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RESEARCH ARTICLE

EFFECT OF NATURAL AND ARTIFICIAL FRUIT RIPENING AGENTS ON THE pH OF SELECTED FRUITS IN PORT HARCOURT, NIGERIA

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ABSTRACT

The effect of natural and artificial fruit ripening agents on the pH of selected fruits has being analysed in Port Harcourt, Nigeria. The pH of orange (Citrus x sinensis), tomato (Solanum lycopersicum L.), lime (Citrus x aurantifolia), pineapple (Ananas comosus), grape fruit (Citrus x paradisi), banana (Musa acuminata), tangerine (Citrus reticulata) and lemon (Citrus x limon L.) was determined by artificially ripening the selected fruits. The fruits were properly washed with water and kept in an air-tight jute bag with 10g of calcium carbide which was not allowed to have direct contact with the fruits for 48hrs at 34± 8^0C, to soften the fruits. Thereafter, water was sprinkled on the fruits at regular intervals for 22hours at 32±8^0C in order to maintain low temperature and to de-green the fruits. A pH stripe was used to test the pH values of unripe banana and tomato, then marched with a pH colour chart and their pH values were both 3. Also, 5 drops of universal pH indicator was mixed with 50ml of unripe orange, tangerine, lime, lemon, pineapple, and grape juices each and the pH values were 3, 3, 2, 2, 3, and 2.3 respectively. 5drops of universal pH indicator was also used to test 50ml of the naturally and artificially ripened tomato, lime, pineapple, orange, banana, lemon, grape and tangerine juices each and their pH values were 4,3,3.7,3.7,3.7,3,3,4 and 4,2.7,4.3,4.7,4.3,3,3.7,3.7 respectively. The results of pH test showed that the pH value of each fruit increased when ripened naturally and artificially. It is therefore recommended that fruits should be eaten only when ripe, to avoid consumption of organic acids which are related to unripe fruits.

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INTRODUCTION

At present, all over the world, emphasis is being placed on malnutrition, food safety, and health security. Consumption of fruit and its processing is on the increase globally. This is due to improved technologies, for ripening of fruits, preservation techniques, transportation, marketing strategies and health benefits. The entire body of fruits is rich in bioactive compounds, such as phenolic constituents, carotenoids, vitamins and dietary fiber (Ayala-Zavala *et al*., 2011). Fruits are essential components of our food and are highly nutritious. They are mostly consumed when ripened. Fruits contain fiber, water, cellulose and various photochemicals which protect human body against various disorders (Dhembare, 2013; Abdullahi *et al*., 2018) as well as carbohydrates, proteins, vitamins, and minerals (Adou *et al*., 2012; Dhembare, 2013) for the general health of the body (Gbarakoro *et al*., 2019). According to Brandy and Holum (1990), fruits contain organic acids such as citric acid, malic acid, ascorbic acid, tartaric acid, etc, present in them.

Fruits contain more of these organic acids at their unripe stage (i.e. premature stage) and as they get matured, they form polymers that contain sugars. For the sugar in the fruits to be released, the fruit produces enzymes such as hydrolase, pectinase, amylase that breakdown the sugar and neutralizes the acid content which then display ripeness (Gbarakoro *et al*., 2019). High acidity is known to be responsible for the distinct sour flavour in most fruits with low pH, as the starch in fruits are transformed into sugar during ripening (Kibrom and Lijalem, 2015). William (2003) reported that the pH value of food depends on the free hydrogen ions present in that food. He explained further that decrease in the concentration of hydrogen ions leads to increase in the pH value of the food. This is the reason why a low-pH food is a high-acid food and vice versa. The pH values of various fruits are listed in Table 1. On the basis of ripening behavior, fruits are categorized into climacteric, depending on their ability to continue to ripen after being harvested and non-climacteric based on their inability to ripen further after being harvested. Ripening of fruits is a natural process that makes the fruits sweeter, less

