APPLICATION OF HIGH CONCENTRATION OZONE GAS TO EXTEND SHELF-LIFE OF FRESH LONGAN

SARANYAPAK CHAMNAN

DOCTOR OF ENGINEERING IN FOOD ENGINEERING
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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF ENGINEERING
IN FOOD ENGINEERING
ACADEMIC ADMINISTRATION AND DEVELOPMENT MAEJO UNIVERSITY
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ชื่อเรื่อง การประยุกต์แก๊สโอโซนความเข้มข้นสูงเพื่อยืดอายุลำไยสด
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บทคัดย่อ

ลำไยเป็นผลไม้ที่เสื่อมเสียตามธรรมชาติ และเกิดโรคหลังจากการเก็บเกี่ยวได้ง่าย ซึ่งเป็นสาเหตุทำให้ลำไยมีอายุการเก็บรักษาสั้นที่อุณหภูมิห้อง งานวิจัยนี้จึงมีวัตถุประสงค์เพื่อประยุกต์การใช้แก๊สโอโซนความเข้มข้นสูงสำหรับยืดอายุลำไยในอุณหภูมิแช่เย็น ในการทดลองส่วนแรกได้นำลำไยพันธุ์ดอมาผ่านการรมด้วยแก๊สโอโซนความเข้มข้น 4,000 ppm นาน 5 นาที และนำไปบรรจุในบรรจุภัณฑ์ 3 ชนิด ได้แก่ ถุงโพลีเอทีลีน (polyethylene, PE) ถุงโพลีโพรพิลีน (polypropylene, PP) และ ใส่ถาดโฟมหุ้มด้วยฟิล์มโพลีไวนิลคลอไรด์ (foam tray wrapped with polyvinyl chloride (PVC) film, WF) จากการวิจัยพบว่าเมื่อระยะเวลาการเก็บรักษานานขึ้น ลำไยจะมีการเกิดโรค การเกิดสีน้ำตาลที่เปลือก และน้ำหนักที่สูญเสียไป เพิ่มขึ้นในทุกทรีตเมนต์ จากบรรจุภัณฑ์ทั้ง 3 ชนิดนี้ จะพบว่าลำไยที่ผ่านการรมด้วยแก๊สโอโซนและบรรจุถุง PE จะมีอายุการเก็บรักษาที่นานที่สุด คือ 36 วัน และสามารถยืดอายุการเก็บรักษาลำไยได้มากกว่าถึง 140% เมื่อเปรียบเทียบกับตัวอย่างควบคุม

สำหรับการทดลองส่วนที่สองได้ทำการศึกษาผลของการรมแก๊สโอโซนความเข้มข้นสูงที่มีต่อคุณภาพของลำไย นำลำไยมาผ่านการรมด้วยแก๊สโอโซนที่ความเข้มข้นต่างๆ ดังนี้ 4,000 8,500 และ 13,000 ppm เป็นเวลา 5 10 และ 15 นาที โดยทำการบรรจุในถุง PE พบว่าลำไยที่ผ่านการรมด้วยแก๊สโอโซนความเข้มข้น 8,500 ppm นาน 5 นาที เป็นทรีตเมนต์ที่ดีที่สุด คือสามารถยืดอายุการเก็บรักษาได้นาน 35 วัน และสามารถยืดอายุการเก็บรักษาได้มากกว่าลำไยที่ไม่ผ่านการรมด้วยแก๊สโอโซน (10 วัน) ประมาณ 57% อายุการเก็บรักษาของลำไยที่ผ่านการรมด้วยแก๊สโอโซนความเข้มข้นสูงในการทดลองส่วนที่สองสั้นกว่าการทดลองส่วนที่หนึ่งอาจจะเกิดความแตกต่างของคุณภาพลำไยในฤดู (ส่วนที่ 1) และนอกฤดู (ส่วนที่ 2)

ในส่วนที่สาม ได้ทำการศึกษาจลนพลศาสตร์การเสื่อมเสียของลำไยที่ผ่านการรมด้วยแก๊สโอโซนความเข้มข้น 8,500 ppm นาน 5 นาที มีค่า rate constants (k) of 0.74×10^{-2} day^{-1} ซึ่งมีค่าน้อยกว่าลำไยที่ไม่ผ่านการรมด้วยแก๊สโอโซนถึง 3 เท่า นอกจากนี้ผลจาก SEM ยังแสดงให้เห็นว่าลำไยที่ไม่ผ่านการรมด้วยแก๊สโอโซนจะมีเส้นขนที่พื้นผิวมากกว่าลำไยที่ผ่านการรมด้วยแก๊สโอโซน

และเส้นขนเหล่านี้อาจเป็นแหล่งที่อยู่ของเชื้อต่างๆ ที่ก่อให้เกิดการเสื่อมเสียของลำไยอย่างรวดเร็ว จากการทำนายอายุการเก็บรักษาของลำไยด้วยสมการโพลีโนเมียล พบว่าลำไยที่ผ่านการรมด้วยแก๊สโอโซนจะมีอายุการเก็บรักษานาน 36 วันซึ่งมีค่ามากกว่าลำไยที่ไม่ผ่านการรมด้วยแก๊สโอโซนถึง 2 เท่า การที่รมแก๊สโอโซนด้วยความเข้มข้นสูงมีผลต่อคุณภาพของลำไยที่เก็บรักษาในตู้แช่เย็น โดยช่วยยืดอายุการเก็บรักษาให้นานขึ้น และยังเป็นมิตรกับสิ่งแวดล้อม นอกจากนี้สามารถนำวิธีการดังกล่าวไปประยุกต์ใช้ และเป็นอีกทางเลือกหนึ่งเพื่อทดแทนการรมลำไยด้วยซัลเฟอร์ไดออกไซด์อีกด้วย

คำสำคัญ : ลำไย, โอโซนความเข้มข้นสูง, บรรจุภัณฑ์ลำไย, ยืดอายุการเก็บรักษา, จลนพลศาสตร์ของการเสื่อมเสีย

Title	APPLICATION OF HIGH CONCENTRATION OZONE GAS TO EXTEND SHELF-LIFE OF FRESH LONGAN
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Degree	Doctor of Engineering in Food Engineering
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ABSTRACT

Longan is a tropical fruit with highly rotten decay and postharvest disease which greatly shortens its shelf-life at room temperature. The objective of this work was to apply the high concentration ozone (HCO) gas to extend shelf-life of longan fruit during cold storage. The first part was conducted on the longan cv. "Daw" by fumigating it at a concentration of 4,000 ppm for 5 min. Longan were packed using 3 different types of packaging materials, namely, polyethylene bag (PE), polypropylene bag (PP) and foam tray wrapped with polyvinyl chloride (PVC) film (WF). Results show that as storage time progressed, all longans became more susceptible to disease incidences, pericarp browning, and weight loss in all treatments. Among the three different types of packaging, the HCO longan stored in PE yielded the longest storage time with a shelf-life of up to 36 days, accounting for 140% longer shelf-life than that of the control.

In the second part, the effects of ozone concentration on fresh quality of longan fruit were studied. Longan was exposed to ozone gas at varied concentrations of 4,000 8,500 and 13,000 ppm with holding time of 5 10 and 15 min and packed with PE bag. Results show that the HCO longan exposed to ozone gas at 8,500 ppm for 5 min was considered an optimal treatment to extend shelf-life up to 35 days, account for 57% longer shelf-life than that of the non-ozonated longan with shelf-life of 10 days. The shorter shelf-life of HCO longan in the second part than that of the first part is possibly due to differences in quality longan between in-season (1^{st} part) and off-season (2^{nd} part).

For third part, the kinetics of deterioration on the HCO longan was studied. At 8,500 ppm for 5 min, the HCO longan exhibited the deterioration rate constants (k) of 0.74×10^{-2} day^{-1}, which were approximately 3 folds lower than that of the non-ozonated longan. The SEM images reveal that the non-ozonated longan was covered with surface epidermal hairs more than the ozonated longan. The existence of epidermal hairs may inhabitant the microorganisms and cause the shelf-life decay. From shelf-life prediction using polynomial equation, the HCO longan had a shelf-life of 36 days, which was 2 folds longer shelf-life than that of the control. The HCO treatment on the quality of fresh longan during cold storage can be further developed as an environmental friendly alternative to sulfur dioxide fumigation to extend the shelf-life of longan.

Keywords : Fresh longan, High concentration ozone, Longan packaging, Shelf-life extension

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CHAPTER 1
INTRODUCTION

1.1 Background of Research

Longan (*Dimocarpus longan* Lour.) the one of economically important fruits in the north of Thailand, which was exported longan fruit 1,022,927 tonnes in 2019 (Office of Agricultural Economics, 2020). Importing countries of Thai longan include China, Vietnam, Indonesia, Hong Kong and Malaysia (Department of International Trade Promotion, 2020). However, the quantity of domestic and export longan fruit is limited by highly rotten nature, susceptible to various postharvest pathogens after just a few days at room temperature, resulting in a short storage life and reducing market value (Saengnil et al., 2014). The main problem resulting in restrictions on the export of longan to long distant markets is rapid pericarp browning during storage (Sardsud et al., 1994). Browning reaction can be related with dehydration, heat stress, senescence, chilling injury or disease (Apai, 2010). Chilling injury symptoms including water soaking and/ or area of browning on the pericarp (Jaitrong, 2006) are normally deserved. After 5 days of storage, the symptoms appear normally on the inner side of pericarp longan fruit. Next, the pericarp of both sides become brown color (Jiang et al., 2002).

Generally, the most common method used to prevent pericarp browning and control postharvest deterioration in longan fruit is sulfur dioxide (SO_2) fumigation. Recently, importing countries such as China, Malaysia and Canada have restricted import regulation of longan, and reduced the maximum permitted residual level of sulfur dioxide. Moreover, consumers are becoming aware of sulfur dioxide residues, due to its negative effect to human body, particularly for asthmatics and sensitive individuals (Apai, 2010). Thus, there is a need to develop alternative methods to replace sulfur dioxide fumigation, with less harmful technology to humans and the environment. With this research, we proposed the use of ozone gas as an alternative to sulfur dioxide fumigation on longan (Whangchai et al., 2006).

Ozone (O_3) is an unstable triatomic oxygen molecule. The high energy such as electrochemical, ultraviolet radiation or electrical discharge is usually a source of ozone (Miller et al., 2013). It is becoming a popular alternative to traditional antimicrobial agents such as chlorine, chlorine dioxide and organic acids because of it is effective antimicrobial property and lack of residual substances (Guzel-Seydim et al., 2004). It can be applied in both gas state or dissolved state in water (Gabler et al., 2010). The ozone gas treatments are generally more effective than aqueous ozone treatments (Akbas and Ozdemir, 2008). Habibi Najafi and Haddad Khodaparast (2009) found that gaseous ozone were able to reduce *Bacillus cereus* in dried figs up to 2 log10 CFU/ g. Whangchai et al. (2011) reported that the eating quality of lychee after treatment with the ozonated water decreased significantly from compared with the control and the ozone fumigated groups.

Ozone is a 'Generally Recognized As Safe' (GRAS) status antimicrobial agent that is used for food treatment, storage, food processing (FDA, 2001) disinfecting water, in the food industry such as sanitation of food plant equipment, surface hygiene and reuse of waste water (Habibi Najafi and Haddad Khodaparast, 2009). Ozone is an effective treatment for increasing shelf-life and decreasing fungal deterioration in the postharvest treatment of fresh fruit such as stone fruit (Palou Lluı´s et al., 2002) and papaya fruit (Ong et al., 2014) because of the lack of residues on the product. The effects of ozone on the reduced growth of microorganisms also have been reported with regard to reduction of total bacterial count, Coliform, *Staphylococcus aureus* and yeast/ mold counts on Iranian date fruits (Habibi Najafi and Haddad Khodaparast, 2009), *Penicillium digitatum, Penicillium italicum* and *Botrytis cinerea* (Ozkan et al., 2011). As the use of sulfur dioxide is prohibited or use to be discontinued, ozone could be an acceptable technology to use with fruit marketed under "organic" classification (Gabler et al., 2010).

Additionally, if ozone treatment is to be used with proper packaging, it may give several benefits for fruit such as control of weight loss, protection from browning skin, reduced contamination during handling and extend shelf-life of fruit (Mario et al., 2010). The proper packaging has a good character of proper permeability where a desirable equilibrium modified atmosphere, when the rate of gas (oxygen and carbon dioxide) transmission through the pack balances the respiration rate of fruit (Kartal et al., 2012).

From a number of researches, ozone exhibit a great potential to solve problems for extending the shelf-life of longan fruit without sulfur dioxide fumigation. The main purpose of this study was to determined appropriate packaging, effective fumigation and kinetics of deterioration under high concentration ozone (HCO) fumigation on the longan during cold storage which may lead to the further developed as an alternative to sulfur dioxide fumigation to prevent desiccation and prolong the shelf-life of longan fruit.

1.2 Objectives of research

The objective of this research was to determine the optimum conditions of ozone fumigation process for extending shelf-life on longan fruit which consists of 3 objectives below:

1. To determine the suitable packaging on quality in fresh longan fruit.
2. To determine the optimum conditions for ozone fumigation on quality of longan fruit.
3. To investigate the kinetics of deterioration of HCO longan during cold storage.

1.3 Scope of research

1. Longan fruit (*Dimocarpus longan* Lour.) cv. ‘‘Daw’’, harvested less than 3 days was obtained from a commercial orchard in the north of Thailand.
2. Longan fruit selected for uniformity of size of >31 mm (grade AA) in diameter, uniform peel-color and non-disease appearance.
3. Ozone used in gas condition and ozone gas fumigation system has flow rate 7.5 L/min, under gas pressure of 11-25 kPa.

1.4 Keywords

Fresh longan, High concentration ozone, Longan packaging, Shelf-life extension, Kinetics of deterioration

CHAPTER 2
LITERATURE REVIEW

2.1 General information of longan fruit

Longan (*Dimocarpus longan* Lour.) is a tree of the *Sapindaceae* family. It is indigenous to the foothills of mountainous areas of northern Myanmar and northeast and southern China. Longan fruit is commercial grow in many countries such as China, Thailand, India and Vietnam as shown in Table 1.

Table 1 Planted area, production and export of longan fruit in different countries.

Country	Year	Planted area (ha)	Production (metric ton)	Export (%)	References
China	1997	444,400	495,800	a	Liu and Ma (2001)
Taiwan	1998	11,808	53,385	-	Wong (2000)
Thailand	1997	41,434	227,979	50	Subhadrabandhu and Yapwattanaphun (2001a), Wong (2000)
Vietnam	1999	41,000	365,000	10	Wong (2000)

a Net importer.

Source: Jiang et al. (2002)

2.1.1 Morphology and botany

Longan is a tropical evergreen tree. Longan tree grows depending on climate and soil type with a typical tree height of 30–40 feet and the round crown. The limited natural flowering period leads to a short production. Recent investigations of longan fruit growth and development indicate that flowering can be regulated by application of chemicals such as chlorate and/or plant growth regulators.

Longan fruit contains a relatively black or brown seed. The fruit is conical heart or spherical shape with a thin pericarp. The pericarp can vary in color from yellowish to light brown, and the skin is smooth (Figure 1). The edible portion of the longan fruit is a fleshy translucent white aril. The pulp is delicate, juicy and sweet.

Figure 1 General appearance of longan fruit.

2.1.2 Fruit growth

Longan fruit have a sigmoidal growth curve. Initially, longan growth from the seed, the pericarp and aril growth, respectively.

2.1.3 Harvest maturity

Longan fruit is non-climacteric, which does not continue to ripen once removed from the tree. Consequently, fruit must be harvested when their skins become yellow-brown and their flesh reaches the optimal eating quality. Maturity can be determined by fruit weight, skin color, flesh sugar concentration, flesh acid concentration, sugar: acid ratio, flavor and/or days of fruit (Table 2). However, harvest maturity is usually assessed on the basis of fruit color and flavor by visual.

Table 2 Fruit characteristics of longan fruits.

	Mean Fruit							
Cultivar	**No. Years Data Collected**	**Weight (g)**	**Length (mm)**	**Width (mm)**	**% Aril**	**% Brix**	**Flesh Texture**	**Comments**
Biew Kiew	5	11.5	25.6	28.0	64.9	20.9	Crisp	Excellent quality
Chompoo I	5	9.4	23.7	25.8	64.4	19.7	Crisp	Sweet, good flavor
Chompoo II	5	8.7	24.4	26.2	62.6	21.5	Crisp	Sweet, good flavor
Dang	5	9.4	23.5	25.6	63.4	19.9	Crisp	Sweet, good flavor
Daw *	4	9.6	24.3	25.8	60.9	19.2	Crisp	Sweet
Haew*	4	9.5	23.8	26.4	63.3	19.6	Crisp	Sweet, good flavor

* Mean of two trees

Samples based on means of 25 fruit for length and width, 10 for brix and 5 for weight and % aril.

Source: Winston and O'Farrel (1989)

2.1.4 Physiology

1) Respiration

Longan fruit is non-climacteric. It gradually increase respiration rate at 25 °C. When fruit stored at 4 °C, it continuously decline and slow down the respiration.

2) Ethylene production

Longan fruit produce ethylene at low levels after harvest (2.3 l/kg per h) when comparison with climacteric fruits. The ethylene production rate of fruit stored at 1 or 4 °C remained relatively constant for 30 days. After 30 days, the ethylene production rate increases and associates with decay.

3) Composition

Longan fruit increases in soluble solid concentration (SSC), titratable acidity (TA) and total sugars during ripening and then gradually decrease after harvest. The main sugars in longan fruit are sucrose, fructose and glucose. Differences the ratio of sugars are a result of differences in invertase activities, maturity and cultivars. TA and SSC of the pulp have been slightly decreased during cold storage.

4) Color

Rapid pericarp browning of longan fruit a few days after harvest is one of the most important problems in marketing. Browning can be associated with desiccation and/or heat stress, senescence, chilling injury and pest or pathogen attack. Browning has been attributed to enzymatic oxidation of phenolic by polyphenol oxidase (PPO). PPO is activated by moisture loss from the fruit. Treatments to reduce desiccation also reduce browning. Many studied use substance for inhibit browning such as propyl gallate (Lin et al., 2015), hydrogen peroxide (Lin et al., 2014) and 2-butanol (Li et al., 2015).

5) Texture

Longan fruit pulp had a little research about the textural changes. Pulp integrity does not appear to be adversely affected by chilling temperatures. When stored at 0 °C, longan fruit maintain good eating quality such as flavor and texture.

6) Disorders

Skin splitting can occur with cultivars, rain or sudden uptake of water during the last stage of fruit development. Disorders effects the pulp faster than the skin, result in skin rupture. Aril breakdown has been observed after storage and over mature fruit.

7) Chilling injury

Longan fruit are more tolerant of low temperatures than other tropical and subtropical fruits. It is difficult to separate effects of chilling injury of longan fruit from desiccation or fruit senescence.

8) Peroxidative activity

Decrease superoxide dismutase activity in longan fruit indicates a decreased ability of harvested fruit to eliminate active oxygen in association with an increased peroxidation of membrane lipids.

2.1.5 Cultivars developed

There are several cultivars of longan fruit in Southeast Asia. However, the diversity among cultivars is lower in other regions. The following are the characteristics of the most commonly cultivated varieties in the world (Mishra et al., 2018).

1) Chuliang

This cultivar is native to Guangdong Province in China of superior quality longan cultivar. Fruit size is large (12.0-16.5 g). Aril constitutes about 69-74% of total fruit weight. The thick, firm and fragrant aril is sweet in taste with TSS content 20-23%. It is suitable for processing. Attractive golden yellow color is formed in aril after drying which fetches good market price. The cultivar produces high and stable yield.

2) Shixia

It is another popular cultivar in Guangdong Province, China. It has a long history of cultivation about 140 years. Fruits are small, but crisp, thick and sweet aril with TSS (19-20%) and with good flavor. It is the best cultivar for consuming as fresh fruit and produces heavy crops regularly on unusually large panicles. It is generally consumed as fresh. The small fruits have sweet aril with TSS content 19-20%. This cultivar is suitable for high density planting.

3) Wuyuan

Wuyuan (syn. Black Round) is another important longan cultivar in Guangdong province, China. Fruit size is medium (15 g) with large seed, soft and juicy aril of average quality with TSS (14-15%). Trees are high yielding. The fruit is suitable for eating fresh and dried. Seedlings are vigorous and consequently useful as rootstock.

4) Fuyan

It is an important longan cultivar in Fujian province, China, occupied about 90% of the area under the province. Fruit is large sized (18 g) with thin skin, small seed and thick crisp aril. Yield is high. It is best used for canning since the fruits have a low TSS value of 15-16%.

5) Wulongling

This is another major cultivar in Fujian province, China. Its history of cultivation can be traced up to more than 150 years. Fruit is medium in size (15 g) with thick skin, good aril recovery and sweet flavor, TSS (21-23%). It has a distinct alternate bearing cropping.

6) Daw

Daw is the most popular longan cultivar of Thailand, accounted for about 73% of the total cultivation area under longan in the country. The name Daw meaning early, indicating it early maturing. Flowering takes place in December and fruit harvesting occurs in late June to early July. Thus, fruits fetch high premium from foreign markets. It is the most regular bearer and has no irregular bearing problem. In addition, the cultivar is relatively free from infection by witches' broom disease. The aril content is low due to big seed, though have a large fruit size. The aril is sweet and with good flavor, is rather tough and not as crispy when compared to the aril of Biew Khiew. Fruits do not keep well on the tree and the seed may even germinate within the fruit. The fruits can be consumed fresh or processed. This cultivar is normally grown in the Northern provinces where the cool winter months are necessary for induction of flowering.

