DEVISING NATURAL METHODS TO GENERATE ETHYLENE GAS FOR FRUIT RIPENING BY USING SOYBEAN OIL

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Abstract

In order to synthesize Ethylene by a natural and easy way, the decomposition of unsaturated fatty acids, present in Soybean oil was carried out catalyzed by Iron powder and Ascorbic acid. A mixture of 50 gm Soybean oil, 50 gm crushed Soybean seeds, 25 cm^3 of Hydrogen peroxide (30%), traces of Iron and Ascorbic acid was prepared, in a closed room (2.2 X 1.80 X 2.5 m.) and Kitagawa precision gas detectors to measure the emitted ethylene. The reaction yielded a range of 450 to 1200 ppm. of ethylene. In a ripening experiment, for 2 years (2005 and 2006), green mature banana "Williams cv." was placed and exposed to gaseous emanation of Soybean oil for 24 hours before being stored partly in cold room at 13°C. and R.H.90%, in addition to a banana ripening treatment by Calcium carbide (common used method) and to non-treated banana as a control.

Results show that gases emitted by Soybean oil treatment were as effective as Calcium carbide treatment in banana ripening and in same aspects were more effective. Banana treated with gaseous emission of Soybean oil had good quality characters and acceptable organoleptic value compared to banana ripened by Calcium carbide, while non-treated banana did not ripen normally and had an unacceptable quality.

More experiments are needed to adapt this method of generating ethylene by Soybean oil for commercial uses.

Key words: Generating Ethylene, Artificial ripening, Soybean oil and Banana fruits.

INTRODUCTION

Plant hormone "Ethylene" is an important substance in plant life. It has many useful aspects when applied externally on plants like fruit ripening stimulation (Banana, Persimmon, Tomatoes and others), flower initiation for some ornamental bromeliad sp., changing self expression (Cucumbers and Pumpkins), degreening (Oranges, Lemons, Grapefruit and others), at harvest and used also for Cherries and Walnuts, (Kauppi, et al, 1998). Ethylene it self is a tiny molecule ($CH_2 = CH_2$), and is produced in industry by cracking ethanol alcohol in presence of a catalyst.

An ethylene releasing compound with a wide commercial use is known as "Ethephon" or 2-chloroethylphosphonic acid (Ethrel), and is applied as an aqueous solution for ripening Apples, Tomato, flowering of Pineapples (Taiz, 2002).

There is a need to generate Ethylene from other sources, especially by simple preparation method, which may replace recoursing to this synthetic and rather expensive material (Ethephon).

Hydrocarbon gases have been generated from peroxidizing lipid compounds called omega-3 and omega-6 fatty acids (unsaturated fatty acids) It is proved that applying linoleic acid and linolenic acid to tissue slices of tomato fruit promoted ethylene production, in presence of lypoxygenase enzyme in these tissues (Sheng, et al, 2000). These gases were released following the decomposition of lipid hydro peroxides enzymatically by addition of excess ascorbic acid. The major hydrocarbon gaseous products in presence of iron or copper catalysis were ethane or ethylene from linolenic acid (Lieberman, 1979). Of the common vegetable oils, Soybean oil contains a significant amount (10%) of linolenic acid, the main substrate for ethylene formation and lypoxygenase enzymes, which catalyze reactions of the decomposition of oxygen and polyunsaturated fatty acids (such as linolenic and linoleic acid). When unsaturated fatty acids react with oxygen, they form hydroperoxides, which may be decomposed by splitting and generate many gases, among which ethylene is found (Ajay A., et al, 2002, Hyodo, et al, 2003 and Sheng, et al, 2000).

The object of this research work is focused on the generation of ethylene from Soybean oil and assessing its efficiency on fruit ripening (banana).

MATERIALS AND METHODS

Materials used

Some preliminary experiments were carried out during the present year for selecting the optimal quantity for each material used in the Soybean oil set up. In the mean time, 5 gm of Calcium carbide placed in a small cup was added to 10 ml of water in a closed cold store room with 3 cartons filled of green mature banana "Williams cv." (5 kg for each).

1- Bananas exposure to ripening gases

All Banana fruits either control and or those ripened by gaseous emissions (Ethylene) from Soybean oil and from Calcium Carbide were subjected to measurements of quality parameters to be certain of the ripening effects of these emissions, either Ethylene (by Soybean oil) or acetylene (by Calcium Carbide).

