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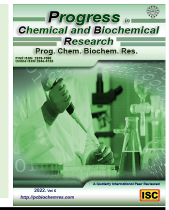

Short Communication Article

The Use of Calcium Carbide in Fruit Ripening: Health Risks and Arsenic Index as a Quantitative Marker for Calcium Carbide Residue

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ABSTRACT

Fruits are important worldwide due to their nutritional, commercial, and nutraceutical values. Doubtless, the increased demand for fruits is instrumental in the use of various artificial ripening methods in their production. The most frequently applied chemical for this purpose is calcium carbide (CaC_2). However, due to its toxicity, the use of calcium carbide in fruit ripening has been banned in many countries, including Nigeria. Despite its limitations, calcium carbide is still illegally used in artificial ripening of fruits and this has elicited great health concerns. Currently, there is little scientific data on the investigation of calcium carbide residue of fruits marketed in Nigeria. This article gives an outline of calcium carbide, its use in fruit ripening and possible health implications. It further identifies arsenic index as a marker for quantifying residue in suspected calcium carbide-ripened fruits.

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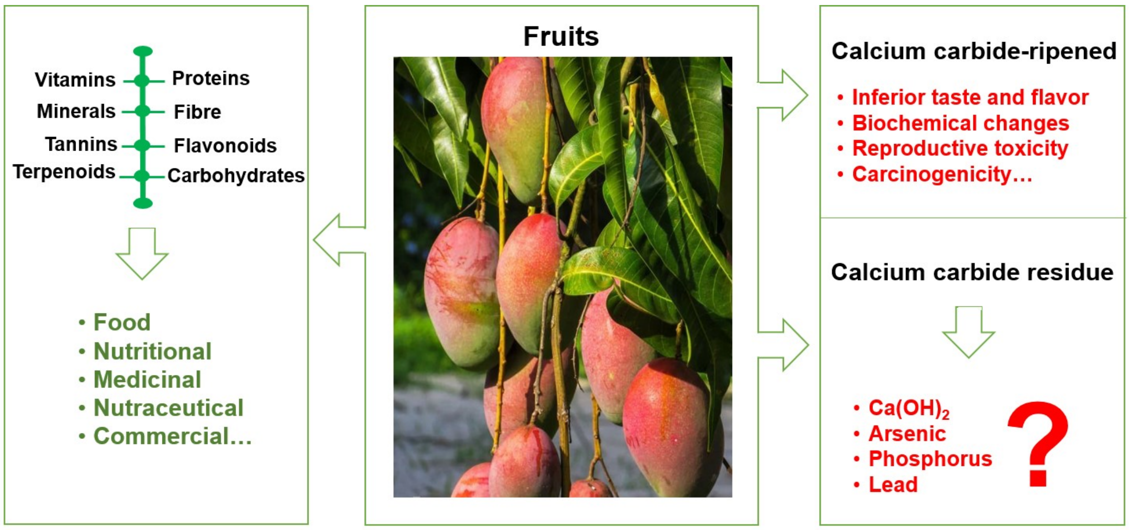
GRAPHICAL ABSTRACT



Introduction

Fruits are of high significance worldwide due to their nutritional and commercial values. Likewise, they are sources of essential nutrients, fortify diet with vitamins and minerals, and provide variety to food and make food appetizing. They further account for a substantial fraction of the world's agricultural output, and, some have acquired great economic importance. Fleshy fruits (like mango, apple, peach, and pear) and juicy fruits (like the citrus and pineapple) are used in producing jams, marmalade, ice creams, yoghurt and juices. In Sub-Saharan Africa, agriculture (fruits production a mainstay) accounts for about 32% of gross domestic product (GDP) [1].

It is noteworthy that Nigeria is richly blessed with abundant tropical fruits. The major fruits grown in the country include banana, mango, citrus, pineapple, and pawpaw. Besides these, a large number of many other fruits are also cultivated across seasons such as watermelon, guava, cashew, coconut, soursop, almond, ackee, African walnut, African pear, and African star apple. These fruits are not only a staple of our diets, but also their production has been a source of livelihood for many households and a source of revenue for the country. In the fourth quarter of 2021, agriculture (including fruit and crop production) contributed 26.84% to overall GDP of the country [2].

The recent interest in nutraceuticals has led to the call for more fruit's consumption around the world. Most fruits contain phytochemicals such as polyphenolics, xanthones, carotenoids, and saponins which have various medicinal properties. There have been reports of a linkage between increased consumption of fruits and decrease in dietary related chronic diseases such as obesity, cardiovascular diseases, diabetes, and some types of cancer. Greater consumption of fruits has been shown to regulate blood sugar [3] as well as lower blood pressure [4].