7) Chompoo

It is another Thai cultivar. It is a mid maturing cultivar. Fruit is medium size, oval shape with greenish light brown skin. Aril is very sweet and slight pink, hence named Champoo. Aril content is high due to small seeds with high TSS (21-22%) and pleasant aroma. It is irregular bearer.

8) Biew Khiew

A late maturing cultivar of Thailand. Fruit is round, large, brownish green color and high aril content. Aril is crispy, pleasant scented and sweet (TSS, 22%) and of excellent quality. Peel is thick, therefore, advantageous to longer shelf-life. It exhibits irregular bearing and is susceptible to witches' broom disorder.

9) Haew

Haew longan is a Thai cultivar which is a late maturing cultivar. It flowers in late January to early February. Fruits mature during mid to late August. Fruit is medium to large size, small seed and average aril content. Aril is firm and of good eating quality. Peel is rough, thick and therefore, advantageous for longer shelf-life.

Haew flowers easily and of high yielding. However, it is an alternate bearer. The fruits are suitable for canning. It required cool winter for flowering induction.

10) Dang

The fruits are harvested during mid July to early August and therefore, classified in mid maturing cultivar of Thailand. Fruit is large with reddish brown rind. Aril content is low due to large seed size. The fruit quality declines with maturity. Yield and quality are similar to Daw. Dang is susceptible to water logging.

11) Baidum

This is also a mid maturing regular bearing cultivar from Thailand. Harvesting of fruits is carried out during the month of mid July to early August. Fruit is medium size with rough rind, small seed and moderate aril content. Aril is of acceptable flavor, crispy, very sweet and is bright white in color. This cultivar is a regular bearer and can withstand drought quite well.

12) Talub Nak

This is an early maturing cultivar whose fruits are harvested in mid to late July. Fruit is medium sized, with small seed and high aril content. Aril is bright white in color and less sweet.

13) Phetsakon

It is an early maturing regular cultivar of longan. Differing to other varieties of Thailand, it is not required cooler climate for induction of flowering. This cultivar is mainly growing in central region of the country in Samut sakhon and Ratchaburi provinces.

14) Fengko

It is the most popular cultivar of longan in Taiwan Province of China, occupied about 98% of the longan area under cultivation. It is a good yielder. Fruit is evenly large sized. Fruit rind is yellowish brown which turns brighter at low temperature. Aril is very sweet, TSS content 20%. Fruits attached firmly with the stalk, not easily detached which is considered as a good quality.

15) Chingko

Another famous cultivar of longan in the Taiwan Province of China. Fruit rind is light brownish green on ripened. However, fruit quality is easily affected by environmental conditions. As compared to Fengko, fruits are easily detached from the stalk and aril is less sweet. Therefore, it is considered to be of a poor quality fruit.

16) Longnhan

A popular cultivar of longan in the Mekong delta, Vietnam. It is a truly tropical longan which can yield two crops per year.

17) Tieuhue

Tieuhue is also a true tropical longan which can yield three crops in two years in the Mekong delta of Vietnam.

18) Longhungyen

It is a popular cultivar of longan in the Northern region of Vietnam. The cultivar thrives only in subtropical conditions and produces only one crop per year.

19) Kohala

It is popular in Florida, USA. Fruits are large size, high aril content with sweet spicy flavored aril. Pruning of panicle (2/3 of the length) in order to increase the fruit size is a common practice in this cultivar.

20) Egami

This cultivar was originated in Hawaii. Kona No. 1 was selected from an open pollinated seedling of unknown origin at Kona Research Station, College of Tropical Agriculture and Human Resources (CTAHR). This Kona No. 1 was named "Egami" in honor of Mr. Yosoto Egami. The panicles bear fruits in large cluster with excellent fruit setting percentage (more than 50 fruits/panicle). Flowering starts in late February and continue to the end of March. Fruits are ripened during August to early October. The aril constitutes 70-75% of total fruit weight with TSS content 18-22%. This cultivar is suitable for drying.

2.1.6 Pathology

Longan fruit are very susceptible to postharvest decay as a result of bacterial, fungal and yeasts infections (Table 3). The most important causing disease organisms include *Botryodiplodia* sp. and *Geotrichum candidum*. About 106 species of microorganism have been isolated from longan fruit, consist of 36 bacteria, 63 mold and 7 yeast species (Jiang et al., 2002).

Table 3 Major postharvest pathogens of longan fruit.

Pathogens	References
Bacteria	
Enterobacter srtohrnrd, *Acinetobacte* sp.	Lu et al. (1992)
Mold	
Botryodiplodia sp.	Jiang (1997)
G. candidum Link ex Pers.	Tsai and Hsieh (1998)
Penicillium sp., *Rhizopus* sp., *Alternaria* sp.	Lu et al. (1992)
Aspergillus sp., Fusarium spp.,	Sardsud et al. (1994b)
Lasiodiplodia theobromae	
Pestalotiopsis sp., *Cladosporium* spp.	Sardsud et al. (1994b)

Source: Jiang et al. (2002)

For many years, the recommended method to control postharvest decay and prevent pericarp browning in longan fruit has been sulfur dioxide (SO_2) treatment. Sulfur dioxide a reducing agent, is able to protect longan fruits from turning brown as a result of reducing PPO activity. It acts as a bleaching agent and also plays a role in decay inhibition (Apai, 2010). Recently, importing countries such as China and Singapore have restricted the import of longan fruit products and other fruits and reduced the maximum permitted residual level of sulfur dioxide. Consumers are becoming cautious regarding sulfur dioxide residues, due to allergenic symptoms. There is a need to develop effective methods to replace sulfur dioxide treatment, with something less harmful to humans and the environment. An alternative method is the use of ozone (Whangchai et al., 2006).

2.1.7 Technology

1) Grading

No official grade or international standards have been set for longan fruit. In practice, fruit are graded on the basis of size or weight. In Thailand, a fruit count in the range of 50–75 fruit per kg is considered as the top grade. Longan fruit is sorted into three size-grades according to commercial marketing practices: AA (diameter greater than 31 mm), A (diameter between 27-31 mm) and B (diameter less than 27 mm) (Jaisin et al., 2013).

2) Treatments

Techniques to reduce browning, control postharvest decay, and extend storage life of longan fruit have included fungicide dips, application of plant growth substances, waxes and chitosan coatings, use of microbial antagonists such as Bacillus subtilis, sulfur fumigation, irradiation and heat treatments. Of these, only fungicide dips and sulfur fumigation have been used commercially.

2.1) Sulfur

SO_2 fumigation has been the most effective practical postharvest treatment for control of color change and inhibit postharvest microbial diseases of fruit. Although recommendations vary slightly, fumigation is achieved by burning of sulfur powder, vaporizing liquid sulfur dioxide, or dissociation of sulfite compounds. However, sodium metabisulfite is less effective and more variable than sulfur dioxide treatment. Sulfur residues were higher in the pericarp than in the aril, and decreased rapidly during the first few days after fumigation of longan fruit. A proposed an alternative improvement of the technology to alleviate the problem by applying a vertical forced-air technique with the sulfur dioxide gas that reduced sulfur dioxide residue in longan fruit. The technique was as effective as the conventional method in preventing postharvest diseases and skin browning of treated fruit. The sulfur dioxide concentration is approximately 3-5 times lower than official recommendations (Phimphimol et al., 2010). In recent years, there has been increasing concern about sulfur residues in fruit, particularly as some people are sensitive to sulfites.

2.2) Fungicides

Longan fruit browning and fungal contamination can be controlled for 5–7 days at ambient temperature or at low temperature by application of fungicides before packaging. Fungicides used commercially include benomyl, thiabendazole and iprodione. However, postharvest fungicides are not readily available in all growing areas to control longan fruit diseases.

2.3) Microbial metabolites and plant extracts

Because SO_2 and fungicide applications are not favored by consumers, regulatory authorities and environmentalists, acceptable alternatives have been investigated. Jiang (2008) reported that the culture supernatant of *B. subtilis* was effective in controlling *Botryodiplodia* sp. Treated longan fruit could be stored for about 30 days at 5 °C, with good turnout quality. However, it showed little effect against disease development on longan fruit. Plant extracts for the control of the decay should be further evaluated, given the extensive world plant resource.

2.4) Irradiation

Irradiation could be a viable alternative to chemical treatments, particular SO_2 fumigation, which is detrimental to fruit quality. Co^{60} irradiation at a relatively high dosage (200–400 Gy) resulted in no visual injury on longan fruit. For most fresh fruits, irradiation is not yet commercially used.

2.5) Heat treatment

Methods for heat treatment of harvested fresh fruit and vegetables include hot water, vapor heat and hot air. Hot water was originally used for fungal control, but has also been extended to insect disinfestation. Short-term high temperature is effective for fungal pathogen control because fungal spores and latent infections are often either on the surface or in the outer layers under the epidermis of fruits and vegetables.

2.6) Plant growth regulators

Application of kinetin at 20 ppm to longan fruit postharvest extended the shelf-life, while postharvest dipping in GA3 at 50 ppm did not prolong storage life. Spraying longan trees with maleic hydrazide at 250 ppm or B9 at 150 ppm 45–50 days after flowering produced smaller fruit, but prolonged their storage life. Treatment with 1-methylcyclopropene, an inhibitor of ethylene reception, reduced the respiration rate of longan fruit, but had no effect on storage life.

2.7) Coatings

Skin coatings have generally been effective in extending storage life of longan fruit. Example, use of waxes reduced water loss, chitosan extended storage life at 5 °C or dipping in acidic chitosan solution could inhibited PPO activity, which would also help delay pericarp browning of longan fruit.

2.8) Disinfestation treatments

Longan fruit is a fruit fly host and, thus, disinfestation is required by many countries, particularly the USA and Japan. Cold storage for 15 days at 1.1 °C has been suggested as a method for insect disinfestation of longan fruit. However, storage at this low temperature resulted in patches of bronze discoloration on the pericarp. Furthermore, fruit can deteriorate rapidly when removed from cold. Hot water treatment could kill China fruit fly without adversely affecting the eating quality and may not be acceptable for marketing of longan fruit. The irradiation is a promising quarantine treatment. The International Consultative Group on Food Irradiation has recommended 150 Gy as a minimum dosage for treating eggs and larvae of fruit flies to prevent emergence of normal adults. Further investigation with regard to optimum doses of irradiation and variable responses of different cultivars is needed.

3) Packaging

Storage in plastic bags was effective in reducing longan fruit moisture loss over a wide temperature range of 3–30 °C. Under conditions minimizing moisture loss, the shelf-life of longan fruit stored at low temperature was limited by a decline in organoleptic quality rather than in visual appearance.

4) Storage

Visual appearance, a reduction in organoleptic quality and the development of disease that causes the longan fruit shelf-life is limited. Rapid moisture loss occurs from fruit during storage despite a pericarp with few stomata or lenticels. Under low humidity, visual appearance declines to unacceptable levels due to skin dehydration and browning. The visual appeal of longan fruit can deteriorate rapidly under ambient conditions within 3–4 days following harvest many researchers suggest that a relative humidity (RH) of 85–95% is an optimal condition for storage (Jaitrong, 2006). Higher humidity is conducive to water soaking and decay. Storage of fruit at lower RH resulted in water loss, causing formation of a dry epidermal layer. Maximum postharvest life of longan fruit is obtained in the lower temperature range of 1–5 °C, where the decline in visual appearance and flesh breakdown eventually limit longevity. The minimum temperature at which fruit can be stored without exhibiting chilling symptoms varies among cultivars (Table 4). Atmosphere control has been reported to modulate the rate of skin color change in longan fruit. Packing within plastic bags and sealed containers can reduce the rate of pericarp color change. However, effects of packaging on RH tend to confound any carbon dioxide and/or oxygen concentration effects.

Table 4 Optimal storage temperature recommendations for longan fruit cultivars.

Cultivar	Optimal storage temperature (°C)	Maximum postharvest life (days)	References
Shixia	1-2	40	Jiang (1999b)
Tongpi	1-3	35	Shi (1990)
Wulongling	3-5	30	Hong et al. (1984), Pan et al. (1996)
Wuyuan	3-5	30	Jiang (1999b)

Source: Jiang et al. (2002)

5) Processing

Dried longan fruit are referred to as longan nut and are popular with Asians. The fruit is often dried outdoor as the controlled conditions are often not available, particularly in countries such as China and Vietnam. The fruit can be blanched and treated with sulfur to help retain their light color during drying. Longan fruit can be also frozen without any adverse effects on the aril. However, if they are frozen whole, the pericarp appears darken on freezing and brown when thawed. Similar treatments to those used for drying can be applied to maintain pericarp color. Longan fruit can be canned in syrup or processed to produce wine or juice. Due to their high SSC content, little sugar additive is required and longan fruit can be canned in their own juice.

2.2 Background of ozone

Ozone is triatomic oxygen (O_3) (Whangchai et al., 2006), generated by the passage of air or oxygen gas through a high voltage electrical discharge or by ultraviolet light irradiation (Figure 2). It can be applied either as a gas or dissolved in water (Gabler et al., 2010). Ozone is one of the powerful oxidants and strong capacity of disinfection and sterilization.

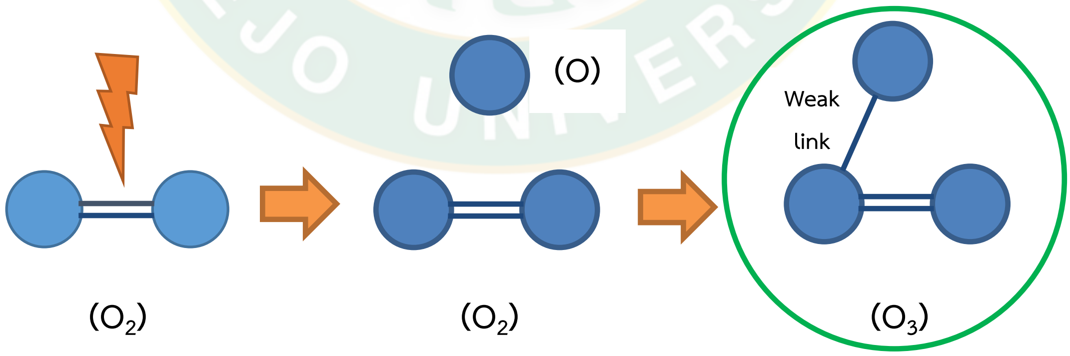


Figure 2 Mechanism of ozone generation.

Source: Gonçalves and Kechinski (2011)

2.2.1 Ozone properties

The disinfectants properties of ozone are superior to oxygen (Table 5). It is a powerful germicide which destroys bacteria and fungi. Other property of ozone is the capacity of absorption of flavors and strange smells in the water. Meanwhile, ozone has a deodorization role of the air. Ozone has a longer half-life in the gaseous state than in aqueous solution (Table 6). Ozone is unstable in pressure and temperature normal conditions. Ozone has been confirmed GRAS status as a food processing aid and is compliant with the Environmental Protection Agency Disinfection by Products Rule (Ong et al., 2014). In addition, ozone could be an acceptable technology to use marketed under "organic" classification (Gabler et al., 2010).

Table 5 Ozone vs. oxygen properties.

Property	Ozone	Oxygen
Molecular Formula	O_3	O_2
Molecular weight	48 $g.mol^{-1}$	32 $g.mol^{-1}$
Color	Light blue	colorless
Smell	Clothes after being outside on clothesline Photocopy machines, smell after lighting storms	odorless
Boiling Point	-111.3 °C	-183 °C
Density	2.141 $kg.m^{-3}$	1.429 $kg.m^{-3}$
Solubility in water (LO_3/LH_2O)	0.64 (190 mgL^{-1})	0.049 (14.6 mgL^{-1})

Source: Gonçalves and Kechinski (2011)

Table 6 Typical ozone half-life vary temperature.

Gaseous		Dissolved in water (pH7)	
Temp (°C)	**Half-life***	**Temp (°C)**	**Half-life***
-50	3 months	15	30 minutes
-35	18 days	20	20 minutes
-25	8 days	25	15 minutes
20	3 days	30	12 minutes
120	1.5 hours	35	8 minutes
250	1.5 seconds	-	-

* These values are based on thermal decomposition only. No wall effects, humidity, organic loading or other catalytic effects are considered.

Source: Gonçalves and Kechinski (2011)

The bactericidal effects of ozone have been studied on a variety of organisms, including gram positive and gram-negative bacteria as well as spores and vegetative cells. Ozone destruction of bacteria is accomplished by attack on the bacterial membrane glycoproteins and/or glycolipids. It oxidized and penetrates bacterial walls, including essential components such as enzymes proteins and DNA (Oner et al., 2011).

The required concentration and time ratio depend on the type of microorganisms, the grade of biological contamination, temperature, pH, turbidity and on the presence of ozone oxidizing substances. The presence of ozone oxidizing substances increases the ozone demand, and this can retard disinfection until the initial ozone demand has been satisfied. A high level of organic substances will have a negative impact on the disinfection rate.

Ozone is an irritate gas with poisonous effect for human. The ozone threshold concentration for continuous human exposure (8 h standard) is 0.075 μLL^{-1} (Gabler et al., 2010).

2.2.2 Ozone applications

Ozone is a powerful antimicrobial substance due to it is potential oxidizing capacity. Ozone use may have many advantages such as food industry application, cleaning-in-place (CIP) and sterilization-in-place (SIP), process water sterilization, and water recycling. For the food industry in applications of ozone include food surface hygiene, sanitation of food plant equipment, reuse of waste water, lowering biological oxygen demand (BOD) and chemical oxygen demand (COD) of food plant waste.

Ozone has been used in the food processing industry such as poultry, meat, seafood, dairy, fruit and vegetable, cereal and beverage. In addition, the application of ozone in the food storage has been applied in freezing chambers and warehouses etc.

In this case, ozone application will only refer to fruit and vegetable industry. Recently, concerns have been raised about the safety of fruits and vegetables for fresh agricultural product and in particular on the intervention methods to reduce and eliminate human pathogens from fresh product. Chlorine is the most widely used sanitizing agent available for fresh product, but it has a limited effect in killing bacteria on fruit and vegetable surfaces. Research and commercial applications have verified that ozone can replace traditional sanitizing agents and provide other benefits. Many research and industrial trials validate the use of ozone in the production industry.

Ozone has been evaluated for postharvest disease control and other storage uses for many years. Some commercial use has occurred with a few commodities such as apples, cherries, onions, carrots, tomato and papaya (Ong et al., 2012). There is increasing interest and empirical activity in the evaluation of ozone for a diversity of water treatment and air treatment uses in postharvest quality management. Examples include ethylene degradation, odor elimination for mixed storage, disinfection of humidification systems, eliminated fungal spore in storage room and treatment of superficial mold after long distance shipping. Ozone treatment has been reported to induce natural plant defense response compounds thought to be involved in postharvest disease resistance.

One way to maintain or even improve the safety of fresh product is to wash vegetables and fruits using ozonated water. Washing system had two types (spray and flume) can be used to reduce microbial counts on the surface of product.

Additional research is needed to define the potential and limits of effective use of ozone for postharvest treatment of whole and minimally processed vegetables and fruits. Minimally processed produce is commonly subject to limited cleaning and sanitizing prior to consumption. Besides, the mechanical damage after processing may cause an increase in respiration, surface dehydration, moisture loss and oxidative browning, and provide attachment sites and nutrients for microbial contamination and growth.

Besides the effectiveness in microorganisms, excessive use of ozone may change the surface color of fruits and vegetables such as peaches, strawberry, persimmon and tomatoes. If appropriate used, ozone can cause some effects on products, such as losses in eating quality. Treatment conditions should be specifically determined for all kinds of products for effective and safe use of ozone.

To prevent the potential contamination and extend the shelf-life of agricultural produce, various chemical treatments have been suggested. Among them, chlorine and associated compounds remain to be the most commonly used sanitizers. Ozone can be employed in cold storage of produce to against mold and bacteria at very low concentration ozone. It can not only destroy mold and bacteria in the air and on the surface of produce. Many studies used gaseous ozone to prevent microbial activity on food surfaces and extend the shelf-life of fruits and vegetables. Numerous experiments have been done on a wide variety of fruits and vegetables, including apples, potatoes, soybeans, strawberry, broccoli, mushrooms, pears, cranberries, oranges, peaches, grapes, corn, and tomatoes (Zambre et al., 2010).

One of the important effects of ozone in cold storage is to slow down the fruit and vegetable ripening process. During ripening, many fruits such as bananas and apples, release ethylene gas which activated the ripening process. Ozone is effective in removing ethylene through chemical reaction to extend shelf-life of fruits and vegetables (Gonçalves and Kechinski, 2011).

2.2.3 Advantages and disadvantages

- Advantages
  - Ozone can be generated on-site
  - Ozone is one of the most active, readily available oxidizing agents
  - Ozone rapidly decomposes to oxygen leaving no traces
  - Reactions do not produce toxic halogenated compounds
  - Ozone acts more rapidly, and more completely than other common disinfecting agents do
  - Ozone reacts swiftly and effectively on all strains of viruses
- Disadvantages
  - High cost compared with other oxidation/ disinfection techniques
  - Ozone is a potent oxidant and can reduce bacterial levels in pure culture, the use in food processing operations
  - This danger was recognized in the early stages of ozone research

2.2.4 Ozone manufacturing process

1) Ozone generation

The ozone production takes place generally by the ventilation of electrical discharges of high voltage in the air or pure oxygen. This radiation affects a common oxygen molecule that is found in atmosphere which produces the split of the molecule and separation of free oxygen atom. These atoms collide with other oxygen molecules, forming therefore ozone molecules.