green, softer (Dhembare, 2013), more palatable, colourful, nutritious, attractive (Gupta, 2017; Abdullahi *et al*., 2018) and attain their desirable flavor, quality, colour, and other textural properties during ripening (Bhattarai and Shrestha, 2015). Ripening is the process of converting starch to sugar. Ripening of fruits lead to increase in acidity values. Naturally, fruits ripen on trees by which the starch in the fruit is broken down to sugars but some chemicals or agents are equally used for artificial ripening process by traders, farmers and transporters. Today, ripening of fruits is of great concern because of its commercial application. Several artificial ripening agents commonly used are available in the markets today. They include calcium carbide (CaC_2), acetylene gas, ethylene, carbon monoxide, potassium sulphate, ethephon, potassium dihydrogen orthophosphate, oxytocin, ethereal, and putrescine (Abdullahi *et al*., 2018). These artificial ripening agents stimulate ripening of fruits and also induce colour changes (Dhembare, 2013). Most farmers apply small dose of ethylene to induce ripening process under controlled conditions of temperature and humidity. Ethylene is a natural hormone and does not pose any health hazard for consumers of fruits. It is a de-greening agent. However, calcium carbide is widely used as artificial ripening agent due to its cheapness and easy availability.

In a study carried out by Dhembare (2013), it was discovered that 80% of fruits are artificially ripened through ripening agents. In another study carried out by Siddiqui (2010), it was observed that most fruit sellers used a deadly chemical, calcium carbide for ripening the fruits. When calcium carbide is dissolved in water, it produces acetylene gas (Dhembare, 2013) which acts as an artificial ripening agent.

$$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$$

Acetylene is believed to affect the nervous system by reducing oxygen supply to the brain (Dhembare, 2013; Abdullahi *et al*., 2018). Siddiqui (2010) noted that calcium carbide is extremely hazardous because it contains traces of arsenic and phosphorus which are toxic and their exposure may cause severe health hazards. Although, it is banned in many countries of the world, it is freely used in India, Pakistan, Bangladesh, Nepal and other countries (Gupta, 2017; Siddiqui, 2010) to treat fruits such as bananas, mangos, papayas and oranges. The study concluded that eating artificially ripened fruits is harmful. In a related study, Abdullahi *et al*., (2018) investigated the effect of artificial ripening of banana (*Musa spp*.) using calcium carbide and noted that the pH contents decrease with increase in CaC_2 concentration. A study conducted by Taposhe *et al*., (2017) on artificial ripening agent and its effect on banana (*Musa spp*.) collected from Tangail area, Bangladesh showed that farmers and traders in this region treated banana with different types of growth hormones and artificial ripening agents. They posited that the temperature at which the banana was stored influenced the ripening changes, as increase in storage temperatures between 14^0C and 30^0C enhanced the rate of ripening and the fruit softened at a faster rate. A related study carried out by Smith and Thompson (1987) showed that high temperature can also damage ripening fruit.

Swanson *et al*., (1980) also worked on pH, acidity and vitamin C content of fresh and canned homegrown fruits in Washington and discovered that the pH of fresh tomatoes increased with maturity while the pH of ripe and overripe tomatoes was 4.6 and 4.74 respectively. This shows that the overripe tomatoes had a significantly greater pH than ripe tomatoes. Gerard *et al*., (2009), assessed the pH and titratable acidity of bananas and used them to estimate the consumption quality and hidden attributes. In their findings, pH of all the studied bananas ranged between 5.38 and 5.94 at harvest. Several previous studies have looked at the effects of tomato cultivar and fruit maturity on pH and other quality parameters. In all tomato cultivars examined; pH increased as the fruits ripened from the green to pink to red stage and continued to increase as the red fruits remained in the vine (Gordon *et al.*, 2011). Moneruzzaman *et al.,* (2008), carried out a research on the effect of stages of maturity and ripening condition on the biochemical characteristics of tomato and discovered that pH of tomatoes increased with the advancement of ripening of tomato fruit. The highest value of 4.16 was observed in matured green tomatoes followed by half ripe 4.21 at 12 days of storage. It was also discovered that tomato fruits ripened artificially by CaC_2 and straw covering after O, 3, 6, 9 and 12 days and recorded the pH values of 4.12, 4.28, 4.31, 4.24 and 4.24 respectively, indicating an increase in pH as the fruits ripened more (Moneruzzaman *et al.,* 2008). Due to daily consumption of unripe, naturally and artificially ripened fruits, this research became necessary to categorically state the actual pH values of the selected fruits. Therefore, this research is aimed at demonstrating the effects natural and artificial fruit ripening agents (such as calcium carbide) have on the pH of some edible fruits.