2- Ten cartons of mature green banana "Williams cv." were exposed to gaseous emissions of Calcium Carbide in a separate space and other 10 cartons were exposed to Ethylene emanated by Soybean oil as described above in a different space. Exposure lasted 24 hours for both treatments, cartons were transferred after wards to cold store at 13° C and R.H. 90% to be stored with other 10 cartons of banana as control.

I-Ethylene generation method by using Soybean oil

Based on the methods described by Lieberman (1979), this system operates at ambient temperature, converting linolenic acid in presence of reduced iron, to the family of hydrocarbon gases including ethylene. The reduced metal catalysts accelerated peroxidation and decomposition of linolenic acid, presumably by formation of peroxides and accompanying free radical chain reactions. The primary source of linolenic acid is soybean oil, crushed Soybean seeds which contains also lypoxygenase and peroxidases enzymes. Hydrogen peroxide also is necessary to form free radicals, which in presence of reduced metal iron and ascorbic acid, synthesize ethylene among other hydrocarbon gases.

The main reaction: using Soybean bean oil + crushed Soybean seeds + H_2O_2 + Iron + Ascorbic acid to generate ethylene involve the following materials. The quantities used as follows:

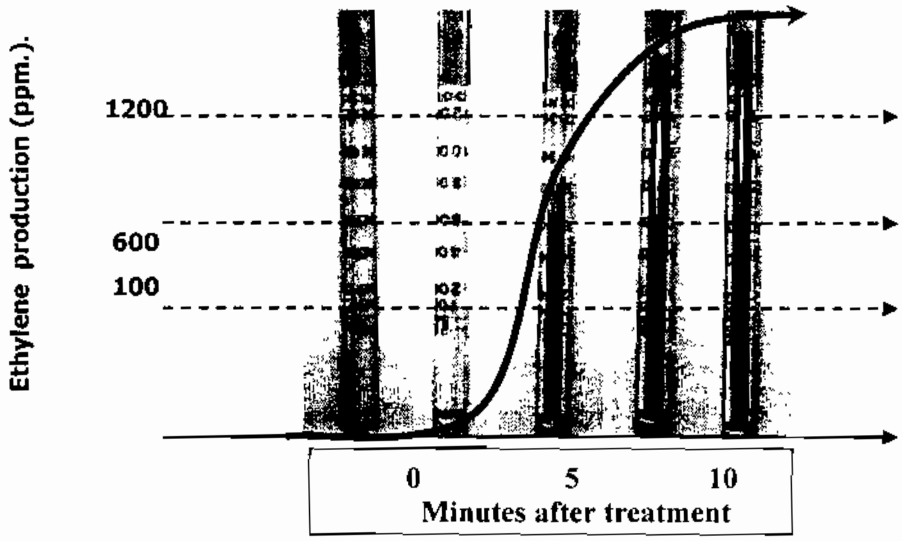
1- 50 gm. of Soybean oil + 50 gm crushed Soybean seeds
2- 25 cm^3 of hydrogen peroxide (30%)
3- 2 mg of iron metal
4- 1 gm of ascorbic acid

The work was carried out in a closed space of 2.2 X 1.80 X 2.5 m., taking clean beaker and the contents 1, 3 and 4 were added first, followed by pouring carefully and slowly hydrogen peroxide in the same open beaker.

A strong reaction was taking place and emission begins to bubble in the oil. The experiment was executed 10 times in a closed store (as shown in Fig. 1) and was repeated in presence of green mature banana.

Ethylene evaluation

Ethylene determination: by using precision gas detectors tubes of the Japanese brand "Kitagawa, 1987". Ethylene concentration was measured in the range of 20 ppm. till 2000 ppm. in closed room. (See picture 1 of the detector tubes). The measurements of ethylene were repeated also in a closed atmosphere of a cold store room where 3 cartons of green mature banana (5 kg for each) were placed and the results are shown in Picture (1).



Picture 1. Kitagawa precision gas detector tubes for Ethylene production.

Table 1. Ethylene production (ppm.) in the closed space according to the time of reaction as measured by Kitagawa instrument.