- The energy absorbed by an oxygen molecule break it in two oxygen atoms.

$$O_2 + hv \longrightarrow O + O$$

- Each one of these atoms is joined to an oxygen molecule to give another one of ozone.

$$O + O_2 \longrightarrow O_3$$

- Finally, the ozone molecule is destroyed again absorbing more ultraviolet radiation.

$$O_3 + hv \longrightarrow O + O_2$$

- Ultraviolet energy is absorbed in a closed cycle of formation and destruction of the ozone

In order to generate ozone, a diatomic oxygen molecule must first be split. The resulting free radical oxygen is thereby free to react with other diatomic oxygen to form the triatomic ozone molecule. However, in order to break the O–O bond, a great deal of energy is required. Ultraviolet radiation (188 nm wave length) and corona discharge methods can be used to initiate free radical oxygen formation and, thereby generate ozone. In order to generate commercial levels of ozone, the corona discharge method is usually used.

1.1) Corona discharge

There are two electrodes in corona discharge, one of which is the high tension electrode and the other is the low tension electrode (ground electrode). These are separated by a ceramic dielectric medium and narrow discharge gap is provided (Figure 3). When the electrons have sufficient kinetic energy (around 6–7 eV) to dissociate the oxygen molecule, a certain fraction of these collisions occur and a molecule of ozone can be formed from each oxygen atom.

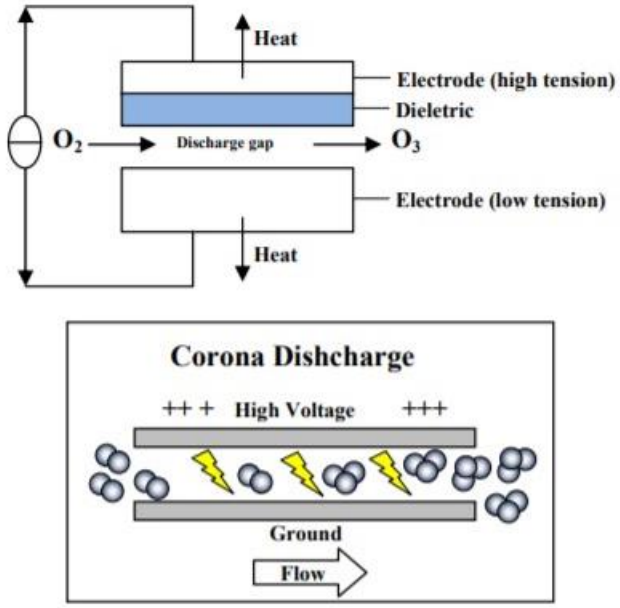


Figure 3 Scheme of corona discharge method.

Source: Gonçalves (2009)

In synthesis, electrical energy flowing across a narrow gap that is filled with oxygen splits the oxygen molecules into oxygen atoms (O). These atoms combine with other oxygen molecules (O_2) to form ozone (O_3), as illustrated in Figure 3. The unstable ozone gas quickly reverts back to molecular oxygen; thus, it cannot be stored in a container. If air is passed through the generator as a feed gas, a 1-4% of ozone can be produced. However, use of pure oxygen allows yields to reach to 16% ozone. Consequently, ozone concentration cannot be increased beyond the point that the rates of formation and destruction are equal. Ozone gas cannot be stored since ozone spontaneously degrades back to oxygen atoms. The advantage of corona discharge is: high ozone concentrations, best for water applications, fast organic (odor) removal and equipment can last for years without maintenance.

1.2) Ultraviolet radiation

The method is based on conversion of oxygen on ozone molecules by lamp of ultraviolet light (wavelength of 188 nm, Figure 4). Nevertheless, the ozone production is of low intensity. At low temperatures, the process of ozone ventilation is made with greater facility. The ozone formed, after certain period of time, is degraded spontaneously in oxygen. The advantages of UV light are: simple construction, lower cost than corona discharge, output hardly affected by humidity and fewer by-products vs. corona discharge.

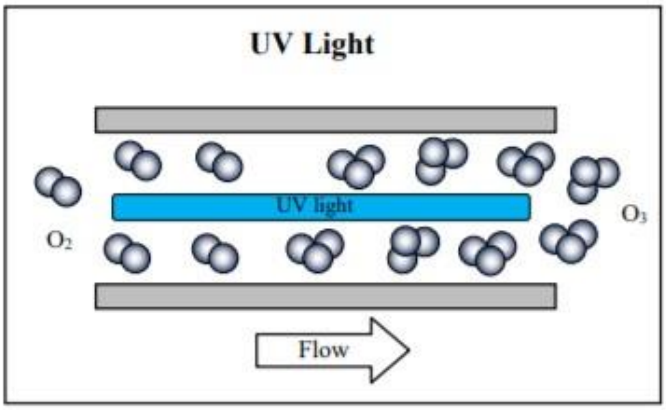


Figure 4 Ultra-violet lamp method.

Source: Gonçalves (2009)

1.3) Electrolytic

Electrolytic generation of ozone has historical importance because synthetic ozone was first discovered by Schönbein in 1840 by the electrolysis of sulfuric acid. The simplicity of the equipment can make this process attractive for small-scale users or users in remote areas. Many potential advantages are associated with electrolytic generation, including the use of low-voltage DC current, no feed gas preparation, reduced equipment size, possible generation of ozone at high concentrations, and generation in the water, eliminating the ozone-to-water contacting processes. Problems and drawbacks of the method include: corrosion and erosion of the electrodes, thermal overloading due to anodic over-voltage.

1.4) Radiochemical

High-energy irradiation of oxygen by radioactive rays can promote the formation of ozone. Even with the favorable thermodynamic yield of the process and the interesting use of waste fission isotopes, the cheminuclear ozone generation process has not yet become a significant application in water or waste water treatment due to its complicated process requirements.

2) Corrosion and degradation of materials

Table 7 Ozone compatibility with surfaces of material.

Material	Compatibility	Material	Compatibility
304 stainless steel	B-Good	Kalrez	A- Excellent
316 stainless steel	A- Excellent	Kel-Fr	A- Excellent
ABS plastic	B-Good	LDPE	C-Fair
Acetal (Delrinr)	C-Fair	Natural rubber	D-Severe effect
Aluminum	B-Good	Neoprene	C-Fair
Bronze	B-Good	Nylon	D-Severe effect
Buna N (Nitrile)	D-Severe effect	Polycarbonate	A- Excellent
Carbon Steel	C-Fair	Polyetherether-Ketone (PEEK)	A- Excellent
ChemRaz (FFKM)	B-Good	Polypropylene	B-Good
Copper	A- Excellent	Polyurethane	A- Excellent
CPVC	A- Excellent	PTFE	A- Excellent
EPDM	A- Excellent	PVC	B-Good
Fluorocarbon (FKM)	A- Excellent	PVDF(Kynar®)	A- Excellent
Hypalonr	A- Excellent	Silicone	A- Excellent
Hytrelr	C-Fair	Viton	A- Excellent

Ratings = Chemical Effect

A = Excellent.

B = Good: Minor Effect, slight corrosion or discoloration.

C = Fair: Moderate Effect, not recommended for continuous use. Softening, loss of strength, swelling may occur.

D = Severe: Effect, not recommended for ANY use.

Source: Gonçalves (2009)

The power of ozone as an oxidant requires careful selection of construction material in design to provide a facility that is resistant to the attacks of gas-phase ozone and ozone dissolved in the liquid being treated (Table 7). Much of the information is basically rule-of-thumb, but there are several published papers on the subject. Operational experience in U.S. installations has provided information that provides design guidance for the various components of an ozonation facility.

When the gas preparation system is from air feed gas, the material selection process should include materials that would be used for conventional compression, drying, and conveyance for ambient air. Carbon steel, cast iron, aluminum, conventional gasketing, and piping coupling techniques are all acceptable for the air preparation system to a point prior to the ozone generators may backflow or migrate upstream of the generators with deleterious effect on that portion of the gas preparation system.

3) Residual ozone destruction

If the contact with reactor vessel is not pressurized as is the cases for most bubble diffuser system, a blower will need to be fitted onto the ozone destroyer to pull a slight vacuum to draw the vent gas into the destroyer. If a degas tank is being employed, as in a side stream injection system, these tanks normally operate under pressure and there should be sufficient pressure to push the vent gas through the ozone destroyer system.

3.1) Thermal

Ozone decomposes spontaneously at elevated temperature to oxygen. Thermal ozone destroyers simply heat the vent gas to the necessary temperature. The systems are the simplest and least expensive on a capital cost basis. They do use more energy than other systems so they are usually only applied to relatively small ozone water treatment systems. Essentially all of the gas that passes through the contact/ reaction vessel must be heated to the decomposition temperature (gas from the ozone generator, water vapor from the reactor vessel and any air that leaks into the contact tank).

3.2) Thermal catalytic

In the presence of a catalyst the temperature needed to decompose ozone is greatly reduced. This reduces the energy required to for the ozone destruct system. However, the capital cost for the catalyst base system is higher than for a pure thermal system. The additional capital cost is easily paid for as the size of the system increases. The catalyst is almost always manganese dioxide. Activated carbon can decompose ozone, but it also burns, so it is not used for this purpose.

3.3) Heat recovery systems

Another way to reduce energy cost in a thermal based ozone destroyer is to heat the incoming vent gas with the treated vent gas. This recapture a portion of the energy used to heat the vent gas and reduces overall energy consumption. These systems are only employed on the largest ozone water treatment systems.

2.2.5 Food industry application

Ozone is a powerful antimicrobial substance due to the its potential oxidizing capacity. Ozone use may have many advantages in the food industry. There are suggested applications of ozone in the food industry such as food surface hygiene, sanitation of food plant equipment, reuse of wastewater, lowering biological oxygen demand (BOD) and chemical oxygen demand (COD) of food plant waste.

Ozone has been shown to deactivate a large number of organisms, including bacteria, fungi, yeast, parasites and viruses, and can also oxidize natural organic compounds as well as synthetic substances, such as detergents, herbicides and composite pesticides. Ozone has been used in the food processing industry, both as gaseous ozone and dissolved in water to reduce bacteria on a wide range of food products and contact surfaces.

The application of ozone in the food storage has been applied in freezing chambers and warehouses (meats, seafood, fruits, vegetables, cheeses, sausages, etc.). The main objective is to reduce the bacteriological index that occur in the mentioned storage systems, obtain greater durability of foods (in refrigeration, freezing or fresh storage) and eliminating bacteria to not allow to growth in meats or others, formation of mold etc.

1) Poultry industry

Ozone has been tested for disinfecting hatchery, hatching eggs, poultry chiller, poultry carcass, broiler, contaminated eggs and surface equipment. The poultry processing industry is critically challenged by competitive economic pressures, food safety and quality issues, and environmental constrains major ones being excessive use and pollution of water. Poultry processors are one of the largest water users in the food industry. Poultry is chilled primarily to reduce the microbial growth rate in order to extend shelf-life and most poultry processed is chilled by immersion using crushed ice and water or chilled water in largest-in-less steel tanks. These tanks are generally designed to mechanically agitate the carcasses and provide counter-current chill water flow. Chilling can be a point where cross contamination between carcasses occurs and as a result of legislative actions, there is a need for identifying suitable disinfectants and water treatment methods for treating poultry chiller water. Ozone appears to be a suitable candidate since ozone is a powerful oxidizing agent that has been used to disinfect, to remove color, odor, and turbidity, and to reduce the organic loads of European wastewater treatment plants.

2) Red meat

Meat is a rich nutrient matrix that provides a suitable environment for proliferation of meat spoilage microorganisms and common food-borne pathogens, therefore adequate preservation technologies must be applied in order to preserve its safety and quality. Food safety is a top priority for authorities and customers worldwide. Moreover, customer demands high quality, convenient, innovative, regular and safe meat products with natural flavor, taste and extended shelf-life. An estimated 30% of fresh produce is lost by microbial spoilage from the time of harvest, through handling, storage, processing, transportation, shelving and delivery to the customer. In order to preserve food, it is necessary for pathogens to be destroyed or inactivated and nonpathogenic microorganisms and enzymes responsible for food spoilage need to be eliminated or at least reduced. The feasibility of using ozone in meat processing has been the focus of several studied, example; the use of ozone in ground beef production process can be effective for reducing microbial pathogens with minimal effects on color or odor characteristics and tested in the process of tenderizing meats to control surface microflora.

3) Seafood industry

In the seafood industry, ozone was tested to disinfect seafood products and to improve sensory qualities. It is well known that molecular ozone and its decomposition products destroy microorganisms due to their effects on microbial intracellular enzymes, nucleic acids and other cell components. In contrast to these positive effects, the possible pro-oxidant effect of ozone on fish constituents has not been extensively studied up to now. In addition, with ozone product obtained is with better sensory aspect and presentation, preventing the formation of mold and putrefaction. Also, a deodorization of cameras is obtained, with the consequent advantage for the maintenance. The most advisable concentration is from 2.5 to 3 ppm between 1 to 3 °C and with relative humidity of 90%. A higher concentration would oxidize fats, producing disagreeable smells. During the freezing process, a concentration from 2 to 3 mg/l is recommended, but 1 ppm is sufficient for the freezing maintenance. A very effective method has been obtained is the intermittent ozonization.

4) Dairy industry

For dairy industry, it is illustrated studies on the effects of ozone for controlling molds on cheddar cheese. Ozone gives the appearance of destroying heavy mold growth and retards the growth of mold and preventing mold from developing on the ends. The sides of the washed cheese are protected from mold growth while mold continued to grow on the ends. Free mold spores is reduced in numbers in the ozone-treated rooms. The use of ozone did not cause any flavor defects in the cheese. Other experiments conducted on cheddar cheese also indicated that the oxidizing action of ozone removes odors otherwise present in storage rooms.

5) Fruit and vegetable industry

Recently, great concerns are raised about the safety of fruits and vegetables for fresh agricultural produces and in particular on the intervention methods to reduce and eliminate human pathogens from fresh produce. Chlorine is the most widely used sanitizing agent available for fresh produce, but it has a limited effect in killing bacteria on fruit and vegetable surfaces. The environmental and health communities have expressed concerns about the residual by-products of chlorine. An alternative treatment is being sought to improve food safety. Research and commercial applications have verified that ozone can replace traditional sanitizing agents and provide other benefits.

Ozone has been evaluated for postharvest disease control and other storage uses for many years. Some commercial uses have occurred with a few commodities such as apples, cherries, carrots, onions, and potatoes. There is increasing interest and empirical activity in the evaluation of ozone for a diversity of water treatment and air treatment uses in postharvest quality management. Examples include ethylene degradation (within a confined reactor), odor elimination for mixed storage, disinfection of humidification systems (including retail super markets), fungal spore elimination in storage room aerosols, and treatment of superficial mold after long-distance shipping of onions. Both effective disease control and phyotoxicity of ozonated air on certain cultivars was reported for table grapes and carrots (bleaching). Ozone treatment has been reported to induce natural plant defense response compounds thought to be involved in postharvest disease resistance. Additional research is needed to define the potential and limits of effective use of ozone for postharvest treatment of whole and minimally processed vegetables and fruits. Minimally processed produce is commonly subject to very limited cleaning and sanitizing prior to consumption. Besides, the mechanical damage after processing may cause an increase in respiration, surface dehydration, moisture loss and oxidative browning, and provide attachment sites and nutrients for microbial contamination and growth.

Besides the effectiveness in microorganisms, excessive use of ozone may change the surface color of some fruits and vegetables. Also, spontaneous decomposition without forming hazardous residues in the treatment medium makes ozone safe in fruits and vegetables. If improperly used, ozone can cause some deleterious effects on products, such as losses in sensory quality. Treatment conditions should be specifically determined for all kinds of products for effective and safe use of ozone. To prevent the potential contamination and extend the shelf-life of agricultural produce, various chemical treatments have been suggested. Among them, chlorine and associated compounds remain to be the most commonly used sanitizers.

Ozone can be employed in cold storage of produce to guard against mold and bacteria at a very low concentration. It can not only destroy mold and bacteria in the air and on the surface of produce but also deodorize. Many early studies used gaseous ozone to prevent microbial activity on food surfaces and extend the shelf-life of fruits and vegetables. One of the important effects of ozone in cold storage is to slow down the fruit and vegetable ripening process. During ripening, many fruits, such as bananas and apples, release ethylene gas, which speeds up the ripening process. Ozone is very effective in removing ethylene through chemical reaction to extend the storage life of many fruits and vegetables.

6) Cereal industry

Ozone treatment of grain is generally applied in silos or vessels. Prior to ozone application, it is necessary to characterize the dynamics of ozone movement through the various grain types to optimize ozone generators for use on large commercial storage bins. Ozone moves through grain slowly because the gas reacts with the chemical constituents present in the outer layer of grain (seed coat). Diffusion of ozone into the grain depends upon the grain characteristics. Adsorption of ozone and subsequent penetration into the grain depends upon several intrinsic and extrinsic factors such as surface characteristics of the grain, microbial contamination, presence of insects and moisture content etc. Ozone adsorption in the grain layer depends on ozone concentration in the feed gas, duration of exposure, gas flow rate, temperature, grain characteristics and the presence of other organic matter such as insects and surface microbial status of the grain. Presence of moisture also plays an important role in ozone reactivity with grain because water solubilizes ozone and increase contact between gas and grain. Within the grain processing industry, ozone is employed as a replacement for the existing fumigants such as methyl bromide and phosphine for the control of storage pests. Ozone in gaseous or aqueous form is reported to reduce levels of the natural microflora, as well as bacterial, fungal and mold contamination in cereals and cereal products, including spores of *Bacillus, Coliform* bacteria, *Micrococcus, Flavobacterium, Alcaligenes, Serratia, Aspergillus* and *Penicillium*. Micro-organisms which are present in food grains either on their surface or internally, deteriorate the nutritional quality of the products and also produce metabolites which are dangerous to human and animal health.

2.3 Background of packaging

Food packaging is defined as food system preparation for transport, distribution, storage, retailing, end-use to satisfy the consumer, protect or preserve quality and extend shelf-life product. Moreover, the current consumer demand for convenient and high quality food products has increased the impact of food packaging.

2.3.1 Packaging systems

We can divide packaging systems into 4 types (Shin and Selke, 2014):

1) Primary packaging

Primary package is the first level package that directly contacts the product. It must be non-toxic, safety and contactable with food. It should not cause any changes in food quality such as color changes, undesired odor, taste and flavor etc.

2) Secondary packaging

The secondary package has two or more primary packages and protects the primary packages from collapse and damage during storage or shipment. Secondary packages are also used to prevent dirt and contaminants.

3) Tertiary package

The tertiary package or distribution package is the shipping container, which contains of the primary or secondary packages. Its main function is to protect the product during distribution and to provide for efficient handling.

4) Unit load

A unit load is a group of tertiary packages assembled into a single unit. The objective is to aid in the automated handling of larger amounts of product.

2.3.2 The packaging system with fruit and vegetables

Maintaining the right temperature, gas mix and moisture in the packaging are important elements to create an efficient extension of the shelf-life for fruit and vegetables. If fruit and vegetables are kept in airtight packaging or another closed container with atmospheric air (20.9% oxygen, 78.1% nitrogen and 0.04 % carbon dioxide) the oxygen will be converted into carbon dioxide due to respiration (Figure 5).

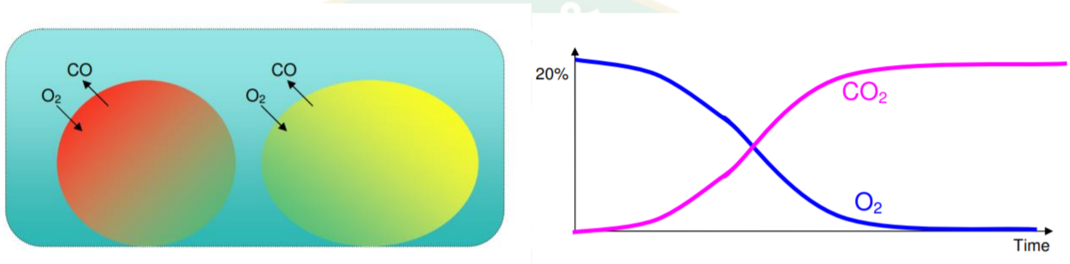


Figure 5 The oxygen and carbon dioxide in packaging with fruit and vegetables

Source: DanishTechnological (2008)

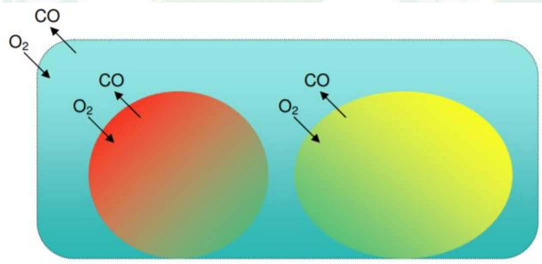


Figure 6 The respiration rate in packaging with fruit and vegetables.

Source: Denish Technological (2008)

The respiration rate or the rate by which the oxygen is converted into carbon dioxide depends on the oxygen concentration. At low oxygen concentrations the respiration usually takes place slower than at high oxygen concentrations. This means that at low oxygen concentrations the ageing process takes place slower, and that the shelf-life is extended. If the oxygen contents become very low, the product cannot breathe. Consequently, the product dies and becomes worthless (Figure 6).

Packaging film for fruit and vegetables are never quite impervious to oxygen, carbon dioxide and water vapors. Even though the packaging film is welded quite tight, these gasses will be transported through the film (dissolved on the one side and liberated on the other). The rate depends on the type of plastic, the thickness of the film and the area, temperature and pressure differences of the gasses on each side of the film. To obtain a sufficient mechanical strength of the packaging, a certain thickness of the packaging is necessary. For quick/ rapid respiring/breathing products it is impossible to make films so thin that the permeability (the transport of gas) becomes high enough to prevent a lack of oxygen inside the packaging. If the product consumes the oxygen in the packaging faster than new oxygen is supplied, the oxygen concentration in the packaging will become so low that the product dies.