MATERIALS AND METHODS

Materials

Some of the materials used for this study include orange, tomato, lime, pineapple, grapefruit, banana, tangerine and lemon. Other materials include calcium carbide, pH stripe, universal pH indicator, jute bag and filter paper.

Methods

Sample Collection and Preparation: Freshly harvested and unharmed unripe and naturally ripened fruits such as tomato, lime, pineapple, orange, banana, lemon, grapefruit and tangerine were purchased from Oil mill market in Port Harcourt, Rivers State, Nigeria. The unripe fruits were properly washed and kept in an airtight jute bag with 10g of calcium carbide which was not allowed to have direct contact with the fruits for 48hrs at 34 ± 8^0C. This was done to soften the fruits. Water was used to sprinkle on the fruits regularly for 22hrs at 32 ± 8^0C in order to maintain low temperature and to de-green the fruits. Unripe and naturally ripened fruit samples were peeled, cut into pieces and manually squeezed to extract the juice. The juice was filtered and transferred into clean beakers. The filtrate was then analyzed for pH.

Test for pH: A pH stripe was used to test the tomato juice; the wet pH stripe was allowed to dry and the colour change was marched with the pH colour chart. The observed value was recorded. This procedure was repeated two more times and the values recorded. Then, 5 drops of universal pH indicator was used to test 50ml of naturally ripened tomato juice; the mixture was shaken and the colour change was marched with the pH colour chart. The observed value was recorded and the procedure was repeated two more times and the values

recorded. This same procedure was used to test the artificially ripened tomato and the observed values were equally recorded. For the unripe, naturally ripened and artificially ripened lime, pineapple, orange, banana, lemon, grapefruit and tangerine; 5 drops of universal pH indicator were used to test 50ml each, the mixtures were shaken and the colour changes were marched with the pH colour chart. The observed values for each of the fruits were recorded and the procedure was repeated twice and the values recorded. Comparative analysis (Mean Test) was used to relate fruit value result with international standard values. Observations in colour changes were also used to make valid decisions.

Table 1. pH Values of Various Fruits

S/N	Food	pH
1	Apples, Red, Delicious (fresh)	3.9
2	Apples, Jonathan, delicious (fresh)	3.33
3	Apples Juice	3.4-4.0
4	Apples Sauce	3.3-3.6
5	Bananas	4.5-5.2
6	Grapefruit (fresh)	3.0-3.3
7	Grapefruit juice	3.0
8	Grapefruit (canned)	3.1-3.3
9	Grapes	3.4-4.5
10	Limes	1.8-2.0
11	Lemon juice (canned)	2.3
12	Mangoes	3.9-4.6
13	Melon, Casaba	5.5-6.0
14	Melon, Persian	6.0-6.3
15	Oranges (fresh)	3.1-4.1
16	Oranges marmalade	3.0
17	Oranges juice	3.6-4.3
18	Papaya	5.2-5.7
19	Pineapple (canned)	3.5
20	Pineapple (fresh)	3.3-5.2
21	Strawberries (fresh)	3.0-3.5
22	Strawberries (frozen)	2.3-3.0
23	Tangerines	4.0
24	Tomato paste (canned)	3.5-4.7
25	Tomato juice	4.1-4.2
26	Tomatoes red, (fresh)	4.2-4.9
27	Tomatoes red, whole (canned)	3.5-5.5
28	Watermelon	5.2-5.8

Source: United States Food and Drug Administration Center for Food Safety and Applied Nutrition Foodborne Pathogenic Microorganisms and Natural Toxins Handbook. http://www.cfsan.fda.gov/~mow/app3a.html, 1992.