Quantities of materials used for Soybean oil (Treatments)	Ethylene production after 5 minutes (ppm.)			Ethylene production after 10 minutes (ppm.)		
	R_1	R_2	R_3	R_1	R_2	R_3
50 gm. Soybean oil + 50 gm crushed Soybean seeds + 25 cm^3 H_2O_2 + 1 gm of V.C. + 2 mg of Iron metal	500 ± 55	450 ± 40	500 ± 120	1200 ± 120	1200 ± 150	1200 ± 133

II- Gaseous emanation from Carbide calcium (commonly used in the past by banana ripeners)

Calcium carbide, when treated with water, produces acetylene gas. This gas has the ability to trigger ripening phenomena in green mature banana fruits, but its strength of ripening acceleration is greatly weaker compared to ethylene aptitude as cited by Kader, et al (1994).

Quality parameters

1- Weight loss percentage was calculated as the difference between fruit weight at the start of storage and fruit weight at the inspection date.

2- Fruit firmness was measured in kg/cm^2 by a hand Magness and Taylor pressure tester equipped with 5/16 inch plunger.

3- Peel color was estimated by a Hunter colorimeter to evaluate color values as hue angle which calculated from "a" and "b" values (hue angle = $\tan^{-1}b\backslash a$). Hue angle (0° = red-purple, 90° = yellow, 180° = bluish-green, 270° = blue) as described by McGuire (1992).

4- Percentage of total soluble solids (T.S.S. %) of the flesh was estimated by a'bbe digital refractometer, according to A.O.A.C., 1980.

5- Acidity percentage of the flesh was determined as malic acid by titration with a solution of 0.1 N., NaOH, according to A.O.A.C., 1980.

6- Total sugars: Soluble sugars were colourimetrically adjusted in the dried fruit pulp extracted with water according to the modification done by Smith *et al.*, (1956). Soluble sugars were calculated as percentages of glucose in fruit dry pulp.

7- Fruit organoleptic quality was determined. The following scores suggested by Nelson and Steinberg (1957) to express the taste condition were taken into account.

A: Astringent.	**B:** Mealy dry
C: Mealy but slight sweet	**D:** Sweet but slight mealy.
E: Sweet.	**F:** Very sweet.

All data for all fruit parameters studied were analyzed as a complete randomized design as described by Snedecor and Cochran, 1980. All measurements were done in triplicate and the data presented are averages of the measurements ± standard deviation. L.S.D. test was performed in order to determine significant differences between means.

RESULTS AND DISCUSSION

1- Total soluble solids (T.S.S. %)

From Fig (1) it is clear that Ethylene emanated from Soybean oil treatment in 1st year was effective in inducing banana ripening as T.S.S.% value increased gradually from 4.53% at start to reach 16.17% after 12 days at 13° C for this treatment. Calcium Carbide treatment emission of ripening gases caused an excessive ripening expressed by a T.S.S. percentage of 17.13% after 12 days at 13° C. Control fruits, unexposed to Ethylene didn't ripen in a satisfactory way and their T.S.S. didn't increase because its very slow maturity metabolism and reached only 5.63 % by end of 12 days of stay at 13° C.

The same pattern was repeated in 2nd year as Ethylene emanated by Soybean oil was almost equal in its effect to that of Calcium Carbide (17.63% for the 1st and 18.67% for the later treatment), while control fruits had their T.S.S.% lagging at 5.8%

because of a slow and irregular maturity operations inside fruit tissues. The above-cited effects of Soybean oil treatment are due to ethylene emission, which stimulates ripening as mentioned by Kader, et al (1994).

2- Acidity percentage

Fruits exposed to gases emissions by Calcium Carbide or by Soybean oil had a lower acidity values compared to those of control, after 12 days of stay at 13° C., in both seasons (Fig 2). Calcium Carbide treated fruits recorded an acidity value of 0.15% and those treated with Soybean oil recorded 0.16% compared to 0.18% for control in 1st season, while in second season Calcium Carbide and Soybean oil treated fruits displayed an acidity value of 0.17% compared to 0.19% for control. The acidity decrease is an indicator of the Ethylene effect on stimulating banana ripening. The results agree with those of Wills, *et al*, (1981).

3- Total sugars percentage

Fruits exposed to gases emission of the Calcium Carbide treatment had the highest total sugar content after 12 days in ambient temperature in both seasons (20.17% and 20.10%) and slightly higher than Soybean oil treated banana (19.27% and 19.40%), while control fruits had only a total sugars percentage of about 4.03% and 4.10% after 12 days (Fig 3).