2.3.3 Packaging requirements for fresh produce

Packaging must be appropriately designed to maintain the quality and prolong the shelf-life of fresh produce. Fresh produce packaging must (FAO, 2011):

- be resistant to low temperature storage
- be resistant to water damage resulting from produce cooling
- be semi-moisture-proof to minimize weight loss and shrinkage of produce during marketing
- be strong enough to protect produce from mechanical damage during distribution
- be able to hold produce in place to prevent abrasion or impact of adjacent produce within the package
- permit ventilation to dissipate heat resulting from produce respiration
- have good gas permeability to avoid the risk of metabolic processes which may occur in the absence of oxygen (anaerobiosis), except in the case of modified atmosphere packaging, of which a degree of gas barrier may be essential
- be biologically and chemically safe as food contact materials

- be compatible with handling and transport equipment – facilitating the use of new modes of transportation, e.g. air transportation of light fibreboard boxes designed in rectangular shapes for efficient area utilization
- provide convenience to consumers during marketing and consumption

2.3.4 Materials and formats for fresh produce packaging

Fresh produce in Thailand ranges from the delicate mangoes to the armoured durian. Each item of fresh produce has its own specific characteristics, and thus has specific packaging requirements. A variety of options are available for the packaging of fresh produce (FAO, 2011).

1) Bulk packaging

Design features of bulk packages include strength, stacking ability, ease of handling and space utilization. Several types of fresh produce bulk packaging are used in Thailand. These include plastic crates, corrugated fibreboard boxes and bamboo baskets. Results of the current survey show that that plastic crates are by far the most widely used form of bulk packaging (Figure 7).

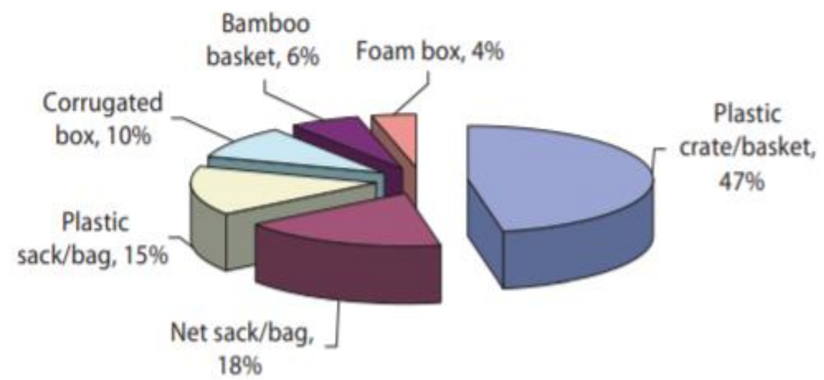


Figure 7 Different types of bulk packaging in wholesale markets of Thailand.

Source: FAO (2011)

Trapezoid plastic crates equipped with steel handles are the most commonly used types of plastic crates in Thailand. Their trapezoid shape allows empty crates to be stored in nested stacks. Large retailers and exporters also make use of round and rectangular nestable plastic crates for the bulk packaging of fresh produce. Solid plastic boxes are used for some produce types but their use in not common. Plastic bags/pouches/sacks are popularly used as packaging for fresh produce, given the convenience they offer in handling and sale. Woven/net plastic sacks are used for produce types that require high levels of ventilation.

Corrugated boxes are commonly used for the packaging of fresh produce destined for export. Solid fibreboard trays and boxes are less popularly use as a bulk packaging option in Thailand when compared to corrugated boxes owing to their comparably higher cost than corrugated boxes. The use of solid fibreboard trays and boxes is generally limited to filling orders from international markets in Europe and North America. Such packing materials are generally imported. Other types of bulk packaging materials used include bamboo baskets and foam boxes.

2) Retail packaging

Retail packaging for fresh produce is available in a range of formats. The selection and use of retail packaging in fresh produce supply chains involves consideration of consumer behavior and social marketing. The selection of a particular type of retail packaging varies according to the target market for the produce. Individual units of packaging are designed to suit specific portions for consumption usually for an individual household before the produce deteriorates. Commonly used retail packaging formats for fresh produce in Thailand can be categorized as: bags or pouches, trays, boxes, cases, cartons and netting or banding.

2.1) Bags, pouches and film wrap

Bags or pouches are generally produced from plastic and paper. The most commonly used form of retail packaging for fresh produce in Thailand is the plastic bag or pouch. Plastic bags and pouches can be used for almost all types of produce and for almost all purposes. In most cases, clear films are used for retail packaging in order to allow consumers to see the produce inside the package, given that appearance is a key quality criterion for the selection of produce by consumers. Bags used for fresh produce packaging in Thailand are commonly made from polyethylene (PE), polypropylene (PP) or polyvinyl chloride (PVC). PE and PP bags (Figure 8) can be easily manufactured at low cost, but lack clarity. Polyvinyl chloride bags are clear but are not considered to be environmentally friendly. Some bags are made from bubble wrapping materials to protect produce from physical damage.

Figure 8 Produce packed in PE and PP bags that are sealed using different methods.

Source: FAO (2011)

2.2) Trays

The semi rigidity of trays offers key benefits including protection and convenience for ready-to eat or ready-to-serve purposes. Trays are usually made from plastic, plastic foam, pulp or paper by a thermoforming process (Figure 9). Plastic trays that are commonly used for fresh produce packaging are made from PE, PP, PET and PS. While popular in the North American and European markets owing to its clarity, PET it is not widely used in Thailand owing to its high cost. Trays can be custom designed for specific applications into a variety of sizes and shapes: rectangular, square and round. Different methods can be used for closure of the packages, such as overwrapping with film, heat-sealed film lids or heat-sealed bags. In the past, trays were closed with wire staples or tape. Wire staples, however, pose a risk to consumers and are no longer used as large retailers are now aware of the risks. The use of tape for sealing is still common in retail markets.

Figure 9 Tray overwrapped with film.

Source: FAO (2011)

Overwrapping is the most common type of produce packaging used in Thailand. The most commonly used overwrap films include PE, LLDPE and PVC. Heat sealing is not as common as overwrapping because it is more costly and complex. Tray heat sealing requires heat sealable materials and additional items of equipment. In recent times, black colored trays have been introduced to the retail packaging of produce, in order to enhance product appeal to consumers.

Foam trays continue to be widely used in Thailand despite the fact that they are not considered environmentally friendly. Their widespread use is largely due to their low cost when compared to other packaging materials. The use of foam trays in supermarkets and superstores has, however, markedly declined since 2009. Plastic foam trays have been slowly replaced with paper trays or mold pulp trays in the past few years owing to increasing consumer awareness of environmental issues in Thailand. The increased demand for paper trays has resulted in a reduction in their prices. Foam and paper trays are generally closed using film overwrapping.

2.3) Boxes, cases and cartons

Retail boxes are produced using either paperboard or plastic, the former being more common. Due to the moisture sensitivity of paperboard it must be coated or laminated with a polymer in order to improve its moisture barrier properties. Retail paperboard boxes are primarily of a full telescope design (FTD). The retail box is used primarily for specialty items– items that are expensive or delicate such as gift packs for strawberries, cherries and mandarin oranges (tangerines). Graphics on retail packages play a key role in the marketing of the product. Retail boxes of packed produce may contain a clear film window for produce display and visibility.

2.4) Net bags

The main advantages of packing produce in nets are ventilation and display. Produce items such as onions and garlic are generally packaged in net bags. Plastic netting is lightweight making it ideal for packing light weight or small units of produce. Plastic foam nets can also be used for cushioning. Plastic netting serves as a popular form of retail packaging for fruits such as tangerines and oranges.

2.5) Bundling

Plastic bands and plastic-covered wire ties are most commonly used to unitize leafy vegetables such as cilantro, parsley and green onions. Vegetable bundles are generally displayed in chilling cabinets in supermarkets where they are routinely sprayed with water to minimize water loss and to refresh the produce. Produce can be bundled in different ways. The most common examples of fruit bundling in Thailand include tying rambutan and longan stalks with rubber bands and using bundling tape to bind a whole banana bunch. Bundled fruits are generally displayed in baskets at both low- and high-end retail markets. Different applications of bundling.

2.6) Comparisons between types of retail packaging

A packaging system is composed of fresh produce and one or more packaging types (primary, secondary, tertiary and quaternary) as previously described. Findings of this survey indicate that different packaging systems are used for different types of fresh produce in Thailand. Survey results of the retail packaging formats of the top ten fruits and vegetables with the highest export values from Thailand in 2009 are summarized in Table 8 and Table 9 respectively.

Table 8 Retail packaging formats of Thai fruits in export value in 2009.

No	Fruit	Volume (ton)	Value (million baht)	Common retail packaging (supermarket/superstore)
1	Pineapple	803,576	25,989.586	Basket/crate display (with or without foam net)
2	Longan	286,328	5,051.021	Basket/crate display (without foam net)
				Plastic bag (perforated)
				Plastic bag (non-perforated)
3	Durian	222,559	3,824.230	Basket/crate display (without foam net)
4	Mango	36,334	1,428.740	Basket/crate display (with or without foam net)
				Tray with film overwrapping
5	Mangosteen	44,268	743.954	Basket/crate display (without foam net)
				Plastic bag (perforated)
				Plastic bag (non-perforated)
				Tray with film overwrapping
6	Tangerine	28,718	590.608	Basket/crate display (with or without foam net)
				Net sack/bag
				Plastic bag (non-perforated)
				Tray packed in net bag
7	Banana	22,904	402.854	Basket/crate display (without foam net)
				Plastic bag (perforated)
				Plastic bag (non-perforated)
				Bubble wrapping bag
				Tray with film overwrapping
8	Litchi	13,491	513.590	Basket/crate display (without foam net)
				Plastic bag (perforated)
				Plastic bag (non-perforated)
9	Rambutan	6,886	126.842	Basket/crate display (without foam net)
				Plastic bag (perforated)
				Plastic bag (non-perforated)
				Tray with film overwrapping
				Bundling tape/rubber band
10	Papaya	3,458	111.885	Basket/crate display (with or without foam net)
				Film overwrapping

Source: FAO (2011)

Table 9 Retail packaging formats of Thai vegetables in export value in 2009.

No	Vegetable	Volume (ton)	Value (million baht)	Common retail packaging (supermarket/superstore)
1	Sweet corn	356,481.483	5,191.311	Tray with film overwrapping Plastic bag (perforated) Plastic bag (non-perforated) Film overwrapping
2	Baby corn	48,614.891	1,556.926	Tray with film overwrapping Plastic bag (perforated) Plastic bag (non-perforated)
3	Onion	39,346.635	390.089	Basket/crate display Net sack/bag Plastic bag (perforated) Tray with film overwrapping
4	Ginger	39,136.549	865.732	Basket/crate display Tray with film overwrapping
5	Chili	24,757.244	1,278.415	Tray with film overwrapping Plastic bag (perforated)
6	Red onion	21,944.370	158.265	Basket/crate display Net sack/bag Tray with film overwrapping
7	Asparagus	13,604.885	804.392	Bundling tape Tray with film overwrapping Plastic bag (perforated) Plastic bag (non-perforated)
8	Tomato	8,865.915	316.411	Tray with film overwrapping Plastic bag (perforated) Plastic clamshell tray
9	Garlic	2,800.653	26.126	Basket/crate display Net sack/bag Plastic bag (perforated)
10	Pepper	2,447.100	82.895	Tray with film overwrapping Plastic bag (non-perforated)

Source: FAO (2011)

3) Unitizing/ palletizing

A unit load refers to a combination of small units/packages into one unit for efficient handling, storage and distribution. Unitizing usually involves placing shipping containers on a pallet. Pallets play an important role in unitizing, distributing and protecting produce. Pallets are primarily made of wood, although some are made from plastic, paper and metal. Various types and sizes of pallets (Figure 10) exist. No global standardized pallet size has been established although there have been attempts to do so. Pallet pooling and exchange systems have been developed to facilitate efficient logistics. Pallet pooling is growing and expanding in many regions in response to global trading.

Figure 10 Stacking packaged produce with and without pallets

Source: FAO (2011)

2.3.4 Types of plastics and general properties

Materials of food packaging are essential to physical damage to product in order to obtain optimal shelf-life. The common form of packaging is the fiberboard carton, tissue paper, wraps, trays or cup. In this research, we want to maintain quality and extend shelf-life of fruits. Most the material packaging use in fruits is plastics.

Plastics are a group of polymers that can be formed into a variety of shapes using control heat and pressure at low temperatures. Each plastic has unique properties based on chemical composition. Thus, plastic for the packaging of a specific fruits are selected to function of the application.

Table 10 Gas permeability and water transmission rate (WTR) of polymeric film

Film	Permeability (cm^3/m^2 d atm) for 25 µm film at 25 °C			WTR (g/m^2/day/atm) at 38 °C, 90% RH
	O_2	N_2	CO_2	
Ethylene-vinyl alcohol (EVAL)	3-5	-	-	16-18
PVdC–PVC copolymer (Saran)	9-15	-	20-30	-
Low-density polythene (PE- LD)	7,800	2,800	42,000	18
High-density polyethylene (PEHD)	2,600	650	7600	7-10
Polypropylene cast (PPcast)	3700	680	10,000	10-12
Polypropylene, oriented (OPP)	2,000	400	8,000	6-7
Polypropylene, oriented, PVdC Coated (OPP/ PVdC)	10-20	8-13	35-50	4-5
Rigid poly (vinyl chloride) PVC	150-350	60-150	450-1,000	30-40
Plasticized poly (vinyl chloride) (PVC-P)	500-30,000	300-10,000	1,500-46,000	15-40
Ethylene - vinyl acetate (EVAC)	12,500	4,900	50,000	40-60
Polystyrene, oriented (OPS)	5,000	800	18,000	100-125
Polyurethane (PUR)	800-1,500	600-1,200	7,000-25,000	400-600
PVdC–PVC copolymer (Saran)	8-25	2-2.6	50-150	1.5-5.0
Polyamide (Nylon-6), (PA)	40	14	150-190	84-3,100

Source: Mario et al. (2010)

Plastics or film should have permeability high gas and anti-fog properties (Table 10) when required extended shelf-life for fruits. The packaging of fresh fruit provides use of polyethylene (PE) and polypropylene (PP) bags because of low water vapor permeability (Mario et al., 2010).

1) Polyethylene (PE)

The plastic most commonly used for food packaging is polyethylene, polymerized from ethylene. PE generally has flexibility, good moisture control, oil and chemical resistance, and good impact strength. The simplest form of PE is a completely unbranched structure of –CH2– units (Figure 11).

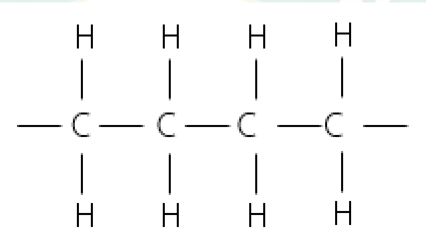


Figure 11 Chemical structure of polyethylene

Source: Carraher (2013)

The branches are few and short (2–4 carbon atoms), the structure can fold and pack tightly and yields call high-density polyethylene (HDPE). HDPE has good oil and grease resistance. It is barrier to oxygen and carbon dioxide though improved over LDPE. The improved stiffness of HDPE makes it suitable for rigid or semi-rigid package applications, such as bottles, tubs, and trays.

Conversely, if there are many long branches, PE becomes low-density polyethylene (LDPE). LDPE is softer and more flexible, and has lower tensile strength than HDPE. LDPE has a low melting temperature, it is a useful material for heat sealing. LDPE also has good impact and tear strength. Applications for LDPE include stretch wraps, shrink wraps, and many types of bags and pouches.

Linear LDPE (LLDPE) is a co-polymer of ethylene and a co-monomer that has short branches of a uniform length, distributed randomly in the polymer molecule. LLDPE has a higher melting temperature and does not heat seal as well as LDPE (Shin and Selke, 2014).

2) Polypropylene (PP)

Polypropylene is polymerized from propylene gas. PP has good chemical and grease resistance. Barrier properties of PP are a good water vapor barrier but a poor gas barrier. The polypropylene structure includes methyl groups (–CH3) attached to every other carbon in the polymer main chain (Figure 12); PP has a lower density and a higher temperature (glass transition and melting) than PE. PP is suitable for products that require moderately high temperatures such as hot filling or reheating in a microwave oven.

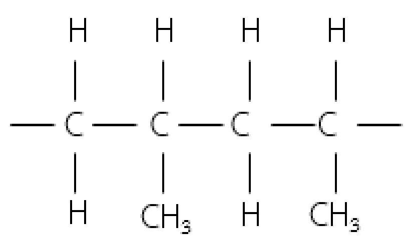


Figure 12 Chemical structure of polypropylene

Source: Carraher (2003)

The oriented polypropylene (OPP) film has use rapidly increased in food packaging applications. OPP film has improved mechanical strength and water barrier properties compared to unoriented (cast) film, but it is not suited for gas barrier properties. (Shin and Selke, 2014).

2.4 Reaction kinetics

2.4.1 Reactions in foods that affect quality

Quality indicators are not constant: the quality of a food changes over time. The most important quality-related changes are (Boekel, 2008):

- Chemical reactions: mainly due to either oxidation or Maillard reactions.
- Microbial reactions: microorganisms can grow in foods; in the case of fermentation this is desired, otherwise microbial growth will lead to spoilage and, in the case of pathogens, to unsafe food.
- Biochemical reactions: many foods contain endogenous enzymes that can potentially catalyze reactions leading to quality loss (enzymatic browning, lipolysis, proteolysis, and more). In the case of fermentation, enzymes can be exploited to improve quality.
- Physical reactions: many foods are heterogeneous and contain particles. These particles are unstable, in principle at least, and phenomena such as coalescence, aggregation, and sedimentation lead usually to quality loss. Also, changes in texture can be considered as physical reactions, though the underlying mechanism may be of a chemical nature.

Table 11 gives an overview of the most important reactions in foods. Another way to look at reactivity and consequences for quality is to look at the various ways in which the main components in foods can react (Table 12). These tables indicate that quality indicators may be affected in many ways. When models are proposed, one should be aware of possible interactions. In many cases, model parameters will in fact embed all kinds of confounding factors.

Table 11 Overview of reactions in foods affecting quality.

Example	Type	Consequences
Nonenzymatic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids, rancid taste
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture
Enzymatic browning	Biochemical reaction of polyphenols	Browning
Separation	Physical reaction	Sedimentation, creaming
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes

Source: Boekel (2008)

Table 12 Reactions of key components in foods.

Component	Reaction	Consequences
Proteins	Denaturation	Gelation, precipitation, solubility, inactivation of antinutritional factors (ANFs)
	Hydrolysis	Formation of peptides and amino acids, texture changes
	Deamidation	Loss of charge and change in reactivity
	Maillard reaction	Crosslinking, loss of nutritional value, browning
Lipids	Oxidation	Loss of essential fatty acids, rancidity
	Fat hardening	Formation of trans fatty acids
	Hydrolysis (usually enzymatically)	Formation of free fatty acids, leading to a soapy off-flavor
Mono- and disaccharides	Maillard reaction	Nonenzymatic browning
	Caramelization	Taste and flavor changes
	Hydrolysis	Sugar inversion
Polysaccharides	Hydrolysis (enzymatically during ripening, chemically during cooking)	Softening of tissue, texture changes
	Physical interaction with other components	Gelation, phase separation
	Gelatinization and retrogradation of starch	Staling of bread
Polyphenols	Enzymatic polymerization	Browning
	Interaction with proteins	Crosslinking, gelation
Vitamins	Oxidation Loss	Loss of nutritional value

Source: Boekel (2008)

2.4.2 Kinetic modeling of food quality attributes

Kinetic modeling implies that changes can be captured in mathematical models containing characteristic kinetic parameters, such as activation energies and rate constants. Modeling in science can serve 3 goals: understanding, prediction, and control. As for understanding, modeling is a tool in applying the scientific method, and in that sensed it can contribute to our understanding of the chemistry and physics taking place in the studied food. If this is the intention of kinetic modeling, it makes sense to make a link to the thermodynamics and chemical kinetics. This will then yield insight in the mechanisms of reactions at the molecular level and results in fundamental kinetic parameters such as activation energies, enthalpies, and entropies. Thus, kinetic modeling of changes in foods can lead to a better understanding at the molecular level of what we observe in foods. One of the ways to get around this problem in food science is that simplified model systems are used rather than real foods. As for the prediction and control purposes of modeling, this serves more an engineering goal.

The goal of fundamental and empirical models alike is to state something quantitatively. Mathematical models consist of equations that provide an output (such as vitamin content) based on a set of input data (for example, time, temperature). It is a concise way to express physical behavior in mathematical terms (Boekel, 2008).

As argued previously, modeling food quality attributes means modeling changes: the quality of a food nearly always changes over time. Food quality modeling is therefore almost synonymous with kinetic modeling. The consequence is that differential equations frequently form the basis for mathematical models; these can sometimes be solved analytically, but if not, it is relatively easy nowadays to solve them numerically with the available software, or even using spreadsheets. We will describe only chemical reaction and physical reaction because it related with this experiment.