RESULTS AND DISCUSSION

Results

The results of pH values of the unripe, naturally and artificially ripened fruits are shown in Tables 2 and 3.

Table 2. Average pH values of fruits

S/N	Fruits (Samples)	pH of unripe fruits	pH of naturally ripped fruits	pH of artificially ripped fruits
1.	Tomato	3	4	4
2.	Lime	2	3	2.7
3.	Pineapple	3	3.7	4.3
4.	Orange	3	3.7	4.7
5.	Banana	3.3	3.7	4.3
6.	Lemon	2	3	3
7.	Grape fruit	2.3	3	3.7
8.	Tangerine	3	4	3.7

DISCUSSION

This study which utilized calcium carbide as the only artificial fruits ripening agent of the selected fruits (tomato, lime, pineapple, orange, banana, lemon, grape fruit and tangerine) showed that the artificially ripened fruits were evenly ripened while the naturally ripened fruits were not evenly ripened. The results of the pH tests of all the fruit categories (unripe, artificially and naturally ripened) showed that the pH of the various fruits increased when getting ripened, thereby decreasing the acid level of the various fruits. The experimental results obtained as shown in Table 2 showed that there was no pH change between the naturally and artificially ripened tomato as both had the same pH value of 4; the unripe tomato recorded a pH value of 3, thereby maintaining moderate acidity level, as pH increased when ripened. These results agreed with a pH of 4.21 for ripened tomato as obtained by Moneruzzaman *et al*., (2008) but was slightly below a pH of 4.6 obtained by Swanson *et al*., (1980). The artificially and naturally ripened lime recorded a pH of 2.7 and 3 respectively indicating a slight difference of 0.3. The unripe lime had a pH of 2. This result also shows that the pH of lime fruit increased when ripened while the acidity reduced. Although, the ripened lime fruits showed acid level, the unripe was strongly acidic.

However, the result of pineapple fruit juice showed that the naturally ripened pineapple had a pH of 3.7 while the artificially ripened pineapple recorded a pH of 4.3 and the unripe had a pH of 3.0, making a significant change in the pH between the naturally ripened with a value of 0.6. This implies that pH increases when the fruit is ripened. Orange fruit showed a pH result of 3.7 for the naturally ripened and 4.7 for the artificially ripened, while the unripe recorded a pH of 3, thereby resulting to a significant difference in pH between the naturally and artificially ripened with pH value of 1. This further proved that acidity level of the fruit reduced when ripened while the pH increased on the other hand and the artificially ripened had a weak acid level, while the unripe and naturally, a moderate acidic level. The pH result of banana recorded a pH value of 3.7 for the naturally ripened banana and 4.3 for the artificially ripened, while the unripe had a pH value of 3.3 producing a significant pH value difference between the artificially and naturally ripened banana, with a pH value of 0.6 and the acidic level of the fruit reduced when ripened as the pH increased, though, they all maintained moderate acidic level. However, these results disagreed with the results of Taposhe *et al*., (2017) which recorded high percentage (78.26%) for moisture content in naturally ripening banana as against 75.05% for ripening agents treated banana. The results indicate that the value gradually decrease with the increase of artificial ripening agents used in banana. They added that artificial ripening agent treated banana is nutritionally poor as compared to naturally ripening banana. Abdullahi *et al*., (2018) used different concentrations of CaC_2 (0-25g/kg) and recorded a pH value which ranged between 7.35-6.93 respectively. They found that concentrations of pH decreased with increase in CaC_2 concentration.