These results constitute strong evidence about the effectiveness of Ethylene emitted by Soybean treatment (or acetylene gas) to trigger and enhance sugars formation in banana fruit during ripening after harvest.

4- Weight loss

As ripening proceeds, banana fruit respire greatly and consume some of its reserve materials, so fruit loss weight during ripening period. After 12 days in ambient conditions, banana treated either by Calcium Carbide or Soybean oil emanations, lost more than 9% of its original weight during both seasons, while control fruits did not lose as much weight as other treated fruits, and recorded (4.67% and 4.87%) in both seasons, respectively (Fig.4). This agrees with Sobieh (1996).

5- Flesh firmness

As shown in Fig (5), fruits exposed to Ethylene emitted by Soybean oil and to acetylene from Carbide Coal have ripened normally after 12 days in ambient conditions and their bulb was soft, as they recorded a range of firmness values from 5.03 to 5.93 kg/cm^2. While control banana stayed firmer with values of 7.07 kg/cm^2 in 1st season and 6.97 kg/cm^2 in 2nd season, indicating a delayed ripened stage.

These results are in conformity with Sobieh (1996) and prove the efficacy of Soybean oil in generating ethylene.

6- Peel color of banana

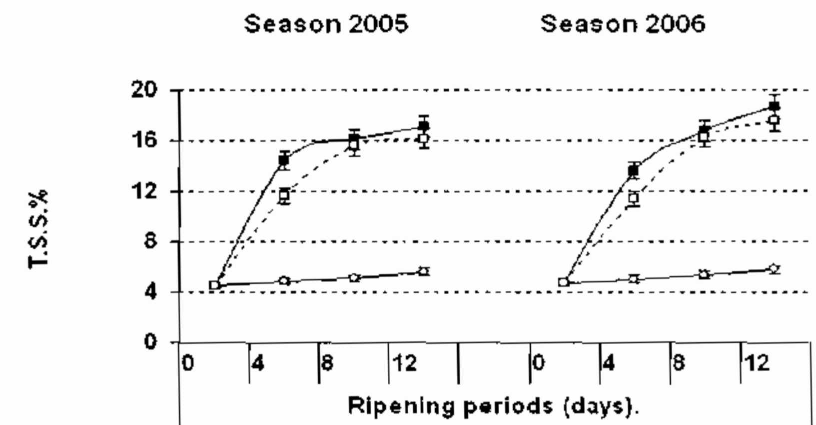
Control, or untreated, banana fruit had a yellow green peel color (as their Hue angle) was around 153.33 – 156.67 degrees on (ELAB diagram of color) by the end of 12 days in ambient conditions. While both treated fruits with emissions of Calcium Carbide or Ethylene from Soybean oil, had developed a more yellowish color, as indicated by their Hue angle of a range of values of 85 to 90 as shown in Fig (6). These results showed the effect of enhancing banana ripening by these emissions of Soybean oil.

7- Eating quality evaluation (Taste)

It's clear from Fig (7) that banana ripened by Calcium Carbide or Soybean oil gases emissions had the best taste after 12 days of storage on 13° C, in both seasons, recording taste values of 4.33 to 5.0., while banana of control had a hardly acceptable taste after this period recording the value of 2.00 (mealy dry). Evaluation of the taste as shown in the Table indicated that after 8 days of storage, banana exposed to gases emission of Soybean oil and Calcium Carbide had reached a good eating quality, compared to a week value for control.

Conclusion

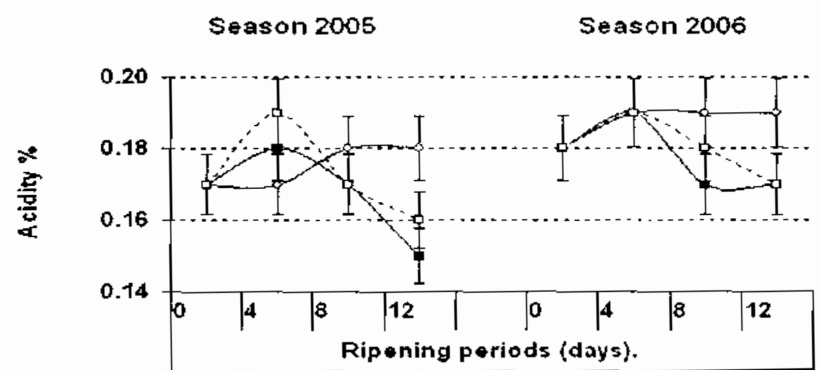
Soybean oil can be used to generate ethylene valid for ripening purposes especially. More experiments are needed to reach a regular and steady ethylene generation from this material by an easy way in the practice of ripening big quantities of banana.