1) Modelling chemical reaction

Reaction kinetics is defined as the study of the rates of chemical reactions and their mechanisms. Reaction rate is simply defined as a change in a measurable quantity divided by the change in time. There are several types of kinetic reaction as follows:

- Zero-order reaction
- First-order reaction
- Second order reaction

1.1) Zero–order reactions

For a zero-order reaction, the integrated rate law shows a straight line corresponding to equation (1).

$$[A] = [A]_0 - kt \quad (1)$$

Where

$[A]_0$ = the initial concentration of A, at time = 0

$[A]$ = the concentration of A, at time

t = Process time

Equation 1 has the form of the algebraic equation for a straight line, y = mx + b, with y = [A], mx = $-kt$, and b = $[A]_0$). The rate constant (k) of a zeroth-order reaction must have the same units as the reaction rate.

1.2) First-order reaction

For the first-order reaction, the reaction rate depends on the concentration of one of the reactants. The integrated rate law for a first-order reaction could be shown in two different equations, exponential equation and logarithm equation. The exponential equation is showed as equation (2).

$$[A] = [A]_0 \, e^{-kt} \quad (2)$$

Where

$[A]_0$	=	the initial concentration of A, at time = 0
$[A]$	=	the concentration of A, at time
t	=	Process time
k	=	the rate constant
e	=	the base of the natural logarithms = 2.718

The integrated rate law is corresponding to the relationship between fumigation time and pesticide concentration. equation (2) shows that the concentration of A will decline in a smooth exponential curve over time. By taking the natural logarithm of each side of equation (2) and rearranging, an alternative logarithmic expression of the relationship between the concentration of A and t will be obtained as shown in equation (3).

$$\ln[A] = \ln[A]_0 - kt \qquad (3)$$

Since equation (3) has the form of the algebraic equation for a straight line, $y = mx + b$, with $y = \ln[A]$ and $b = \ln[A]_0$, therefore a plot of ln[A] versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$.

1.3) Second-order reaction

For the reaction 2A$\longrightarrow$ products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[c]} = \frac{1}{[c]_0} + kt \qquad (4)$$

Since equation (4) has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[A]$ and $b = 1/[A]_0$, therefore a plot of 1/[A] versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of 1/[A]

2) Modelling physical reaction

Physical processes frequently lead to quality change. Examples are creaming or sedimentation, fracture phenomena, viscosity changes, gelation of biopolymers, crystallization, and moisture migration. Modeling these phenomena are not easy because the changes are rather complex and may be accompanied by chemical changes. As an example, 2 models are presented for predicting viscosity of dispersions. The first one is an equation derived by Einstein for dilute dispersions:

$$\frac{\eta}{\eta_s} = 1 + 2.5\varphi \qquad (5)$$

in which η represents the viscosity of the dispersion, η_s the viscosity of the solvent, and φ the volume fraction of the dispersed particles. The interesting aspect of this equation is that only the volume fraction, but not the size of the dispersed particles, is of importance in determining the viscosity.

However, this equation is only valid for very dilute dispersions (φ< 0.01) and, therefore, not very suitable for foods. For more concentrated dispersions, an empirical relation has been derived, which is the so-called Eilers equation:

$$\frac{\eta}{\eta_s} = [\ 1 + (\frac{1.25\varphi}{1-\frac{\varphi}{\varphi_{max}}})\ ] \qquad (6)$$

This equation works quite well for foods. Such equations can thus be used to predict the rheological properties of a food if one knows the volume fraction of dispersed particles. As indicated previously, there are numerous models describing physical phenomena, such as aggregation and flocculation, crystallization, drying and dehydration. A critical remark here is that physical quality indicators are frequently modeled as if they concern a simple chemical reaction. A case in point is texture changes, for instance, during cooking of potatoes. The reason why there is softening of tissue is the result of very complicated processes, among which is the degradation of pectin. However, this is not what is measured; one uses a physical device to measure texture. This can, for instance, be modeled as a 1st-order reaction, and the resulting rate constant is then further evaluated in the Arrhenius equation.

2.5 Literature review

2.5.1 Effect of chemical treatment on quality of longan fruit

Jiang et al. (2002) suggested that sulfur dioxide (SO_2) fumigation has been the most effective practical postharvest treatment for control of color change in fresh longan fruit. Fumigation is achieved by burning sulfur powder at ambient temperature for 20–30 min with no humidity control, vaporizing liquid SO_2 held in a pressurized cylinder, or dissociation of sulfite compounds. However, sodium metabisulphite is comparatively less effective and more variable than SO_2 treatment. Fumigated fruit absorb about 30–50% of the SO_2 dosage. Fruit sulfur residues were maximal at 150–300 ppm immediately after fumigation, in the pericarp higher than the aril. In recent years, there has been increasing concern about sulfur residues in fruit, particularly as some people are sensitive to sulfites.

Whangchai et al. (2005) reported that when dipping in 1.5 N hydrochloric acid (HCl) for 20 min and rinsing in water can be considered for commercial application in extending shelf-life, controlling fruit decay and maintaining fruit qualities (color and eating) of longan fruit during 7 days storage at 25 °C following 45 days storage at 5±1 °C.

Lin et al. (2015) found that the addition of 0.5 mmol/L propyl gallate significantly retarded the browning index in the pericarp of propyl gallate-treated longan fruit when compared with the control, maintained higher activities of the active oxygen scavenging enzymes, preventing polyphenol oxidase (PPO) and peroxidase (POD). It is possible that propyl gallate treatment could be a feasible technique for controlling pericarp browning and extend the storage life of longan fruit.

Saengnil et al. (2014) suggested that longan cv. Daw were fumigated with 0 (control), 2.5, 5, 10 and 25 mg/L chlorine dioxide (ClO_2) for 10 min, packed in cardboard boxes and stored at 25±1 °C, RH 82±5% for 7 days. The 10 mg/L ClO_2 treatment was the most effective at extending shelf-life from 1 to 5 days, when compared with the control, by reducing pericarp browning, the activities of polyphenol oxidase (PPO) and peroxidase (POD), disease development, maintaining the highest total phenolic content and quality acceptance (odor and flavor) of longan fruit.

Li et al. (2015) found that when added 2-butanol (a phospholipase D inhibitor) at different concentrations (0.05%, 0.10% and 0.15%) in longan fruit and stored at ambient temperature (25 °C), the 0.05% 2-butanol treatment had the most positive effects on fruit quality, with treated fruit showing a significant delay changes in weight, titratable acidity content, total soluble solids content, lowest rate of pericarp moisture loss. It also maintained higher ascorbic acid contents and lower browning index than the control. This treatment maintained high contents of phenolics and flavonoids and inhibited browning, pulp breakdown and respiration.

2.5.2 Effect of ozone on fruit

Whangchai et al. (2005) found that when exposed ozone gas 20 ppm for 15, 30 and 60 min on postharvest diseases of longan fruit (fungi *Lasiodiplodia* sp. and *Cladosporium* sp.). In vitro studies showed that ozone exposure for 60 min significantly reduced mycelial growth of *Lasiodiplodia* sp. and completely inhibited *Cladosporium* sp. Exposing longan fruit to ozone for 60 min after inoculation with *Lasiodiplodia* sp. and *Cladosporium* sp. was the most effective of controlling the diseases incidence of postharvest. Therefore, application of ozone could be considered as a possible alternative method to control postharvest decay and prolong storage life of longan fruits.

Whangchai et al. (2006) suggested that longan fruit were fumigated with ozone 200 ppm for 60 min and stored at 5 °C for 3 weeks. The result showed that pericarp browning increased with increasing of storage period. Ozone treatment was effective inhibited browning compared to control fruits.

Gabler et al. (2010) reported that the concentrations used in fumigation table grapes with ozone up to 10,000 μLL^{-1} and stored after fumigation for 28 days at 0.5 °C, it was exceeded those required to kill exposed conidia. The rachis of grapes fumigated with ozone was sometimes harmed with the development of thin longitudinal darkened lesions. Rachis injury appeared irregularly, and was not always associated with a particular ozone dose or cultivar.

Ozkan et al. (2011) found that conidia of table grapes died more rapidly during ozone exposure at higher humidity than at lower humidity, and *P. digitatum* and *P. italicum* were more resistant to ozone than *B. cinerea.* Table grapes inoculated with *B. cinerea*, the number of infected grapes was reduced from 92.5% to 5.0% by 2000 $\mu LL^{-1} \times h$ of ozone. Ozone treated grapes that did develop infections had small, non-sporulating lesions, while the control grapes were covered with aerial mycelium and conidia.

Aday and Caner (2014) suggested that ozone treatments on strawberry during storage prevented the mold growth compared with control. This result is probably due to the effect of antimicrobial activity of ozone on fruits. They believe that, gaseous phase of ozone can be used instead of aqueous form to see significant differences on quality of fruits.

2.5.3 Effect of packaging on fruit and vegetable

Mangaraj et al. (2012) found that modified atmosphere (MA) packaging with selective permeability for extending storage life of litchi fruit. A mathematical model for MA packaging of fruit applying a respiration equation based on enzyme kinetics coupled with the Arrhenius model was developed. The MAP system increased the shelf-life of litchi fruit by 100–150% that of unpacked fruit at various storage temperatures with a quality comparable with freshly harvested fruit. The effect as well as 2-3 factor interaction of temperature, packaging system and storage periods were found to have significant effects on quality parameters of fruit ($p<0.01$).

Sahoo et al. (2015) reported that packaging of pointed gourds created a suitable headspace environment with low oxygen and high carbon dioxide concentrations. MAP in PP film with pin holes under refrigerated (4–6 °C, 45%RH) condition was significantly improved shelf-life of pointed gourds up to 16 days. While, LDPE film with pin holes under ambient (23–35 °C, 45–75% RH) conditions could extend shelf-life of pointed gourds up to 4 days.

Chitravathi et al. (2015) reported that the physicochemical characteristics of modified atmosphere packed and control chilies also showed significant ($p<0.05$). Chilies packed in microporous, PE-LD, polyolefin and anti-fog films had shelf-life of 16, 18, 22 and 28 days, respectively. In addition, control samples had shelf-life 15 days. Anti-fog (RD45) film was effective to maintain postharvest quality of green chilies during low temperature storage (8±1 °C, 85–95%RH).

Larsen and Wold (2016) suggested that the low oxygen concentration and high carbon dioxide concentration in laser perforated packages stored at retail conditions, when measured in these carrots high ethanol content could indicate anaerobic respiration. These carrots also had significantly higher scores for ethanol odor and flavor. Percentage diseased carrots were highest in the laser perforated packages. The overall quality of carrot was best maintained in needle perforated packages with a gas atmosphere close to air, giving no major weight loss, no ethanol formation and the lowest incidences of storage diseases at both chill and retail conditions.

Palou et al. (2003) found that fumigation oranges with ozone gas 2.5 gh^{-1} and stored at 12.8±1 °C, sporulation of *P. digitatum* and *P. italicum* was significantly inhibited by ozone gas exposure only on packed in RPCs with naked fruit. Ozone penetration inside the packages and unimpeded contact to the decayed area on the fruit are needed for ozone gas to be effective in controlling sporulation. It was related to the vented area of each type of package. The practical use of ozone gas exposure during storage for the treatment of fresh fruit is limited to highly vented packages or open-top containers.

2.5.4 Kinetic of quality and deterioration on fruit and vegetable

Pinheiro et al. (2013) found that the storage of whole tomato at different temperatures (2, 5, 10, 15, and 20 °C) conditions, storage at all temperatures had significant impact on the quality parameters. A fractional conversion model fitted well the experimental data on color parameters (a* and h° value), firmness and weight loss. Shelf-life threshold could be established using h° color parameter as standard indicator of quality tomato. The storage temperature effect was described by the Arrhenius law. The storage temperature of 10 °C was the one that preserved tomato quality, avoiding chilling injuries and extending shelf-life. These results represent a good predictive tool for tomato quality estimation along the food chain.

Noiwan et al. (2017) reported a study of the various storage temperatures (13, 20, 27 and 34 °C) on biochemical, physical and physiological changes of mango fruits. Mangoes stored at low temperature revealed a decrease in their respiration rates. The lower respiration rates delayed ripening, ethylene production, weight loss, peel and flesh color changes, firmness, and total soluble solid content (SSC) as well as titratable acidity (TA). A second-order kinetic model, a Gaussian model, and a first-order kinetic model fitted well with response quality parameters on firmness, SSC and TA. The data reveal that stored mango fruit at 13 °C effectively prolongs the quality attributes and extends the shelf-life of mango fruit.

Wang et al. (2018) reported that study of the temperature stored at 4, 15, 25, and 35 °C on quality of strawberry during storage. The results showed that firmness, total sugar content (TSC), titratable acidity (TA), and ascorbic acid (AA) content of strawberry had high correlations with the aerobic plate counts (APC) changes. A kinetic model of microbial growth was established based on modified Gompertz model in order to predict the shelf-life of postharvest strawberry. This mathematical model at different temperatures fitted into the modified Gompertz model with a high correlation coefficient (R^2>0.99). Predicted values were compared with observed values, and bias factors and accuracy factors were all in the acceptable range, indicating that this model had practical application.

Giannakourou and Taoukis (2019) reported the kinetics of deterioration (e.g., activation energy, shelf-life, etc.) on frozen food of plant origin. The scope is to provide a critical assessment and a comprehensive meta-analysis of the literature information on quality loss modeling of frozen foods. Therefore, common quality indices for specific systems were reviewed, fundamental methodologies used to build kinetic models were assessed, and alternative approaches to improve practical applications of these models are proposed. Alternative methodologies were described in order to take into account the calculated uncertainty of model parameters when assessing the remaining shelf-life of the product at any point within the cold chain. Results demonstrated the improved predictions obtained, with broader and more realistic confidence intervals.

Van Dijk et al. (2006) reported a development of practical applicable models capable to describe and to predict the temperature dependent firmness and moisture loss of tomatoes during storage at four different temperatures (3, 12, 20 and 25 ^{o}C) up to four weeks. The first type of model was based on fundamental laws of chemical kinetics, assuming plausible chemical reaction mechanisms. These reaction mechanisms describe the processes underlying either firmness, or moisture loss. For these kinetic models, both for firmness, and moisture loss, two independent processes were assumed. Throughout the entire temperature range its contribution increases at increasing temperature. The second type of model was based on Partial Least Squares Regression analysis, relating the data on firmness to the near infrared spectral data. Their difference in nature the kinetic models describe the firmness change and moisture loss in time at constant external condition.

CHAPTER 3
RESEARCH METHODOLOGY

The research works of application gaseous ozone technology for extending shelf-life of longan fruit was divided 3 parts showed in Figure 13.

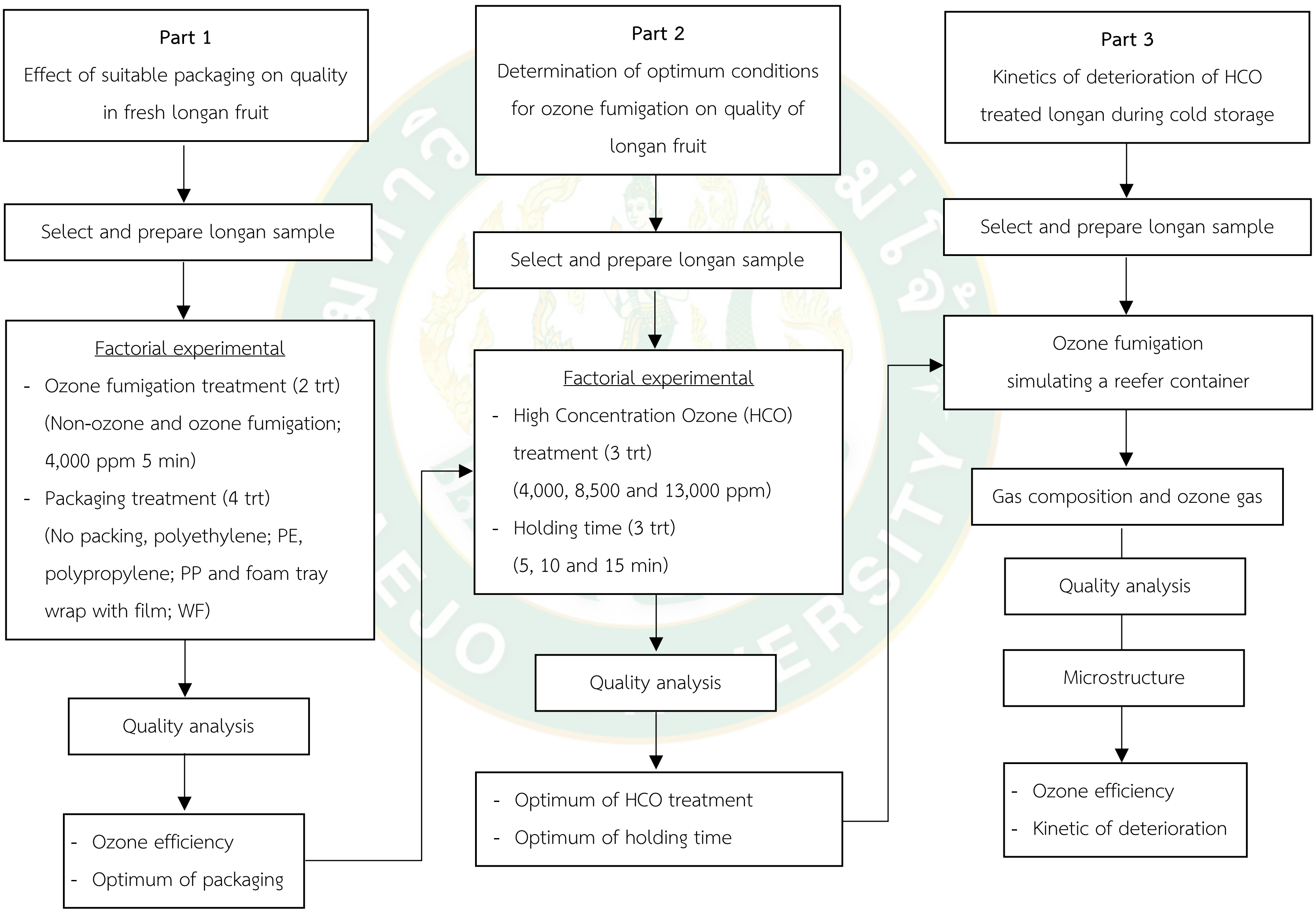


Figure 13 Research diagram and framework.

3.1 Part 1: Effect of suitable packaging on quality in fresh longan fruit

The objective of Part 1 was to evaluate the effectiveness of fumigation with gaseous ozone, and the optimum in packaging, on the quality of freshness of longan during cold storage. Therefore, the experimental method was set up to compare packaging types between non-ozonated and ozonated fumigation assisted accordingly.

3.1.1 Longan fruit sample

The on-season longan (*Dimocarpus longan* Lour.) cv. ''Daw'' with the age less than 3 days after harvested from orchards in Chiang Mai, Thailand was used in this experiment. The fruit was graded by size of >31 mm (grade AA) in diameter (Jaisin et al., 2013), uniform peel-color and non-disease appearance.

3.1.2 Ozone fumigation system

The ozone fumigation system as shown in Figure 14 consisted of a corona discharge ozone generator from purified oxygen gas. The generator connected with the control system using Labview^{TM} program with wireless network. The system connected to fumigation chamber of 0.4×0.4×1.2 m^3. The system conveyed ozone gas by silicone tube. The optimum flow rate of ozone gas was 7.5 L/min and system pressure (11-25 kPa). The output of generate ozone gas was 5.5 g/h (Changchai et al., 2015). Ozone concentration was measured by an ozone-gas sensor connected with data logger. This data logger calibrated by ozone gas-sampling pump with a detector tube (model GV-100, Gastec Corporation, Japan) to measure concentration of ozone in a range of 2,000-20,000 ppm.

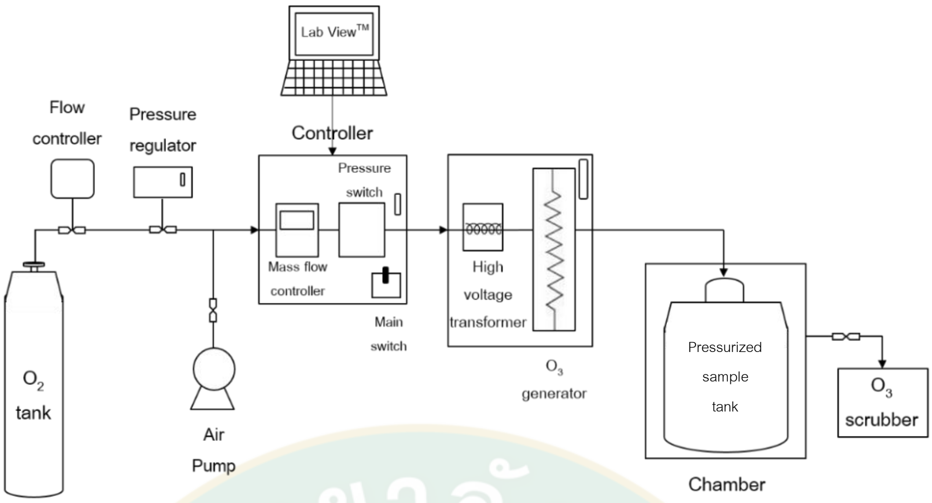


Figure 14 The scheme diagram of ozone gas fumigation system process.

