit is further exemplified by the internal ethylene concentration found at several stages of development and ripening. The internal ethylene concentration of climacteric fruits varies widely, but that of non-climacteric fruits changes little during development and ripening (Burg and Burg, 1962). Ethylene, applied at a concentration as low as 0.1 - 1.0 micro litres per litre for one day, is normally sufficient to hasten full ripening of climacteric fruits, but the magnitude of climacteric is relatively independent of the concentration of applied ethylene. In contrast, applied ethylene merely increases the respiration of non-climacteric fruits, the magnitude of the increase being dependent on the concentration of ethylene. Moreover, the rise in respiration in response to ethylene may occur more than once in non-climacteric fruits in contrast to the single respiration increase in climacterics (Baile, 1964).

Table No. - 2

Internal ethylene concentrations measured in several climacteric and non-climacteric fruits

Fruits	Ethylene (μl/L)
Climacteric	
Apple	25-2500
Pear	80
Peach	0.9-20.7
Avocado	28.9-74.2
Banana	0.05-2.1
Tomato	3.6-29.8
Non-climacteric	
Lemon	0.11-0.17
Lime	0.30-1.96
Orange	0.13-0.32
Pineapple	0.16-0.40

(Burg and Burg, 1962)

2.3.1 Ethylene biosynthesis:

Ethylene has been shown to be produced from methionine via a pathway that includes the intermediates S-adenosyl-methionine (SAM) and 1-aminocyclopropane-1-carboxylic acids (ACC). The conversion of SAM to ACC by the enzyme ACC synthase is thought to be the rate-limiting step in the biosynthesis of ethylene. However, addition of ACC to pre-climacteric (unripe) fruit generally results in only a small increase in ethylene evolution showing that another enzyme, the ethylene forming enzyme (EFE) is required to convert ACC to ethylene, EFE has not been identified but it is known to be labile and is thought to be membrane-bound. Factors that affect the activity of ACC synthase include fruit ripening, senescence, auxin, physical injuries, and chilling injury (Wills *et al*., 1989).

2.3.2 Mode of Action:

It has been proposed that two systems exist for the regulation of ethylene biosynthesis: System 1 is initiated or perhaps controlled by an unknown factor, probably involved in the regulation of senescence. System 1 then triggers System 2 which is responsible, during ripening of climacteric fruits, for the production of the large amounts of ethylene that are necessary for the full integration of ripening. Non-climacteric fruits do not have an active system 2; the treatment of climacteric fruits with ethylene circumvents system 1 (Wills *et al*., 1989).

3. Artificial Ripening

Artificial ripening is done to achieve faster and more uniform ripening. It is the process by which ripening is controlled and product may be achieved as per requirement by controlling the different parameters.

Climacteric fruits, particularly tropical and subtropical species, are frequently harvested when less than fully ripe and then transported, often over considerable distances, to areas of consumption. Here these fruits are ripened to optimum quality under controlled conditions of temperature, relative humidity, and with some fruits, through the addition of ripening gases. A further advantage of controlled ripening is to improve uniformity of ripening of fruit. The use of relatively high ripening temperature may also minimize the development of rots in ripe tropical fruits. In contrast, non-climacteric fruits generally undergo little or no desirable change in composition after harvest and must not be harvested until fit for consumption.

A significant proportion of the world production of bananas of approximately 18 million tonnes is ripened under controlled conditions. The banana is unusual in that it can be picked over a wide range of physiological ages from half grown to fully-grown and ripened to excellent quality with the aid of ethylene. Acetylene, generated by adding water to calcium carbide, produces a ripening response, but in practice at least a concentration 100 times higher is required (Wills *et al.,* 1989).

The concentrations of ethylene required for the ripening of various commodities vary but in most cases are in the range of 0.1 to 1 ppm. The time of exposure to initiate full ripening may vary, but for climacteric fruits exposure of 12 hours or more are usually sufficient. Full ripening may take several days after the ethylene treatment.

In general optimum ripening conditions are given in table.

Table No -3

General optimum ripening conditions for different fruits

Parameters	Value
Temperature	18 to 25^{o}C
Relative humidity	90 to 95 %
Ethylene concentration	10 to 100 ppm
Duration of treatment	24 to 72 hours depending on fruit king and maturity stage
Air circulation	Sufficient to ensure uniform distribution of ethylene, which reduces the effectiveness of ethylene

(Reid, 1992)

3.1 Sources of ethylene

1. ***Explosion proof ethylene mixture***: - 6% ethylene in carbon dioxide by weight

2. ***Ethylene generator***: - ethanol is heated in the presence of catalyst to produce ethylene.

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

3. ***Ethephon***: - Chemical name- 2-chloroethane phosphonic acid, commercial name- Ethrel, Florel, Cepa
   It is acidic in water solution and above pH 5 it liberates ethylene.

4. ***Use of ripe fruit***: - Ripe fruits with ethylene production can be used to ripen or degreen other fruits.