	0	4	8	12		0	4	8	12
Control	4.53	4.83	5.07	5.63		4.67	5.03	5.37	5.80
Calcium Carbide	4.53	14.43	16.10	17.13		4.67	13.63	16.77	18.67
soybean oil	4.53	11.67	15.60	16.17		4.67	11.40	16.30	17.63
L.S.D. at 5%		1.59	0.33	0.55			1.71	0.80	0.74

The vertical lines at each point represent the standard deviation of the means.

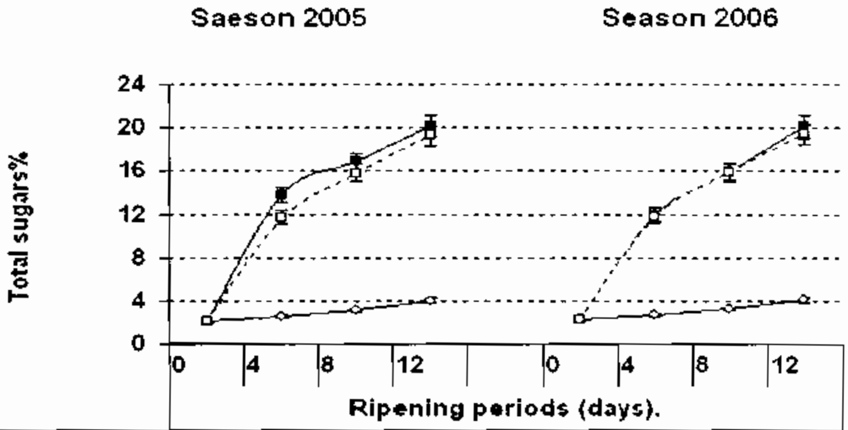
Fig (1): Effect of ripening method on T.S.S.% of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	0	4	8	12		0	4	8	12
Control	0.17	0.17	0.18	0.18		0.18	0.19	0.19	0.19
Calcium Carbide	0.17	0.18	0.17	0.15		0.18	0.19	0.17	0.17
soybean oil	0.17	0.19	0.17	0.16		0.18	0.19	0.18	0.17
L.S.D. at 5%		0.001	0.001	0.001				0.001	0.001

The vertical lines at each point represent the standard deviation of the means.

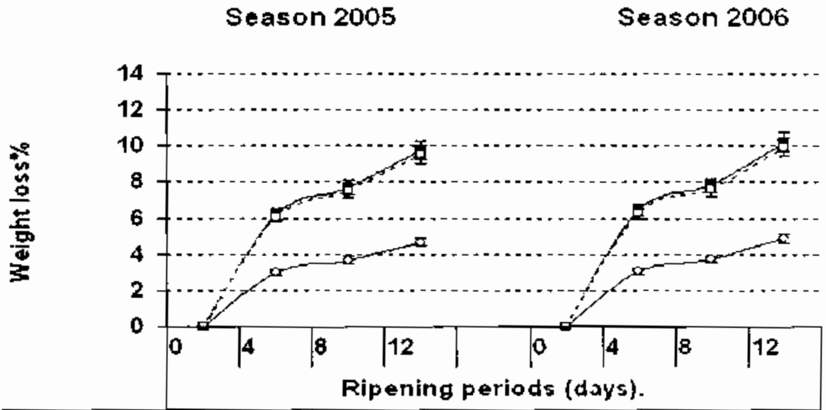
Fig (2): Effect of ripening method on acidity % of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	2005: 0	4	8	12		2006: 0	4	8	12
Control	2.07	2.60	3.10	4.03		2.23	2.67	3.23	4.10
Calcium Carbide	2.07	13.73	16.83	20.17		2.23	12.00	15.93	20.10
soybean oil	2.07	11.71	15.83	19.27		2.23	11.74	15.89	19.40
L.S.D. at 5%		3.70	0.71	1.32			0.24	0.66	0.57

The vertical lines at each point represent the standard deviation of the means.