3.1.3 Ozone fumigation process and packaging study

Longan fruit with a batch size of 3 kg was filled in a polycarbonate container (1/4 tank). For fumigation process, the longan sample was fumigated with ozone gas at a concentration of 4,000 ppm and held under pressure for 5 min. Longan fruit with pressurized and without fumigation were of packed size of 200g per pack. Accordingly, the longan was packed using 3 different types of packaging, namely, polyethylene (PE) bag, perforated polypropylene (PP) bag and foam tray wrapped with polyvinyl chloride (PVC) film (WF) (Figure 15). PE and PP bag had perforated by size diameter of 0.5 mm amount 4 hole/ side of bag (8 hole/ bag) and the perforated: bag in ratio of area equal 1:500 (Figure 16). Then, sealed bag when the longan was packed already and stored all treatment at 5±1 °C until the end of shelf-life. Treatments according to packaging type were defined by codenames as follows:

Untreated with gaseous ozone:

NC = control without packaging NE = packed with PE

NP = packed with PP NF = packed with WF

Treated with ozone gas:

OC = control without packaging OE = packed with PE

OP = packed with PP OF = packed with WF

Perforated polyethylene (PE)

(B) Perforated polypropylene (PP)

(C) Foam tray wrapped with PVC film (WF)

Figure 15 Packaging material of this experiment
(A) perforated polyethylene (PE), (B) perforated polypropylene (PP) and (C) foam tray wrap with PVC film (WF).

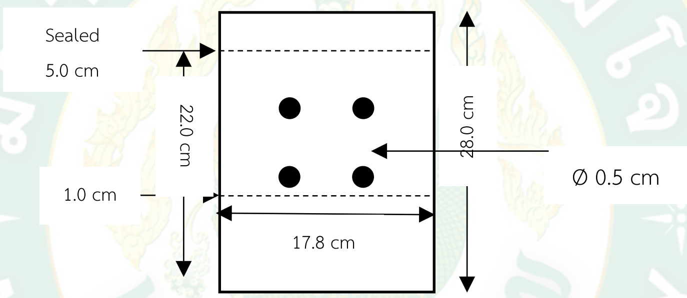


Figure 16 Size and perforation characteristics of PE and PP bag.

Table 13 Permeability of gas through plastic films.

Permeability	**PE**	**PP**	**PVC**
Water (g·µm/m^2·d·kPa) at 37.8°C	66-99	16.5-26	330-2,000
Oxygen (cc(STP)·µm/m^2·d·kPa) at 25°C	1,940	622	389-3,900
Carbon dioxide (cc(STP)·µm/m^2·d·kPa) at 25°C	10,490	2,100	1,170-2,330

Source: Hernandez (1997)

The properties of these films used for packaging experiments are given in Table 13. The fruit was determined for its quality analysis immediately after fumigation and every three days for disease incidence, pericarp browning, weight loss, firmness, color and shelf-life evaluation.

3.1.4 Quality analysis

1) Disease incidence

Disease incidence of 10 longan fruits from each treatment was assessed by measuring lesion area of fungal infection on each fruit surface (Aday et al. 2011; Apai, 2010; Whangchai et al., 2006). Disease incidence was scored into levels as: Level 0 = no disease, Level 1 = 1-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Disease incidence was expressed as by equation (7).

$$Disease\ incidence\ (score) = \left(\frac{\sum(Level\ of\ disease\ incidence)}{Total\ longan}\right) \tag{7}$$

Fruit evaluated at score $\geq$0.20 were considered unacceptable for marketing.

2) Pericarp browning

Pericarp browning of 10 longan fruits from each treatment was determined by estimating the browning area appeared on each fruit pericarp due to deterioration of longan shelf-life during storage (Apai 2010; Whangchai et al., 2006). The measurement was scored into 5 levels with respect to its browning area as: Level 1 = 0-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Pericarp browning was expressed as by equation (8).

$$Pericarp\ browning\ (score) = \left(\frac{\sum(Level\ of\ pericarp\ browning)}{Total\ longan}\right) \tag{8}$$

3) Weight loss

For weight loss, samples were weighed using 2 digit-digital balance model CP3202S (Sartorius AG, Germany). After weighing, the packages were returned to storage cabinet at 5±1 °C. The same package in was repeatedly weighed every 3 days throughout storage time. Weight loss was expressed as by equation (9).

$$Weight\ loss\ (\%) = \left(\frac{initial\ weight - final\ weight}{initial\ weight}\right)\ x\ 100 \qquad (9)$$

The result was reported by a mean of three replicates (n = 3) (Karakosta et al., 2018).

4) Firmness

Firmness analysis of 5 longan fruits from each treatment was selected at random where each fruit was penetrated on one side using a Texture Analyzer with ±0.1 g accuracy (model TA.XT-PLUS, Stable Micro Systems, UK). The firmness test applied a cylinder plunger SMS-P/2 probe (2 mm diameter), compressed by 20%strain using cross-head speed of pre-test, test, and post-test speed of 3 mm/s, 1 mm/s and 10 mm/s, respectively.

5) Color

The color of longan fruits was measured on the surface using a spectrophotometer with ±5 nm accuracy (model Mini Scan XE PLUS 45/0-S, Hunter Lab, USA). For each measurement, nine longans were sampled the means of L* (lightness) and b* (yellowness and blueness) were reported according to the consumer preference on visual appearance of longan fruit with a yellow to light brown color (Jiang et al., 2002).

6) Shelf-life evaluation

The shelf-life of longan fruit was determined by disease incidence, immediately after fumigation and every 3 day-intervals during storage. The fruit was considered to be at the end of its shelf-life when disease incidence of the fruit was evaluated with score ≥0.20.

3.1.5 Statistical analysis

The experiment was designed using factorial experimental design in a randomized complete block design (RCBD). Data were statistically analyzed by analysis of variance (ANOVA), and was carried out using SPSS 16.0. Duncan's Multiple Range Tests (DMRT) at a significance level of 0.05. Among the various treatments, the p-value less than 0.05 was considered as a significant difference. The result from this part will use in the second part.

3.2 Part 2: Determination of optimum conditions for ozone fumigation on quality of longan fruit

The objective of Part 2 was to study the effect of high concentration-ozone (HCO) on the quality of fresh longan during cold storage. Therefore, the experimental method was consisted of 2 factors;

1. Concentration of ozone gas fumigation
2. Exposed time of ozone gas fumigation

3.2.1 Longan fruit sample

The off-season longan (*Dimocarpus longan* Lour.) cv. ''Daw'' with age less than 3 days after harvested from orchards in Chiang Mai, Thailand was used in this experiment. The fruit was graded by size of >31 mm (grade AA) in diameter (Jaisin et al., 2013), uniform peel-color and non-disease appearance before HCO treatment.

3.2.2 Ozone fumigation system

The ozone fumigation system as shown in Figure 14 consisted of a corona discharge ozone generator from purified oxygen gas. The generator connected with the control system using Labview™ program with wireless network. The system connected to fumigation chamber of 0.4×0.4×1.2 m^3. The system conveyed ozone gas by silicone tube. The optimum flow rate of ozone gas was 7.5 L/min and system pressure (11-25 kPa). The output of generate ozone gas was 5.5 g/h (Changchai et al., 2015). Ozone concentration was measured by an ozone-gas sensor connected with data logger. This data logger calibrated by ozone gas-sampling pump with a detector tube (model GV-100, Gastec Corporation, Japan) to measure concentration of ozone in a range of 2,000-20,000 ppm.

3.2.3 HCO treatment

Longan was batched in a size of 3 kg and filled in a 20 L of polycarbonate container (1/4 tank). For HCO treatment, the batched longan was fumigated with pressurized ozone gas at concentration 4,000, 8,500 and 13,000 ppm and held under pressure for 5, 10 and 15 min as shown in Table 14.

Table 14 Treatment conditions of HCO fumigation on longan fruit.

No	Ozone gas concentration (ppm)	Exposure time (min)	Total time (min)	Code
1	-	-	0	Control
2	4,000	5	10.45	04/05
3	8,500	5	13.15	08/05
4	13,000	5	20.00	13/05
5	4,000	10	15.45	04/10
6	8,500	10	18.15	08/10
7	13,000	10	25.00	13/10
8	4,000	15	20.45	04/15
9	8,500	15	23.15	08/15
10	13,000	15	30.00	13/15

After each HCO fumigation, the batch of longan was divided into 200g and packed in optimum packaging (from Part 1), then longan fruit was stored at 5±1 ^{o}C until the end of shelf-life. The fruit was analyzed for its quality immediately after fumigation at day 0 and every 5 day on pericarp browning, disease incidence, weight loss, total soluble solid content (TSS), color, sensory evaluation and shelf-life evaluation.

3.2.4 Quality analysis

1) Disease incidence

Disease incidence of 10 longan fruits from each treatment was assessed by measuring lesion area of fungal infection on each fruit surface (Aday et al. 2011; Apai, 2010; Whangchai et al., 2006). Disease incidence was scored into levels as: Level 0 = no disease, Level 1 = 1-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Disease incidence was expressed as by equation (7). Fruit evaluated at score ≥0.20 were considered unacceptable for marketing.

2) Pericarp browning

Pericarp browning of 10 longan fruits from each treatment was determined by estimating the browning area appeared on each fruit pericarp due to deterioration of longan shelf-life during storage (Apai 2010; Whangchai et al., 2006). The measurement was scored into 5 levels with respect to its browning area as: Level 1 = 0-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Pericarp browning was expressed as by equation (8).

3) Weight loss

For weight loss, samples were weighed using 2 digit-digital balance model CP3202S (Sartorius AG, Germany). After weighing, the packages were returned to storage cabinet at 5±1 ^{o}C. The same package in was repeatedly weighed every 5 days throughout storage time. Weight loss was expressed as by equation (9). The result was reported by a mean of three replicates (n = 3) (Karakosta et al., 2018).

4) Total soluble solid (TSS) content

Total soluble solid (TSS) content was measured from longan juice extract using a hand refractometer model N-1α (Atago Co. Ltd, Japan). Result of TSS content was expressed as percentage of TSS (Aday et al. 2014; Apai 2010).

5) Color

The color of longan fruits was measured on the surface using a spectrophotometer with ±5 nm accuracy (model Mini Scan XE PLUS 45/0-S, Hunter Lab, USA). For each measurement, nine longans were sampled the means of L* (lightness) and b* (yellowness and blueness) were reported according to the consumer preference on visual appearance of longan fruit with a yellow to light brown color (Jiang et al., 2002).

6) Sensory evaluation

Sensory evaluation of longan was assessed by trained panel of 6 researchers using a 9-point hedonic scale, every 5 days during storage. The attributes to characterize the sensory evaluation included fruit pericarp color, aromatic odor, flavor, firmness and overall acceptance (Apai, 2010). Longan fruit were randomly selected and rated for its fresh quality which was scaled into 9 levels: Level 1 = poor, Level 5 = acceptable and Level 9 = excellent. Acceptance score less than 4.00 was considered as the cut-off point for acceptance of the lot of each treatment.

7) Shelf-life evaluation

Shelf-life of longan fruit was determined by disease incidence and acceptance score, immediately after fumigation and every 5 days during storage. The fruit was considered end of shelf-life when disease incidence of fruit evaluated at score is $\geq$0.20 and acceptance score less than 4.00.

3.2.5 Statistical analysis

The experiment was designed using factorial experimental design in a randomized complete block design (RCBD). Data were statistically analyzed by analysis of variance (ANOVA), and was carried out using SPSS 16.0. Duncan's Multiple Range Tests (DMRT) at a significance level of 0.05. Among the various treatments, the p-value less than 0.05 was considered as a significant difference. The result from this part will use in the third part.

3.3 Part 3: Kinetics of deterioration of HCO treated longan during cold storage

The objective of Part 3 was to study of kinetics of deterioration HCO treated longan during cold storage, which may lead to the further alternative method to sulfur dioxide fumigation to prolong shelf-life of fresh longan.

3.3.1 Longan fruit sample

The off-season longan (*Dimocarpus longan* Lour.) cv. ''Daw'' with age less than 3 days after harvested from orchards in Chiang Mai, Thailand was used in this experiment. The fruit was graded by size of >31 mm (grade AA) in diameter (Jaisin et al., 2013), uniform peel-color and non-disease appearance.

3.3.2 Ozone fumigation system

The ozone fumigation system as shown in Figure 14 consisted of a corona discharge ozone generator from purified oxygen gas. The generator connected with the control system using Labview™ program with wireless network. The system connected to fumigation chamber of 0.4×0.4×1.2 m^3. The system conveyed ozone gas by silicone tube. The optimum flow rate of ozone gas was 7.5 L/min and system pressure (11-25 kPa). The output of generate ozone gas was 5.5 g/h (Changchai et al., 2015). Ozone concentration was measured by an ozone-gas sensor connected with data logger. This data logger calibrated by ozone gas-sampling pump with a detector tube (model GV-100, Gastec Corporation, Japan) to measure concentration of ozone in a range of 2,000-20,000 ppm.

3.3.3 Kinetics of deterioration

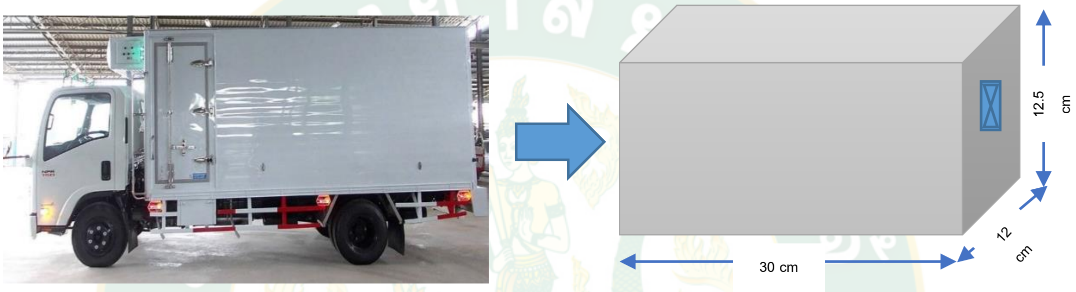
The main export market of longan fruit was China and most of them would longan transport from Thailand to China with reefer container (2 °C) about 30 days. Kinetic deterioration of HCO longan during transportation by simulating a 20' RF reefer container was study. The model of this work was developed by the deterioration of the longan transport simulation system.

1) Model assumptions

The geometry of the longan transport simulation system (Tupperware + longan + PE bags + headspace) was considered in this study. The biological phenomenon (gas composition and deterioration) was taken into account in the modelling approach are schematically represented in Figure 17.

2) Limitation of modelling

This model was close system, it consists of Tupperware and fan for reefer container simulation. The size (width x length x height) of Tupperware and 20’ RF reefer container were 12.00 x 30.00 x 12.50 cm and 2.20 x 5.50 x 2.25 m, respectively. The Tupperware was replaced 20’ RF reefer container in ratio of size and volume equal 18:1 and 6,050:1, respectively. The fan used for circulated air inside the Tupperware. This model packed longan in perforated PE bag was replaced plastic crates.



20’ RF
(W x L x H = 2.20 x 5.50 x 2.25 m)

Plastic container (Tupperware)
(W x L x H = 12.00 x 30.00 x 12.50 cm)

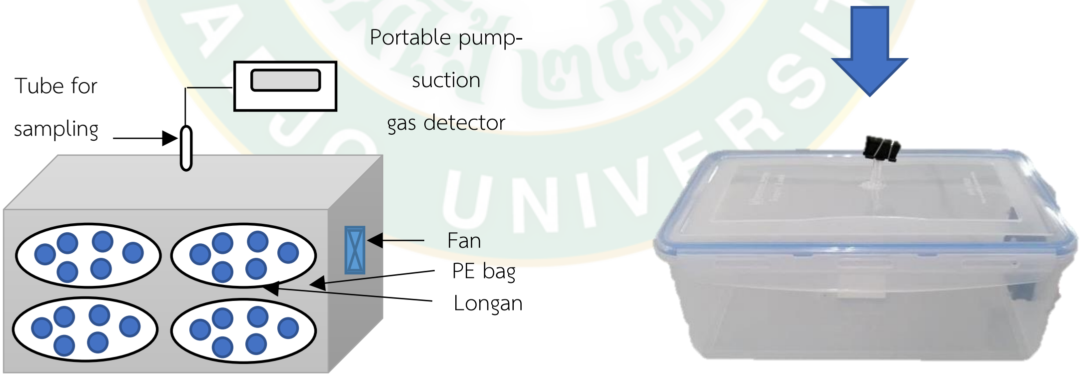


Figure 17 Longan transport simulation for kinetic of deterioration modelling.

Three kilograms of longan fruit was filled in a 20 L of polycarbonate container (1/4 tank). The longan sample was fumigated with pressurized ozone gas concentration (from Part 2). Longan fruit with and without fumigation were packed in suitable packaging (from Part 1) and packed size 200g/ bag. 4 bags of longan sample were put in Tupperware and stored at 2±1 °C for 30 days as shown in Figure 17. Fan was turned on during storage time for circulated air in the Tupperware. Its quality was analysis every 3 days for kinetic of deterioration, gas evaluation, disease incidence, pericarp browning, weight loss, color and overall acceptance. Microstructure by scanning electron microscopy (SEM) of longan was determined immediately after fumigation.

1) Kinetic of deterioration

Kinetic of deterioration in longan fruit was analyzed every 3 days. The rate constant of surface deterioration is calculated given by equation (10) (Matar et al., 2018):

$$\frac{dD}{dt} = k_D D \frac{D_{max} - D}{D_{max}} \delta_{CO_2} \qquad (10)$$

Where D is the percentage of surface deterioration (%) at time t (s), D_{max} is the maximum percentage of deterioration (%) and this work experimental data D_{max} equal 100%, k_D represents the deterioration rate constant (day^{-1}) and δ_{CO2} is a dimensionless weighting parameter representing the inhibiting effect of carbon dioxide on the deterioration rate.

The δ_{CO2} parameter is calculated given by equation (11):

$$\delta_{CO_2}(t) = 1 - \frac{X_{CO_2}(t)}{X_{CO_2\,max}} \qquad (11)$$

Where X_{CO2} is the quantity (%) of CO_2 in the headspace at time t (s), X_{CO2max} represents the maximal quantity (%) of CO_2 withstanding by the microorganisms and x_{CO2max} equal 30% from the study of (Garcia et al., 2002).

2) Gas evaluation

Gas evaluation consist of carbon dioxide, oxygen and ozone gas concentration, which using a portable pump-suction gas detector model HT-R-CO2, HT-E-O2 and HT-E-O3 (AGI, China), respectively. Gas sampling was asses all gas in the headspace through tube fitted with Tupperware (Figure 17) every 3 days, which was scaled into percentage.

3.3.4 Quality analysis

1) Disease incidence

Disease incidence of 10 longan fruits from each treatment was assessed by measuring lesion area of fungal infection on each fruit surface (Aday et al. 2011; Apai, 2010; Whangchai et al., 2006). Disease incidence was scored into levels as: Level 0 = no disease, Level 1 = 1-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Disease incidence was expressed as by equation (7). Fruit evaluated at score greater than 0.20 were considered unacceptable for marketing.

2) Pericarp browning

Pericarp browning of 10 longan fruits from each treatment was determined by estimating the browning area appeared on each fruit pericarp due to deterioration of longan shelf-life during storage (Apai 2010; Whangchai et al., 2006). The measurement was scored into 5 levels with respect to its browning area as: Level 1 = 0-20%, Level 2 = 21-40%, Level 3 = 41-60%, Level 4 = 61-80%, and Level 5 = 81-100%. Pericarp browning was expressed as by equation (8).

3) Weight loss

For weight loss, samples were weighed using 2 digit-digital balance model CP3202S (Sartorius AG, Germany). After weighing, the packages were returned to storage cabinet at 2±1 ^{o}C. The same package in was repeatedly weighed every 3 days throughout storage time. Weight loss was expressed as by equation (9). The result was reported by a mean of three replicates (n = 3) (Karakosta et al., 2018).

4) Color

The color of longan fruits was measured on the surface using a spectrophotometer with ±5 nm accuracy (model Mini Scan XE PLUS 45/0-S, Hunter Lab, USA). For each measurement, nine longans were sampled the means of L* (lightness) and b* (yellowness and blueness) were reported according to the consumer preference on visual appearance of longan fruit with a yellow to light brown color (Jiang et al., 2002).

5) Overall acceptance

Overall acceptance of longan was assessed by trained panel of 6 researchers every 3 days during storage. Overall acceptance aims to determine the disease incidence, pericarp color, aromatic odor, flavor and firmness (Matar et al., 2018). Longan fruit were randomly selected and rated for its quality which was scaled into percentage. Fruit evaluated at score less than 45% were considered unacceptable for marketing.

6) Microstructure

For micro-structure, SEM evaluation of longan with and without HCO fumigation were conducted using Scanning Electron Microscope model JSM-5410LV (JEOL, Japan) at 10 kV with protocol from (Chu et al., 2017). Sample of the longan epicarp was cut in a small piece with size of 5x5 mm with a thin blade and dried with a vacuum dryer model VO500 (Memmert GmbH + Co.KG, Germany) and coated with gold of 20 nm thickness in an ion sputter coater model JFC-1200 (JEOL, Japan).

7) Predict of shelf-life

Predict of shelf-life on longan fruit was determined by disease incidence and overall acceptance, immediately after fumigation and every 3 days during storage. The fruit was considered end of shelf-life when disease incidence of fruit evaluated at score is $\geq$0.20 and overall acceptance less than 45%.

CHAPTER 4
RESULT AND DISCUSSION

4.1 Effect of suitable packaging on quality in fresh longan fruit

The objective of Part 1 was to evaluate the effectiveness of fumigation with gaseous ozone, and the optimum in packaging, on the freshness of longan during cold storage. Therefore, this experiment was compared packaging between non-ozonated and ozonated fumigation.