Lemon fruit produced a pH value of 3 for the naturally ripened and artificially ripened, and 2 for the unripe fruit juice and there was no change in pH value between the artificially and naturally ripened fruit but the pH value increased when ripened while the acidity reduced, causing both the naturally and artificially ripened to be moderately acidic and the unripe strongly acidic. The pH result of the grape fruit showed that the naturally and artificially ripened fruit juices recorded pH values of 3 and 3.7 respectively while the unripe had a pH of

Table 3. Average pH values, Observed Colours, Inference and Conclusion

S/N	Fruits (Samples)	Avg. pH value of unripe fruits	Avg. pH value of nat. rip. fruits	Avg. pH value of art. rip. fruits	Colour change observed			Inference	Conclusion
1.	Tomato	3	4	4	orange	Beige	Beige	No difference in pH value of nat. & art. ripened fruits; the pH value of ripped increased.	Both nat. & art. ripened fruits were moderately acidic; the unripe fruit was also moderately acidic. Acidity decreased when ripened.
2.	Lime	2	3	2.7	Pink	Orange	Orange	Slight pH change in the art. ripened, but pH changed when ripened (art. & nat.) compared to unripe.	Both (nat. & art) ripened, and are moderately acidic. Unripe was strongly acidic. pH also increased when ripened.
3.	Pineapple	3	3.7	4.3	Orange	Beige	Beige	Slight difference between pH values of art. & nat. ripened but significance change in pH of unripe and nat. ripened.	Both unripe, art. & nat. ripened were moderately acidic and pH increased when ripened.
4.	Orange	3	3.7	4.7	Orange	Beige	Yellow	Significant change in pH of art & nat. ripened orange but slight change between nat. ripened & unripe orange.	Unripe & nat. rip. are moderately acidic while art. is weakly acidic. Acidity also reduced when ripened.
5.	Banana	3.3	3.7	4.4	Orange	Beige	Beige	Significant change in pH between art. & nat. ripe banana; slight change in pH between unripe and nat. rip. banana.	Both unripe art. & nat. ripened are moderately acidic. Acidity reduced when ripened.
6.	Lemon	2	3	3	Pink	Orange	Orange	No difference in pH value of art. & nat. ripened lemon but significant change between unripe & ripened (nat. & art) lemon.	Both art. & nat. ripened are moderately acidic, but unripe was strongly acidic. Acidity reduced when ripened.
7.	Grape fruit	2.3	3	3.7	Pink	Orange	Beige	Significant change in pH between art. & nat. ripened grape; also significant change in pH between unripe & ripened (nat. & art.) grape.	Both art. & nat. ripened are moderately acidic, but unripe was strongly acidic. Acidity reduced when ripened.
8.	Tangerine	3	4	3.7	Orange	Beige	Beige	Slight change in pH of nat. & art. ripened tangerine, but significant change of unripe & rip. (nat. & art.) tangerine.	Both unripe art. & nat. ripened are moderately acidic. Acidity reduced when ripened.

2.3. Also there was a significant difference in pH value between the ripened fruit juice with a pH value of 0.7 and the acidity reduced when ripened, while the pH level increased; both ripened fruit juices had moderate acidic level, while the unripe was strongly acidic. Tangerine fruit showed a pH result of 4 and 3.7 for the naturally and artificially ripened fruits juices respectively and a pH value of 3 for the unripe fruit juice, indicating a slight difference in pH between the naturally and artificially ripened fruit juices. Though, all unripe, naturally and artificially ripened juices maintained a moderate acidic level, the acidity reduced when ripened. Obviously, the pH values of all the fruits tested fell within the recommended ranges as shown in Table 1.

Conclusion

This study has shown that artificially and naturally ripening of fruits can produce an effect on the pH of the fruits by increasing their pH, thereby reducing their acidity level on the other hand. Although, all the pH values obtained were acidic between the ranges of 2 to 4.7, unripe fruits were more acidic than naturally and artificially ripened fruits. Due to the hazardous and carcinogenic effects calcium carbide have on humans, its use for ripening of fruits should be based on scientific and academic researches only and not for commercial use or for human consumption. Therefore, fruits should mainly be eaten when properly ripened in order to enjoy it and reduce high intake of acids that is commonly related with unripe fruits. Further studies should be carried out to ascertain how safe it is to use calcium carbide in commercial fruit ripening.

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