The increased demand for fruits is certainly vital in the use of various artificial ripening methods in their production. Fruit vendors artificially ripen immature ones to meet the demand of consumers and make high profit of seasonal fruits [5]. The most commonly used chemical for this purpose is calcium carbide. However, due to its toxicity, its application in fruit ripening has been banned in many countries [6, 7]. Despite its ban, calcium carbide is still being used illegally in artificial ripening of fruits and this has elicited great health concerns. The National Agency for Food and Drug Administration and Control (NAFDAC) has repeatedly warned fruit producers and vendors to desist from using calcium carbide to ripen fruits. In April 2018, the Nigerian lawmakers further urged NAFDAC and the National Orientation Agency (NOA) to carry out massive enlightenment to sensitize the public on the risks of using noxious chemicals such as calcium carbide to ripen fruits [8]. Currently, there is few scientific data on the investigation of calcium carbide residue of fruits marketed in many countries, including Nigeria. Here, an outline is given of calcium carbide, its usage in fruits ripening, possible health implications and arsenic index as a marker for quantifying residue in suspected calcium carbide-ripened fruits.

Calcium carbide

Calcium carbide (CaC_2) is a chemical compound of industrial significance. In its pure form, calcium carbide is a colorless solid, but its technical grade is grey or brown. Calcium carbide is produced industrially from a mixture of lime (CaO) and coke (as given by eqn (1)) in an electric arc furnace at approximately 2000 °C which usually produces about 80–85% calcium carbide by weight, and the rest being impurities [9]. During the production, impurities contained in the charge components such as sulfur and phosphorus are further reduced and dissolved in molten calcium carbide, forming calcium sulfide (CaS) and calcium phosphide (Ca_3P_2). The other impurities are from lime and coke including aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), and arsenic [10].

$$CaO + 3C \rightarrow CaC_2 + CO \qquad (1)$$

In the industry, calcium carbide content of the product is assayed by measuring the amount of acetylene produced on hydrolysis and is mainly used in the production of acetylene and calcium cyanamide.

Production of acetylene: Calcium carbide reacts with water producing acetylene (C_2H_2) and calcium hydroxide ($Ca(OH)_2$) (eq. (2)).

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \qquad (2)$$

This reaction was initially reported by Friedrich Wohler in 1862 [9] and is the basis for the industrial manufacture of acetylene as the major industrial application of calcium carbide. Acetylene is used in its torches for welding and in manufacturing polyvinyl chloride (PVC) plastics.

Nitrogen fixation and production of calcium cyanamide: In 1893, Henri Moissan observed that calcium carbide absorbed the atmospheric nitrogen and in 1898, Fritz Rothe found that the compound formed by this absorption was calcium cyanamide ($CaCN_2$) (as given by eq. (3)) [11].

$$CaC_2 + N_2 \rightarrow CaCN_2 + C \qquad (3)$$

This discovery led to the development of a commercial process for the production of calcium cyanamide, a fertilizer, from calcium carbide. In the soil, calcium cyanamide is decomposed to produce urea and ammonium carbonate, which are both considered as the potent fertilizers.

The other applications of calcium carbide are in steel making, carbide lamps, and the artificial ripening of fruits. In steel making, calcium carbide is used for desulfurization of iron, as a fuel to extend the scrap ratio to liquid iron and as a powerful deoxidizer at ladle treatment facilities [12]. In carbide lamps, drips of water on calcium carbide are used for producing acetylene gas, which burns and produces light.

Artificial fruit ripening

Ripening is the final stage of the maturation process of fruits, when a fruit changes color, softens and develops the flavor, texture, and aroma which constitute the optimum eating quality [13]. In nature, fruits ripen after attainment of the proper maturity by a sequence of physiological and biochemical events, and thus the process is irreversible. For cosmetic and economic purposes, fruit vendors use artificial means to delay or hasten fruits ripening.

Once harvested, fruits may be highly perishable, with short shelf life and transportation stress leading to post-harvest losses. To avoid this, sometimes fruits are harvested immaturely and ripened artificially when needed. The commonly used chemicals to induce ripening are inter alia, ethylene gas, ethephon, ethylene glycol, ethereal, and calcium carbide [5]. Technical grade calcium carbide is the most commonly and widely used, probably because it is cheap and readily available.

Researchers have observed that plants produce ethylene (C_2H_4) which is transferred from one cell to another in fruits to achieve ripening [14]. In artificial ripening, calcium carbide is sprayed with water to release acetylene (C_2H_2) which has similar effects as the endogenous ripening agent, ethylene [15].