4.1.1 Disease incidence

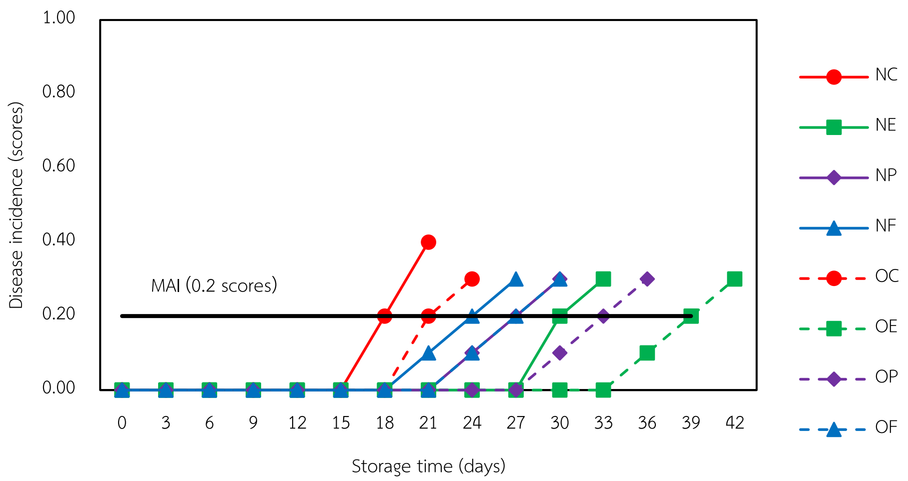


Figure 18 Effect of ozone fumigation and packaging materials on disease incidence of longan.

Note: MAI = Maximum acceptable disease incidence at which ≥0.2 scores of consumers rejected the product.

The first parameter related with the shelf-life of the fruit was defined as disease incidence. For Figure 18, disease incidence of longan all treatments increased when storage time increased. The disease incidence of NC sample increased rapidly in 15 days. Longans treated with gaseous ozone exhibited less disease incidence than those of untreated samples when stored at 5 ^{o}C. The OE sample had the longest storage time (36 days) up to disease incidence 0.2. Our result corresponds to (Ong et al., 2012) who found that ozone treatment reduced disease incidence up to 40% in papaya fruit. Other researchers also reported that ozone fumigation reduced the microorganism population in fruits such as longan fruit (Whangchai et al., 2006), date fruit (Habibi Najafi and Haddad Khodaparast, 2009), strawberry (Aday and Caner, 2014) and table grapes (Gabler et al., 2010) because it destroyed microorganisms by oxidizing the cellular components of cell (Victorin, 1992). Ozone affected to disrupt cellular components of microorganisms when cellular components destroyed, microorganisms could not live. In our study, longan fruit packed in PE exhibited the least disease incidence when compared to PP, WF and without packaging. Since PE had more carbon dioxide (CO_2) permeability than other films (Table 13), it is possible that carbon dioxide might permeate to environment easier than those packed in other packaging. As a result, the ozonated longan packed in PE emerged disease incidence slower than the others. The low percentages of diseases incidence in PE also slow down the rate of pathological disorder in PE films as well.

4.1.2 Pericarp browning

The pericarp browning of longans under all treatments increased throughout shelf-life (Figure 19). At day 3, the longan fruit fumigated with gaseous ozone significantly exhibited less pericarp browning than that of non-fumigate longan fruit ($p<0.05$). When stored for 15 days, the OE sample exhibited the least pericarp browning score of 1.80, whereas the NC sample exhibited the highest pericarp browning score of 4.40. Correspondingly, Whangchai et al. (2006) reported that with the increase of storage time, longan fruit treated with low concentration ozone showed an increase in pericarp browning because of the time limit in ozone efficiency to inhibit browning of longan fruit.

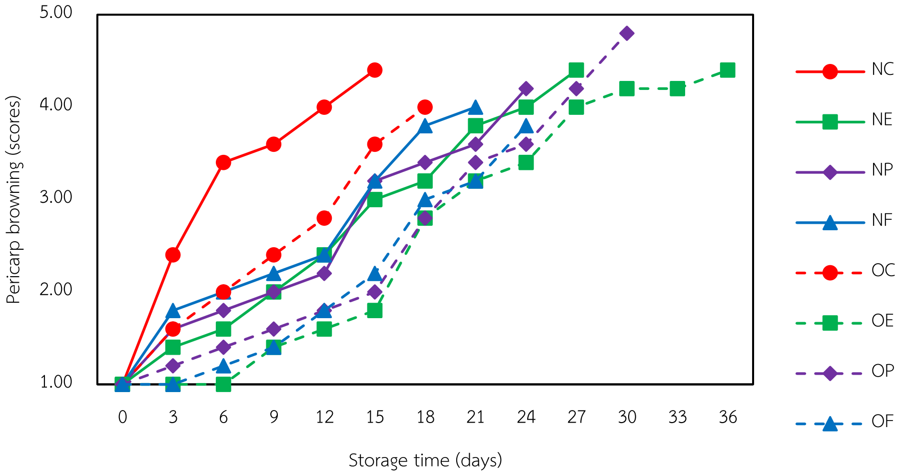


Figure 19 Effect of ozone fumigation and packaging materials on pericarp browning of longan.

4.1.3 Weight loss

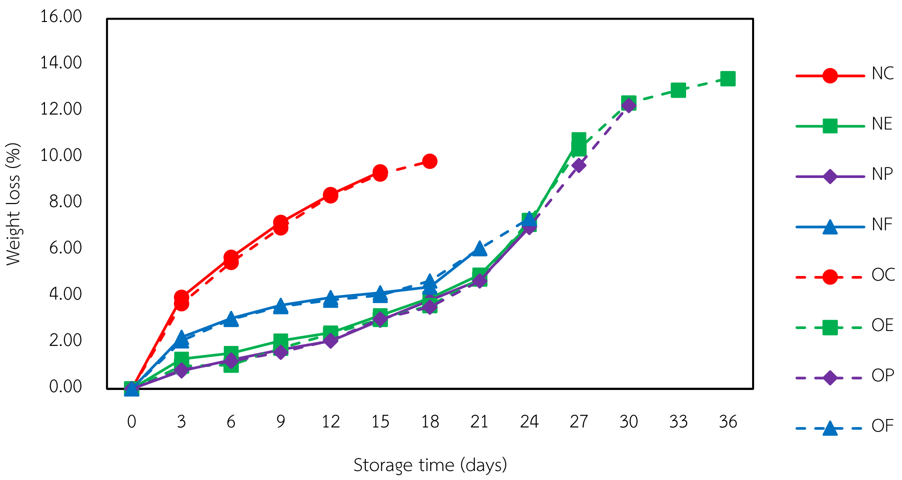


Figure 20 Effect of ozone fumigation and packaging materials on weight loss of longan.

Gaseous ozone treatments did not significantly affect ($p \geq 0.05$) the weight loss of longan fruit; however, the type of packaging significantly did ($p<0.05$). During 15 days in storage, longan fruits with no packaging was susceptible to weight loss more than those packed in WF, PE, and PP, respectively. The NC sample had the highest weight loss of 9.39% in 15 days. These results agreed with Mistriotis et al. (2016) who suggested that unwrapped samples (cherry tomatoes and peaches) had more weight loss than samples packed in PLA and OPP film. When storage time lengthened, longan fruit under all treatments was susceptible to weight loss. The OE sample had the highest weight loss of 13.42% in 36 days, as shown in Figure 20. An increase in weight loss of longan is normally due to evaporation and respiration (water and heat production), but under different packaging types, it yielded different responses (Chitravathi et al., 2015).

4.1.4 Firmness

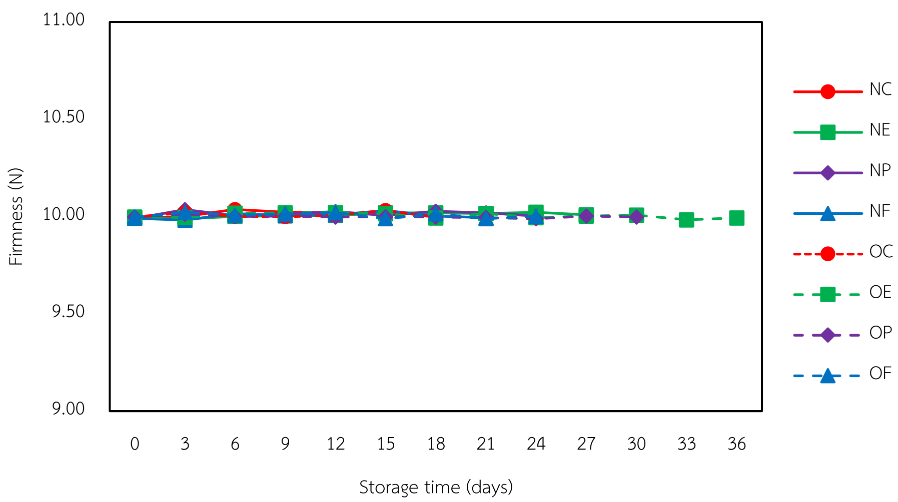


Figure 21 Effect of ozone fumigation and packaging materials on firmness of longan.

Firmness can be defined as the parameter which is related to cell wall strength and intercellular adhesion (Toivonen and Brummell, 2008). In Figure 21, gaseous ozone treatments and packaging types did not significantly affect ($p \geq 0.05$) the firmness of the longan fruit. During storage at 5 °C, the firmness of longan was within a range of 9.98 to 10.04 N. Longan fruit changed slightly in firmness but with no significant difference ($p \geq 0.05$). The firmness did not change, may be has thick cuticle and pericarp as a result to protect water loss and regulate the exchange of water and highly responsive to the external conditions (Lara et al., 2019) thus lesser loss of moisture from the surface of longan fruit. In contrast to other fruits, A day and Caner (2014) reported that significant difference in firmness values was observed between ozone treated and ozone untreated strawberries. All treated strawberries had higher firmness values than the control group. Sahoo et al. (2015) also reported that pointed gourd in all packaging types had peak force decreased during storage under ambient and refrigerated storage condition.

4.1.5 Color parameters

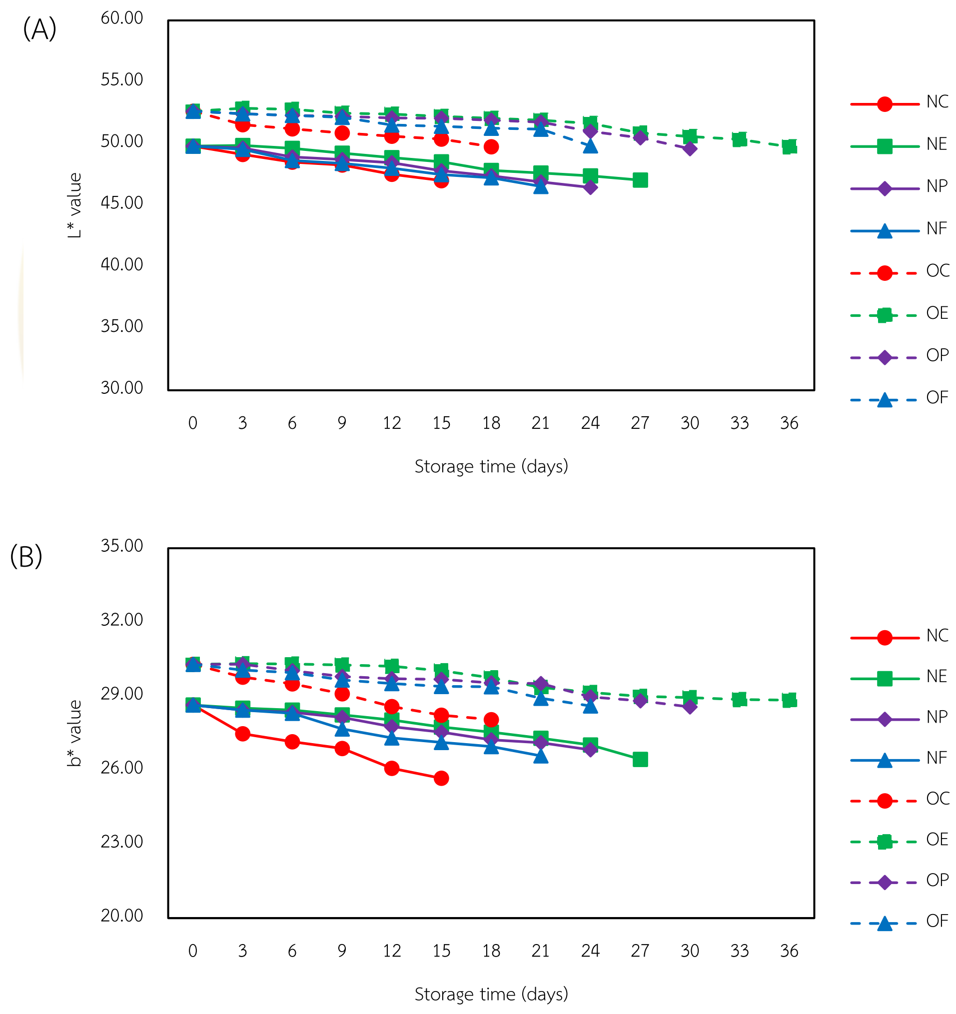


Figure 22 Effect of gaseous ozone and packaging type on color parameters; (A) L* value and (B) b* value of longan.

Color is the one factor in deciding visual attributes for buying and selling of longan fruit (Apai, 2010). At day 0, longan fruit without ozone fumigation possessed the L* and b* of 49.80 and 28.64. When fumigated with ozone gas, the longan had increased in L* and b* to 52.64 and 30.29, respectively. Ozone may cause an increase in L* of longan due to the bleaching effect (Forney, 2003). During storage at 5 ^{o}C, the ozonated longan stored in PE, PP, WF and without packaging had more L* and b* (light yellow-brown color) as well as a longer shelf-life than those of the untreated longan (dark brown color), as shown in Figure 22 (A) and 22 (B). Similar trend was also observed by Aday and Caner (2014) who suggested that strawberries with ozone treatments and storage times were significant factors affecting the L*.

4.1.6 Shelf-life

The shelf-life of longan fruit due to effects of ozone treatment and storage packaging type was determined by disease incidence, as shown in Figure 18 and Table 15. Longan fumigated with ozone gas had a longer shelf-life than untreated samples. The ozonated longan packed in PE had a longer shelf-life than that of PP, WF and those with no packaging when stored at 5 ^{o}C. Among three different types of packaging, the ozone fumigated longan stored in PE yielded the longest storage time up to 36 days, equivalent to 140% longer shelf-life than that of the control. According to Zambre et al. (2010), tomatoes treated with ozone gas and stored at 15 ^{o}C had a prolonged shelf-life of tomato by 22 days, which corresponded to our result when applied ozone with longan. The longer shelf-life of longan was possibly due to a reduction in the surface microbial count in combination with proper modified atmosphere effect inside the package. The modified gaseous composition in the different packaging created a suitable headspace with low oxygen and high carbon dioxide, which resulted in maintaining the quality and marketability of vegetables (Sahoo et al., 2015). Our results also agreed with that of Mangaraj et al. (2012) who found that the modified atmosphere packaging extended shelf-life of the litchi fruit from 100 to 150% compared with unpackaged fruit.

Table 15 Shelf-life at various treatment of longan fruit during storage at 5°C.

Non-Ozone treatment	Shelf-life (days)	Ozone treatment	Shelf-life (days)
NC	15	OC	18
NE	27	OE	36
NP	24	OP	30
NF	21	OF	24

From results in Part 1, it was found that longan with ozone fumigation attained the disease incidences, weight loss and shelf-life more positive result than the longan without ozone treatment, which depend on the type of packaging materials. Therefore, it can be concluded that the optimum treatment was that the use ozone fumigation combined with PE packaging yielded the best shelf-life of longan and would be use in Part 2.

4.2 The optimum HCO treatment for using ozone gas on quality of longan fruit

The objective of Part 2 was to study the effect of high concentration-ozone (HCO) on the quality of fresh longan during cold storage. Therefore, the experiment was consisted of 2 factors; concentration and exposed time of ozone gas fumigation. All samples were packed with PE packaging as a selected result from Part 1.

4.2.1 Disease incidence

Disease incidence of longan fruit (control and HCO treatments) increased when increasing of storage time. Control sample had increased rapidly disease incidence in 20 days, but at a less rapid rate in the treatment groups. While, HCO treatments had disease incidence started in 30 days (04/05 and 04/10), 35 days (08/05, 08/10 and 04/15) and 40 days (13/05, 13/10, 08/15 and 13/15) (Figure 23). In our tests, we obtained acceptable reduction of disease incidence after fumigation with ozone gas treatment for over 30-40 days when compared with the control (15 days) with storage at 5 °C. This result corresponded to the work by Taimaneerak et al. (2018) who reported that none of longan treated with ozone had disease incidence immediately after fumigated for 5 days at 25 °C. It was also agreed with Whangchai et al. (2006) who found that longan fruit were fumigated with ozone for 60 min, had the greatest reduction in microorganism population. It is possible that ozone may destroy microorganisms by oxidation of cellular components such as sulfhydryl groups of amino acids in enzymes and oxidation of the cell membrane (Victorin, 1992). The ozone treatment with long exposure time could damages the cellular membrane of microorganism such as fungi that penetrate into the fruit through lenticles, making fruit less susceptible to decay (Underhill and Simons, 1993). Slightly different with disease incidence result, longan with and without ozone concentration 4,000 ppm for 5 min packed in PE bag from Part 1 has less disease incidence than Part 2. This variation is possibly due to the variation of batch of longan between in-season and off-season harvesting times. The poor development of the pericarp in the off-season longan fruit in Part 2 caused higher incidence cracking than the on-season longan fruit (Yang et al., 2010). When longan fruit had more incidence cracking probably caused higher disease incidence of longan fruit as confirmed by results in this work.

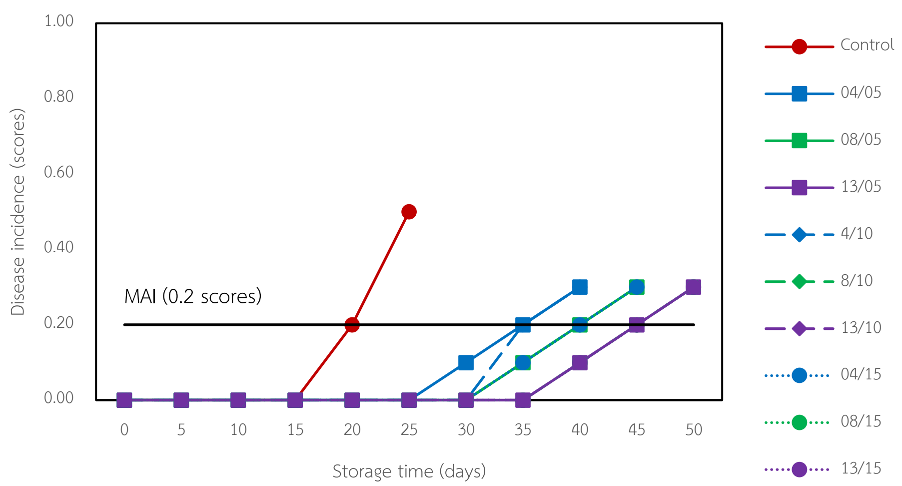


Figure 23 Effect of HCO treatment on disease incidence of longan.

Note: MAI = Maximum acceptable disease incidence at which ≥0.2 scores of consumers rejected the product.

4.2.2 Pericarp browning

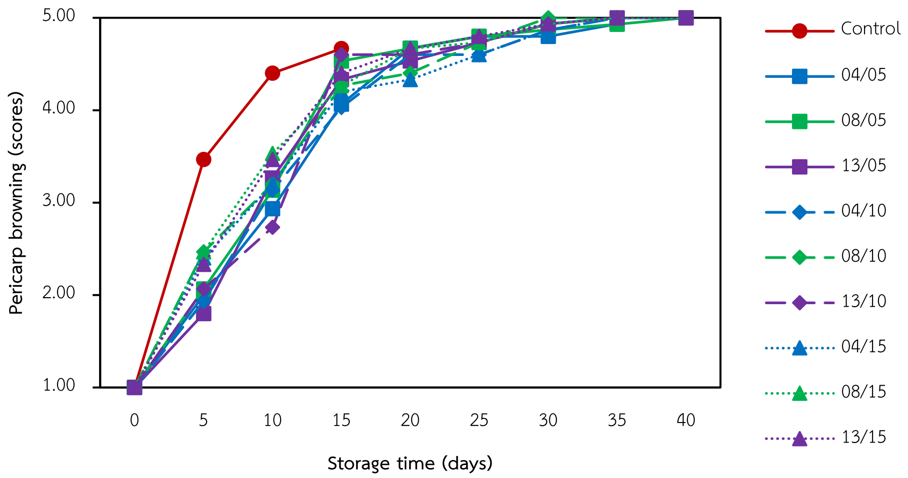


Figure 24 Effect of HCO treatment on pericarp browning of longan.

Pericarp browning in longan fruit occurs rapidly and becomes a major postharvest problem. Browning is evident as dark and water-soaked areas on pericarp, which caused by temperature stress, decay and senescence (Bhushan et al., 2015). From Figure 24, the pericarp browning of the both HCO longan and control increased during shelf storage. At day 0-10, the control had more pericarp browning significantly ($p<0.05$) than that of HCO treated samples. When stored for 15 days, the control had highest pericarp browning with score of 4.67. In contrary, the 04/05 HCO longan was susceptible to the least pericarp browning of 4.07. Our results agreed with Whangchai et al. (2006) who report that longan fruit fumigated with 200 ppm ozone for 60 min, it had slowed down pericarp browning when increasing of storage time, because of ozone efficiency in inhibiting browning of longan fruit. Thus, our HCO treatment exhibits the potential to inhibit browning compared to control. When storage time increased, the control longan fruit suffered the pericarp browning on the control faster than ozone treated treatment. Since the browning is a results of oxidation and polymerization of phenolic compounds, caused by polyphenol oxidase (PPO) and peroxidase (POD) (Saengnil et al., 2006), the ozone was able to inhibit the PPO and

POD enzymes (Miller et al., 2013). As a result, ozone could prevent pericarp browning of longan fruit.