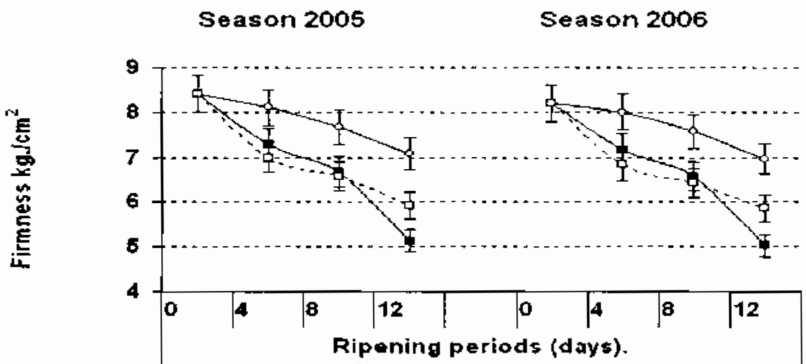
Fig (3): Effect of ripening method on total sugars % of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	2005: 0	4	8	12		2006: 0	4	8	12
Control	0.00	2.97	3.67	4.67		0.00	3.07	3.73	4.87
Calcium Carbide	0.00	6.23	7.70	9.80		0.00	6.44	7.84	10.22
soybean oil	0.00	6.07	7.50	9.54		0.00	6.27	7.63	9.95
L.S.D. at 5%		0.22	0.41	0.41			0.32	0.16	0.42

The vertical lines at each point represent the standard deviation of the means.

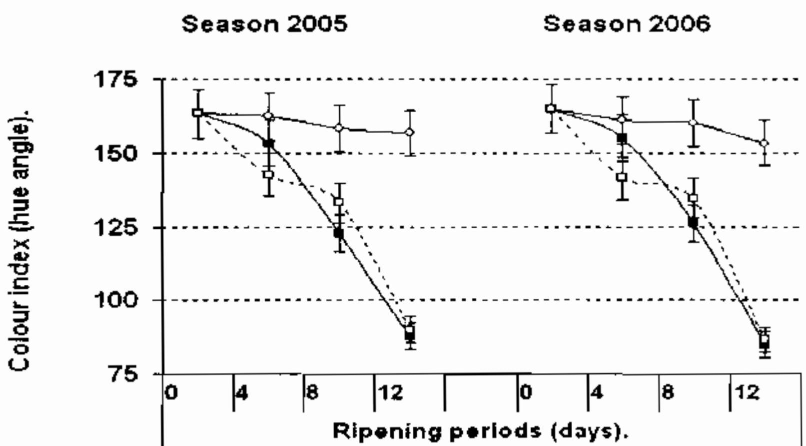
Fig (4): Effect of ripening method on weight loss% of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	Season 2005 (0)	(4)	(8)	(12)		Season 2006 (0)	(4)	(8)	(12)
Control	8.40	8.10	7.67	7.07		8.20	8.00	7.57	6.97
Calcium Carbide	8.40	7.27	6.67	5.13		8.20	7.17	6.57	5.03
soybean oil	8.40	7.00	6.57	5.93		8.20	6.83	6.43	5.87
L.S.D. at 5%		0.50	0.59	0.27			0.54	0.63	0.12

The vertical lines at each point represent the standard deviation of the means.

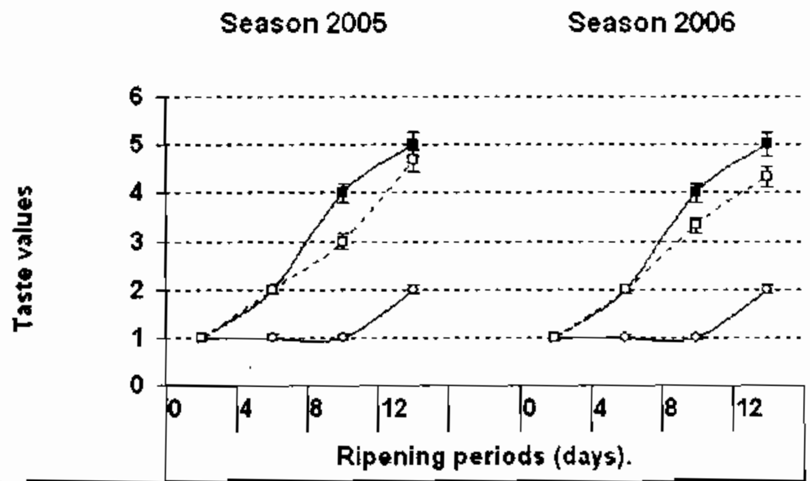
Fig (5): Effect of ripening method on firmness kg./cm² of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	Season 2005 (0)	(4)	(8)	(12)		Season 2006 (0)	(4)	(8)	(12)
Control	163.3	162.3	158.3	156.7		165.0	161.0	160.0	153.3
Calcium Carbide	163.3	153.3	122.7	87.7		165.0	155.0	126.0	85.0
soybean oil	163.3	142.7	133.0	90.0		165.0	141.3	134.7	86.7
L.S.D. at 5%		6.39	7.80	6.84			3.16	8.96	4.03