Health risks associated with calcium carbide-induced fruit ripening

Technical grade calcium carbide emits an unpleasant odor reminiscent of garlic in the presence of trace moisture [16]. As a result, fruits ripened with calcium carbide, though may develop uniform attractive surface color, are usually inferior in taste and flavor [5]. Studies [17–19] have also indicated that the use of calcium carbide for fruit ripening could alter the nutritional quality, proximate composition, physicochemical properties, and shelf life of such fruits.

In spite of the foregoing, the use of calcium carbide as a ripening agent is discouraged worldwide mainly due to the associated health hazards. Calcium carbide is a corrosive chemical and when ingested could alter hematological and biochemical profiles as well as reduce sperm count [20, 21]. The heavy exposure to calcium carbide also poses carcinogenic risk to different organs, including liver, kidney, lung, and intestine and it might weaken the immune system [22–24]. In addition, calcium carbide contains traces of arsenic and phosphorous, and once dissolved in water, it produces acetylene gas [13]. Acetylene is a mild asphyxiant and its acute exposure may cause dizziness, headache, fatigue, tachycardia, tachypnoea, nausea, and vomiting; while in high concentrations, it could cause loss of consciousness and death [25]. The chronic exposure to acetylene may produce mood disturbance and loss of memory [5]. Phosphorus is an essential nutrient required for a wide range of functions within the body. However, the excessive retention of phosphorus in the body could cause various cellular and tissue damages, including increased cell death, renal dysfunction, vascular calcification, and impaired fertility [26]. Arsenic is a potent toxicant on both acute and chronic exposures. Acute exposure to arsenic is associated with nausea, vomiting, abdominal pain, and severe diarrhea; while in high doses, it could lead to encephalopathy and peripheral neuropathy [27]. The chronic exposure to arsenic could cause cancer and impairment of various systems in the body, including dermal, cardiovascular, respiratory, gastrointestinal, and neurological systems [27].

Few studies have been carried out to evaluate the toxicological effects associated with consumption of calcium carbide-ripened fruits. In a sub-acute study [28], calcium carbide-ripened pawpaw, mango, and plantain were orally administered as juice to male and female rats for 30 days. The study reported changes in some hormonal parameters, oxidative stress enzymes, haematological indices, and morphologies of ovaries and testes in rats. Notably, the calcium carbide-ripened fruits increased white blood cell count, platelet count, and estrogen levels in female rats and degenerated germ cells in the testes of male rats. The authors [28] cautioned that consumption of calcium carbide-ripened fruits could weaken immune system and impair reproductive function, especially in males. In a similar study [29], calcium carbide-ripened banana was orally fed to pre-pubertal female mice for three days. The study indicated that the calcium carbide-ripened fruit induced changes in serum estrogen levels, uterus weight, and morphologies of uterus, ovaries, and cervix in the female mice. The authors [29] cautioned that consumption of calcium carbide-ripened fruits could impair female reproductive physiology and accelerate puberty onset.

Arsenic index as a quantitative marker for calcium carbide residue

The illegal use of calcium carbide in the artificial ripening of fruits and associated health hazards necessitate the development of analytical methods for the detection and determination of calcium carbide in suspected fruits. This however poses a complex challenge. The instability of calcium carbide makes its analysis difficult. Calcium carbide undergoes hydrolysis to give acetylene (C_2H_2) and calcium hydroxide ($Ca(OH)_2$) (as given by eq. (2)).

In the industry, calcium carbide is assayed by measuring the amount of acetylene produced on the controlled hydrolysis. In fruits, the instability, diffusion, and trace quantity of acetylene make it difficult to quantify.

Calcium carbide residue could also be expressed in terms of released calcium hydroxide. Calcium hydroxide is assayed by measuring the equivalent calcium ions. However, the elemental analysis of fruits' peel for calcium content would be misleading and an incorrect index for calcium carbide residue because fruits naturally contain calcium.