5. ***Calcium Carbide***: - When hydrolyzed, it produces acetylene, containing trace amounts of ethylene that are sufficient to be used in fruit repining. Acetylene, the end product of Calcium Carbide and Water provokes the same effects as the fito-hormone ethylene, but neither Calcium Carbide nor synthetic ethylene when used to "ripen" less mature fruit, produce results that approach those of fruit picked closer to it's peak.

$$CaC_2 + H_2O \longrightarrow CaCO_3 + C_2H_2$$

Comparative effectiveness of ethylene and related compounds are given below: -

Table- 4.
Comparative effectiveness of ethylene and related compounds

Compound	Relative Activity (moles/unit)
Ethylene	1
Propylene	130
Vinyl chloride	2370
Carbon monoxide	2900
Acetylene	12500
1- butene	140000

(Burg and Burg, 1966)

3.2 Use of Calcium Carbide and its implications

3.2.1 Identification: -

Calcium carbide is a greyish black, lump shaped solid or crystal (sugar or sand like), which has slight garlic like odour. It is readily produced by heating calcium oxide with charcoal under reducing conditions. It is commonly used to make acetylene and other chemicals and in metallurgy.
It is considered as cheap source of ripening agents and also easy method to use by general people, but they are not conscious about the hazard that it can commence.

3.2.2 Hazard Summary: -

Calcium Carbide is extremely hazardous compound. The health hazard aspect of calcium carbide can be described on the following way:

1. ***Acute health effects***

The following acute (short term) health effect may occur immediately or shortly after exposure to calcium carbide: -

- Contact can severely irritate or burn the eyes and skin causing permanent eye damage and ulcers on skin.
- Exposure can severely irritate the mouth, nose and throat causing sores cough and wheezing.
- Irritate the lungs causing coughing and/or shortness of breadth. Higher exposure may cause a build up of fluid in the lungs (pulmonary oedema), a medical emergency, with severe shortness of breath.

Calcium carbide contains traces of Arsenic and Phosphorus. Early symptoms of Arsenic or phosphorus poisoning include vomiting, diarrhoea with or without blood, burning sensation of the chest and abdomen, thirst, weakness and difficulty in swallowing and speech and garlic like odour of breath. Other effects include numbness in the legs and hands, general weakness, cold and damp skin and low blood pressure. While most cases of arsenic and phosphorus poisoning are detected before they become fatal. If not treated in time, these can prove fatal. " Pregnant women are particularly vulnerable. The chemical residue in the fruit could lead to miscarriage."

2. Chronic Health effect

The chronic (long term) health effect can occur at some time after exposure to calcium carbide and can last for months or years. Calcium carbide has not been tested for its ability to cause cancer and reproductive hazard but may cause bronchitis to develop with cough, phlegm, and /or shortness of breath.
(Adapted from "Hazardous Substance Fact Sheet", New Jersey Department of Health and Senior Services, March 2003)

3.3 Safety aspects in handling Carbide to control hazards

The hazardous aspect of calcium carbide is in both inhalation and intake of residue but acetylene gas seems to be in practice and does not indicate the negative impact on the fruit intake. Even literatures show that calcium carbide is still being practiced outside. The exposure hazards of carbide may be controlled by using prescribed personal protective equipments, following standard procedures of workplace control, practices, handling and storage. The major hazard from the consumption of calcium carbide treated fruit is the residual effect, so using the carbide in closed and separate atmosphere to release acetylene and use the gas in separate ripening room seems to be safe. Literatures show that carbide wrapped in newspaper can be used as the generator in separate section. Water vapour from the fruit releases sufficient amount of gases from carbide to cause ripening. 100gm of carbide can be used per 50 kg of fruit.

4. Food Regulation on the use of calcium carbide

Considering the possibilities of aforementioned hazardous effects, the use of carbide has been banned in many countries of the world. Rule no. 44-AA of the Prevention of Food Adulteration Act (PFA India) and subsequent rules have strongly prohibited the use of carbide gas in ripening of fruits expressing that " No person shall sell or offer or expose for sale or have in his premises for the purpose of sale under any description, fruit which have been artificially ripened by use of acetylene gas, commonly known as carbide gas". Similarly, Part 7, Rule no 19 (d) of Nepal Food Regulation 2027 has strongly prohibited the use of carbide gas in ripening of fruits. Thus it is not advised to use such chemicals so as to ripen the fruits.

4.1 Detection of Artificially ripened fruits

Although the use of carbide has been banned under the food act and is punishable, but a few seems to care. Artificially ripened fruits are much likely to occur on market. It is suggested that naturally ripened fruits are not uniformly yellow. Artificially ripened fruits bear white streaks on the skin, whereas naturally ripened fruits would be mix of green and yellow. Close scrutiny can make it possible to identify fruits that have been treated with carbide. When tomatoes are uniformly red, or mangoes and papayas are uniformly orange, one could easily make out that carbide may have been used. Banana can also be identified if the stem is dark green while the fruits are all yellow.
Suspected sample may be tested for the phosphorus and arsenic residue on the surface of the fruits on the lab.

5. Concluding Remarks

From the facts, as discussed above, it is concluded that the fruits and fruit vegetable such as tomatoes are being treated with calcium carbide to ripen them fast. The use of carbide, considering its hazardous aspects, lack of knowledge about its standard procedures for safety use among concerning people and being banned by the regulation, is to be strictly monitored and controlled.

While purchasing fruits and fruit vegetables, that are prone to artificial ripening in the Nepalese food chain, it is advised not to select homogenously ripened and eye catching bright coloured fruits. In case of banana if the stems are green and the fruits are well ripened then it could be suspected of the use of carbide.

Washing and peeling operations before eating a fruit, in case of suspicion, could help in minimising the risks associated with the use of carbide.

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