The vertical lines at each point represent the standard deviation of the means.

Fig (6): Effect of ripening method on colour index (hue angle) of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.



	Season 2005: 0	4	8	12	Season 2006: 0	4	8	12
Control	1.00	1.00	1.00	2.00	1.00	1.00	1.00	2.00
Calcium Carbide	1.00	2.00	4.00	5.00	1.00	2.00	4.00	5.00
soybean oil	1.00	2.00	3.00	4.67	1.00	2.00	3.33	4.33
L.S.D. at 5%		0.001	0.001	0.755		0.001	0.755	0.755

The vertical lines at each point represent the standard deviation of the means.

Fig (7): Effect of ripening method on tast values of "Williams" banana cultivar fruits at 13°C in seasons of 2005 and 2006.

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طرق طبيعية لتوليد غاز الإثيلين لإنضاج الفاكهة بإستخدام زيت فول الصويا

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من اجل تخليق غاز الإثيلين بطرق سهلة وطبيعية تم اللجوء إلى طريقة تجزئة الاحماض الدهنية الغير مشبعة ،استخدم زيت فول الصويا ومجروش بذور فول الصويا فى وجود برادة الحديد وحمض الاسكوربيك كعوامل حفّازة ، حيث تم إضافة ٢٥ سم^3 من محلول فوق اكسيد الأيدروجين (٣٠٪) إلى خليط من ٥٠ جرام من زيت فول الصويا و٥٠ جرام من مجروش بذور فول الصويا فى وجود آثار من برادة الحديد وحمض الأسكوربيك فى حجرة مغلقة ذات ابعاد ٢,٢ X ١,٨٠ X ٢,٥٠ متر و إستخدمت انابيب Kitagawa لقياس تركيز غاز الإثيلين حيث تراوح تركيز الإثيلين المنبعث فى جو الغرفة مابين ٤٥٠ : ١٢٠٠ جزء فى المليون.

وفى تجربة لمدة عامين متتاليين (٢٠٠٥ و ٢٠٠٦ م) لإستخدام غاز الإثيلين المنعث فى الإنضاج ، تم تعريض جزء من ثمار موز صنف ويليامز مكتملة النمو خضراء لتلك الغازات المنبعثة من معاملة زيت فول الصويا والجزء الآخر تم تعريضها للغازات المنبعثة من معاملة كربيد الكالسيوم (المعاملة الشائعة الإستخدام) لمدة ٢٤ ساعة بالإضافة إلى الثمار الغير معرضة لأى غازات (كمعاملة كنترول) ثم خزنت جميع المعاملات على ١٣°م ورطوبة نسبية ٩٠٪.

أوضحت النتائج المتحصل عليها أن الغازات المنبعثة من زيت فول الصويا كانت فعّالة فى إنضاج ثمار الموز كتلك المنبعثة من كربيد الكالسيوم ، وكانت الثمار المعرضة للغازات المنبعثة من زيت فول الصويا ذات جودة عالية وخصائص اكلية مقبولة مقارنة بتلك المعرضة للغازات المنبعثة من كربيد الكالسيوم ، بينما الثمار الغير معاملة (الكنترول) لم تنضج طبيعياً وذات صفات رديئة وطعم غير مقبول.

والمطلوب المزيد من الأبحاث على إستخدام الغازات المنبعثة من زيت فول الصويا فى الإنضاج الصناعى على النطاق التجارى.