Arsenic and phosphorous–often as arsine (AsH_3) and phosphine (PH_3) or calcium phosphide (Ca_3P_2)– are usually present in calcium carbide as impurities [13, 30]. These impurities might find entry into calcium carbide-ripened fruits and may be determined as estimates for calcium carbide residue. In a study on estimating arsenic, phosphorus, and calcium contents of mango fruits due to ripening by calcium carbide, out of different combinations, the fruits ripened by using calcium carbide either as solution or in the form of sachet contained arsenic content between 34.73–83.43 ppb, while the fruits ripened without using calcium carbide did not contain any arsenic residue, and the quantities of calcium and phosphorus found in the calcium carbide-ripened fruits were not considerably different from that of the untreated fruits [31]. This indicates that determination of arsenic in ripened fruits can be used as a tool for detecting calcium carbide-ripened fruits, while quantification of calcium and phosphorus will not be suitable for calcium carbide detection. This phenomenon was explored by Lakade *et al*. [32] to develop a gold nanoparticle-based colorimetric method for detecting the use of calcium carbide in artificially ripened fruits. Their analyses demonstrated that calcium carbide-ripened fruits contained higher amounts of arsenic compared to naturally ripened fruits. The group further affirmed this observation in a follow-up study [33] and incorporated same to develop a near-infrared (NIR) spectroscopic method for the detection of calcium carbide in calcium carbide-ripened fruits. Hassan *et al*. [34] also reported the elevated levels of arsenic and lead in calcium carbide-ripened mangoes and suggested the use of both elements as indicators of applying calcium carbide for fruit ripening. The use of arsenic level as an indicator of calcium carbide residue in fruit, however, is dependent on the presence and level of arsenic in technical grade calcium carbide used for the ripening of such fruits. Vemula *et al*. [35] noted that since arsenic content in different samples of technical grade calcium carbide is not uniform, the chance of contamination by arsenic is always questionable. The authors hypothesized that different ripening agents may produce unique metabolites which may be identified and targeted as markers for the use of such ripening agents. Based on this, they identified two isomers of 3,5-dimethyl-1,2,4-trithiolane in sapota fruits ripened with technical grade calcium carbide which contained divinyl sulfide as impurity. The authors suggested the use of these trithiolane isomers as chemical markers for identification of fruits ripened with technical grade calcium carbide. Interestingly, the trithiolane isomers were not detected in fruits ripened with high purity grade calcium carbide that did not contain divinyl sulfide as impurity. This indicates that the use of trithiolane isomers as markers for calcium carbide residue in fruit is also dependent on the presence and level of divinyl sulfide in technical grade calcium carbide used for ripening such fruits.

Given that there is more evidence supporting the elevated levels of arsenic in calcium carbide-ripened fruits, it could be considered, in the meantime, as a marker for identifying fruits ripened with calcium carbide.

Arsenic determination in fruits

Arsenic determination in fruit samples can be done using spectroscopic techniques, including inductively coupled plasma-optical emission spectrometer (ICP-OES), inductively coupled plasma-mass spectrometer (ICP-MS), inductively coupled argon plasma-atomic emission spectrometer (ICP-AES), hydride generation-atomic absorption spectrometer (HG-AAS), and electrothermal atomization-atomic absorption spectrometer (ET-AAS). There are several methods for the digestion and preparation of samples for arsenic determination, such as described by AOAC [36], Koreňovská [37], and Adepoju-Bello *et al*. [38]. An adapted method that could be used is as follows.

Preparation of standard solution: Commercially available 1000 ppm standard stock solution of arsenic is used in preparing working solutions (0.1–10 μg/mL) by dilution with ultrapure water. The standard working solutions are then analyzed and used for preparing calibration curve.

Sample preparation and analysis: Fruit samples are peeled, separated, oven dried, and pulverized. The powdered fruit sample (0.5 g) is transferred into a digestion tube and 20 mL of conc. HNO_3 is added. The digestion tubes are arranged on the digester assembly and primed to 140 °C for 2 hours, then later primed to 180 °C until digestion is completed. The digested samples are allowed to cool and made up to 20 mL with conc. HNO_3. Each digestion mixture is vortexed for 10 min and filtered. The resultant filtrate could then be analyzed on ICP-OES, ICP-MS, ICP-AES, HG-AAS, or ET-AAS for arsenic determination and the responses are recorded. The responses and regression equations from the calibration curves are used to determine the concentrations of arsenic in the samples.

Conclusion

The use of calcium carbide for fruit ripening has been known for many years and has been banned in many countries due to the associated health risks. However, there is a dearth of robust scientific data on the investigation of calcium carbide residue in fruits marketed in different parts of the world. This could partly be attributed to the lack of suitable analytical methods for detecting and determining calcium carbide residue in suspected fruits. This study presented evidence demonstrating the use of arsenic index as a marker for calcium carbide residue in suspected fruits and outlined a method for analyzing same. This could be considered by food control and regulatory authorities for detecting fruits ripened using calcium carbide. Despite this, more studies are recommended on the development of robust analytical methods for evaluating calcium carbide residue in suspected fruits.

Declarations of interest: none

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