4.2.3 Weight loss

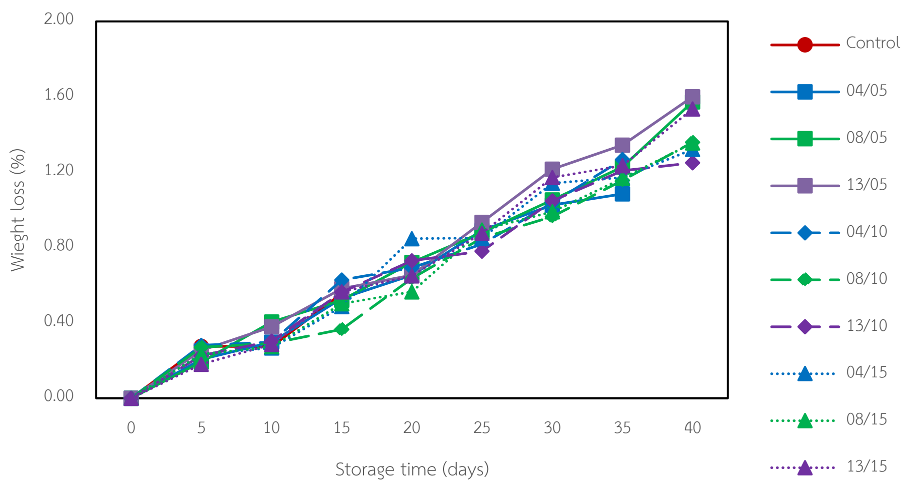


Figure 25 Effect of HCO treatment on weight loss of longan.

The HCO treatments did not affect of the weight loss of longan fruit. When storage time increasing, weight loss in all treatment increasing. During 15 days, samples in all treatment had weight loss in range of 0.49-0.63%. The 13/05 HCO treatment had the highest weight loss of 1.60% at 40 days (Figure 25), but it was not difference significantly from other treatments. The weight loss of HCO treatment on longan corresponds with the ozone fumigation treatment on papaya reported by Ong et al. (2014) where the papaya was exposed continuously to ozone fumigation for 96 h at various ozone concentration and stored for 14 days. Ozone concentration gave a small effect on weight loss of papaya fruit as the fruit naturally lost weight during storage in all treatment. Also Guo et al. (2010) found that the weight loss rate of longan pericarp increased, when increase storage time at 4$\pm$1 °C, corresponding to our results from control.

4.2.4 Total soluble solid content (TSS)

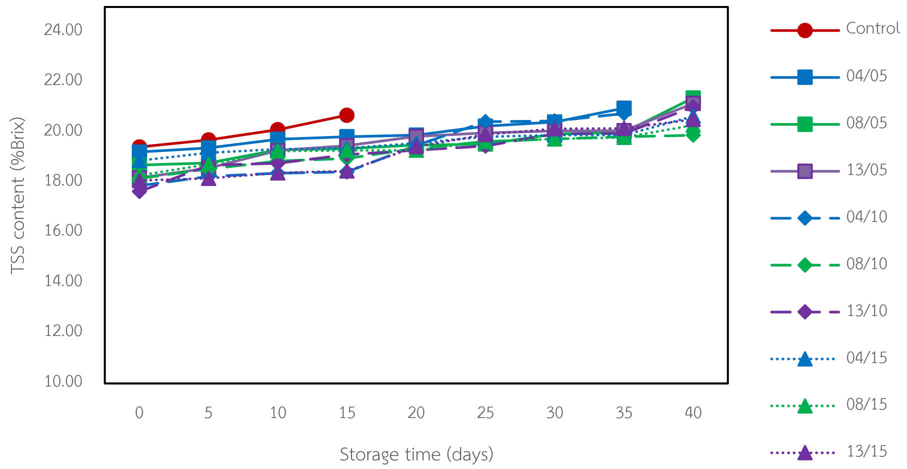


Figure 26 Effect of HCO treatment on TSS content of longan.

TSS content of fruit is one of the most important parameter associated with the texture and consumer acceptability (Voća et al., 2008). The HCO treatments gave no significant effect on the TSS content ($p \geq 0.05$) as shown in Figure 26. When storage time increased, TSS content increased tend in all samples but insignificantly. The variation in TSS content was possibly due to the alterations in other soluble ingredients more than sucrose, which is a major component for TSS content (Ray et al., 2005). Our results are agreed with Aday and Caner (2014), who found that TSS content of ozone treatments on strawberry during storage was not significant difference. Same as all lychee samples on control and treated with ozone with no adversely affected on TSS content report by Whangchai et al. (2011).

4.2.5 Color parameters

Color is the key element in food quality consumer behavior and acceptability. The L* and b* color of control and HCO treated longan fruit was reported. When storage time increased, color parameters decreased. Control sample had less color parameter L* than HCO treatments significantly ($p<0.05$) but not the b* ($p \geq 0.05$) in Figure 27 (A) and 27 (B). An increased in L* may be due to the bleaching effect of ozone which oxidizing pigments rapidly (Taimaneerak et al., 2018). This effect was also reported by Daş et al. (2006) on treated cherry tomatoes with the high ozone concentrations. On the contrary, ozone treatment had not significantly changes in color of dried figs (Akbas and Ozdemir, 2008), carrots (Sharpe et al., 2009) and chili (Sintuya et al., 2018).

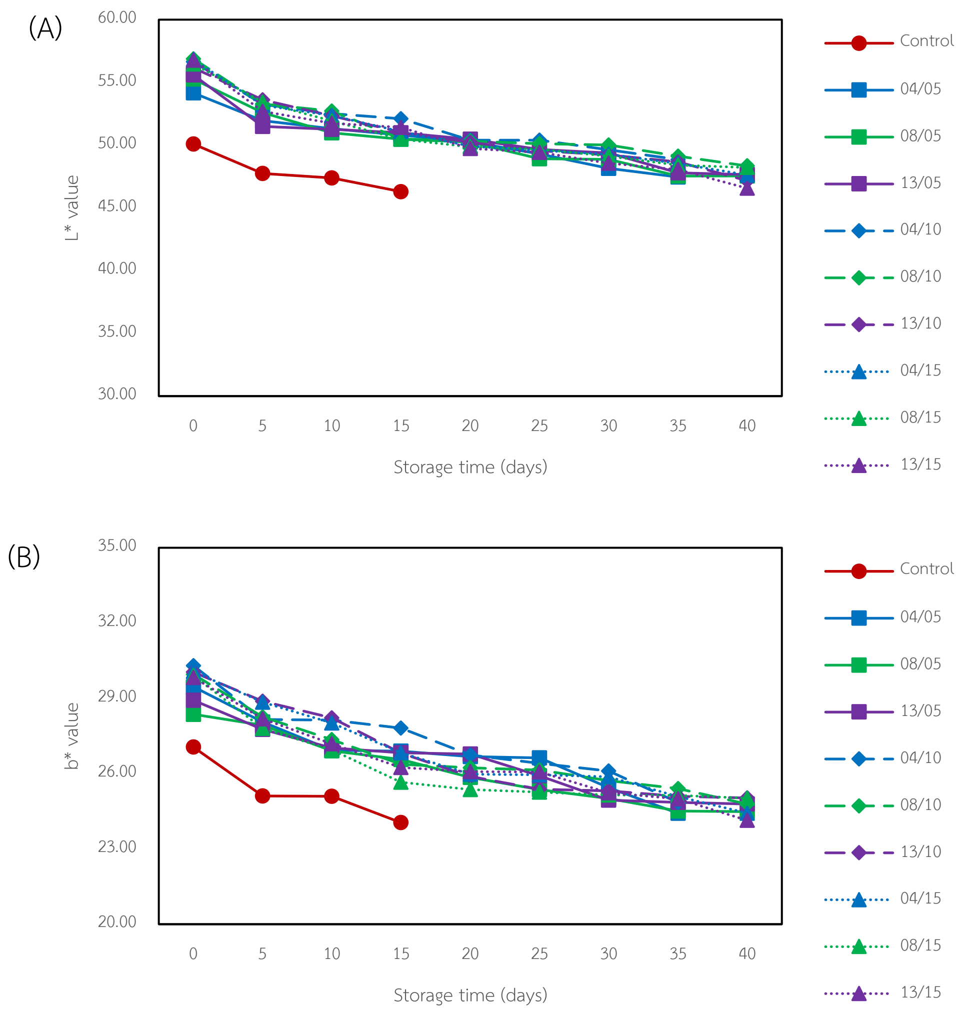


Figure 27 Effect of HCO treatment on color (A) L* value and (B) b* value of longan.

4.2.6 Sensory evaluation

Sensory evaluation of longan fruit consisted of fruit pericarp color, odor, flavor, firmness and acceptance by trained panelists. When storage time increased, sensory score of longan fruit all treatment decreased. HCO treatments had effect on pericarp color, odor (0 day), flavor (15th days) and acceptance score of longan fruit significantly ($p<0.05$) in Table 16. The control had less pericarp color score than treated ozone samples significantly ($p<0.05$). Pericarp color score was corresponding with L* value, when storage time increased both of pericarp color score and L* value decreased. Control sample had higher odor score (0 day) than HCO treatments significantly ($p<0.05$) in initial storage because the longan treated with ozone had less longan odor than control which affected the odor scores. Since ozone is one of the powerful oxidants, oxidation of the volatile compounds released by the fruit could be a reason for a reduction of fruit aromatic volatile compounds (Karaca and Velioglu, 2007). When storage time increased, the smell of longan gradually decreased, possibly due to ozone natural degradation in the air. Similarly, previous research by Karaca and Velioglu (2007) who reported that ozone treatment reduced 40% the emission of volatile esters in strawberries. For this reason, the HCO treatments on longan fruit yielded the odor scores in the same manner for all treatments at 15 days. Flavor (0 day) and firmness of all HCO treated longan decreased gradually with storage period and the HCO treatments did not significantly affect ($p\geq0.05$) flavor, firmness and eating quality at each period of storage time. The HCO treatments had more acceptance (15 days) score than without ozone treatment significantly ($p<0.05$). In day 0, acceptance score of longan fruit was slightly difference all treatment. Similar trend was also observed by Whangchai et al. (2011) who reported that the eating quality of lychee after fumigation with the ozone gas and control was not significant difference. Also our results corresponded to the work by Tzortzakis et al. (2007) who found that tomato fruit was exposed ozone concentration in range of 0.005-1.0 $\mu molmol^{-1}$ could maintain the firmness in comparison with tomato stored in traditional storage.

Table 16 Effects of HCO treatment on sensory evaluation for 15 days of longan.

Sensory evaluation	Days	Treatment									
		Control	04/05	08/05	13/05	04/10	08/10	13/10	04/15	08/15	13/15
- Pericarp color	0	2.00 ± 0.60^{c}	4.33 ± 1.67^{ab}	5.58 ± 2.43^{a}	5.00 ± 2.26^{ab}	5.00 ± 1.76^{ab}	5.25 ± 1.60^{a}	5.08 ± 2.23^{ab}	4.83 ± 1.53^{ab}	3.92 ± 1.24^{b}	4.75 ± 1.22^{ab}
	15	1.67 ± 0.65^{c}	2.75 ± 1.14^{b}	3.50 ± 1.17^{ab}	3.00 ± 1.04^{ab}	3.17 ± 1.27^{ab}	3.33 ± 1.07^{ab}	2.92 ± 0.78^{ab}	2.83 ± 0.94^{ab}	3.33 ± 1.15^{ab}	3.83 ± 1.34^{a}
- Odor	0	6.33 ± 1.61^{a}	4.50 ± 0.52^{b}	4.75 ± 1.06^{b}	4.67 ± 1.07^{b}	5.08 ± 1.44^{b}	4.67 ± 0.90^{b}	4.67 ± 1.50^{b}	5.00 ± 1.41^{b}	4.67 ± 1.44^{b}	4.58 ± 1.38^{b}
	15^{ns}	4.67 ± 1.72	4.33 ± 0.65	4.33 ± 0.78	4.50 ± 0.80	4.33 ± 0.65	4.25 ± 0.67	4.25 ± 0.45	4.25 ± 0.45	4.50 ± 0.90	4.50 ± 0.80
- Flavor	0^{ns}	5.58 ± 1.00	6.33 ± 1.56	5.92 ± 1.00	5.83 ± 0.94	5.83 ± 0.89	6.17 ± 0.94	6.00 ± 1.13	5.83 ± 0.94	6.00 ± 1.04	5.83 ± 0.83
	15	5.08 ± 1.00^{b}	6.00 ± 0.95^{a}	5.67 ± 0.65^{ab}	5.58 ± 1.31^{ab}	5.25 ± 0.83^{ab}	5.00 ± 1.00^{b}	5.33 ± 0.90^{ab}	5.42 ± 0.67^{ab}	5.50 ± 0.67^{ab}	5.50 ± 0.80^{ab}
- Firmness	0^{ns}	4.58 ± 1.51	5.08 ± 1.83	5.33 ± 1.23	5.00 ± 1.13	5.33 ± 1.04	5.67 ± 1.50	5.42 ± 1.56	5.42 ± 1.31	5.33 ± 1.15	5.33 ± 1.23
	15^{ns}	4.25 ± 1.14	4.58 ± 0.90	5.17 ± 0.94	4.33 ± 1.07	4.75 ± 1.30	4.75 ± 0.74	4.67 ± 1.00	4.58 ± 1.16	4.83 ± 1.27	4.42 ± 1.31
- Acceptance	0	5.08 ± 1.38^{b}	5.67 ± 1.61^{ab}	5.75 ± 0.87^{ab}	5.42 ± 1.00^{ab}	5.83 ± 0.94^{ab}	6.33 ± 0.65^{a}	5.83 ± 1.34^{ab}	6.08 ± 0.67^{a}	5.58 ± 1.08^{ab}	6.00 ± 0.95^{a}
	15	3.75 ± 1.60^{b}	5.08 ± 0.67^{a}	5.25 ± 0.87^{a}	5.08 ± 1.08^{a}	5.17 ± 0.89^{a}	4.92 ± 0.94^{a}	4.67 ± 1.03^{a}	5.08 ± 1.00^{a}	4.92 ± 0.90^{a}	5.00 ± 1.13^{a}

Data are means ± SD of three replicates

^{ns} means in the same row with different letters are not significantly different ($p \geq 0.05$)

$^{a-c}$ means in the same row with different letters are significantly different ($p<0.05$)

4.2.7 Shelf-life

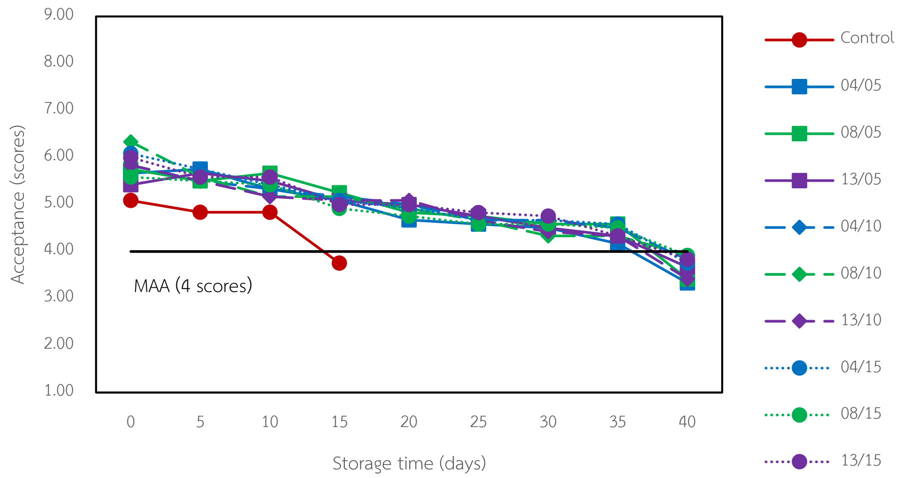


Figure 28 Effect of HCO treatment on acceptance scores of longan.

Note: MAA = Maximum acceptable acceptance scores at which less than 4 scores of consumers rejected the product.

Shelf-life of longan fruit was considered from a combination of disease incidence and acceptance sensory score. In Figure 23, disease incidence of the HCO longan was observed on day 30th (04/05 and 04/10), day 35th (08/05, 08/10 and 04/15) and day 40th (13/05, 13/10, 08/15 and 13/15). On the other hand, the acceptance score of longan in all treatments decreased when storage time increased. The control sample had less acceptance score (day 15th) than that of all HCO treatment. For this research, the acceptance score of the control sample was 10 days but all HCO treated longan had acceptance scores of 35 days storage at 5 °C (Figure 28). Shelf-life of the control was 10 days, while those of the HCO treatments were 30 days (04/05 and 04/10) and 35 days (08/05, 13/05, 08/10, 13/10, 04/15, 08/15 and 13/15) when storage at 5 °C shown in Table 17. With slightly different shelf-life result, longan treated with HCO at 4,000 ppm for 5 min from Part 1 (36 days) has more shelf-life than Part 2 (30 days) because the criteria to consider shelf-life of were different. Compared to Part 1 which considered only disease incidence, the criteria used in Part 2 was considered from a combination of disease incidence and acceptance score. This would give more accurate acceptance results towards consumer preferences. Another factor was quality of longan harvesting season. The off-season longan fruit had higher incidence cracking than the on-season longan fruit (Yang et al., 2010), which hade longan was more susceptible to cracking, caused the higher disease incidence and shorter shelf-life.

Table 17 Effect of HCO treatment on shelf-life of longan.

Code	Shelf-life (days)	Code	Shelf-life (days)	Code	Shelf-life (days)
Control	10				
04/05	30	04/10	30	04/15	35
08/05	35	08/10	35	08/15	35
13/05	35	13/10	35	13/15	35

Longan with HCO fumigated had longer shelf-life than those of untreated sample. Our result found much longer shelf-life of HCO longan fruits to previous report by Whangchai et al. (2011) which the eating quality of ozone treated lychee was only 6 days. Also, Zambre et al. (2010) found that tomatoes treated with ozone gas and stored at 15 ^{o}C prolonged shelf-life of strawberry by 12 days. Ozone at appropriate concentrations could induce resistance to pathogens by induction of the phytoalexins reveratrol and pterostilbene (Sarig et al., 1996), which extended shelf-life of longan fruit. The longer shelf-life in our work was due to a reduction in surface microbial count. Among HCO treatments, 08/05 sample was found as the optimal condition because the longest storage shelf-life and shortest total time for HCO fumigation of longan fruit (Table 14) compared with other treatments.

From results Part 2, the HCO treatments affected the fresh quality of longan fruit. The optimum HCO fumigation in this study was ozone concentration of 8,500 ppm and holding time 5 min because the longest shelf-life and shortest total time for HCO fumigated of longan fruit was obtained. This condition was to be used the next Part 3.

4.3 Kinetics of deterioration after HCO fumigation on the longan during cold storage

The objective of Part 3 was to study of kinetics of deterioration HCO longan during cold storage by simulating the container transportation. In this study, the optimal condition from Part 2 was applied with gaseous ozone concentration of 8,500 ppm for 5 min.

4.3.1 Gas composition

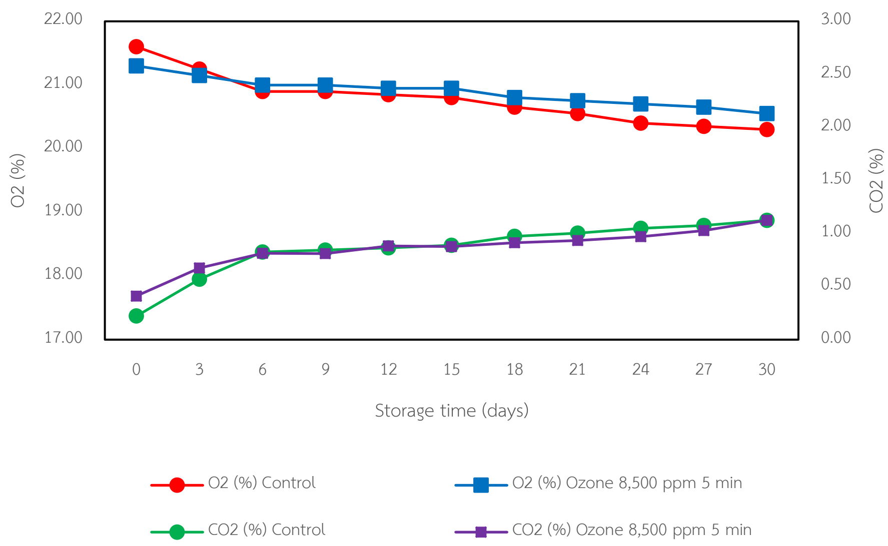


Figure 29 Relationship of gas composition during storage of longan fruit.

Figure 29, show the gas composition of HCO longan fruit during storage at 2 °C for 30 days. The respiration rate of HCO longan was determined by the gas composition in the container simulation. Ozone gas was not measured in this study due to rapid ozone decay into oxygen within 2 hours. Gas composition of oxygen and carbon dioxide concentration showed a no difference among all treated samples. The oxygen and carbon dioxide concentration were in range of 20.30-21.60% and 0.22-1.13%, respectively. When storage time increased, the carbon dioxide concentration increased but the oxygen concentration decreased. Our result corresponds to that of carrot samples which decreased in oxygen concentration and increased in carbon dioxide concentration during storage (Larsen and Wold, 2016). The low oxygen and high carbon dioxide concentration indicated a shift from aerobic to anaerobic metabolism in carrot sample, becaused it underwent the carbon dioxide production as a result of higher respiration.

4.3.2 Kinetics of deterioration

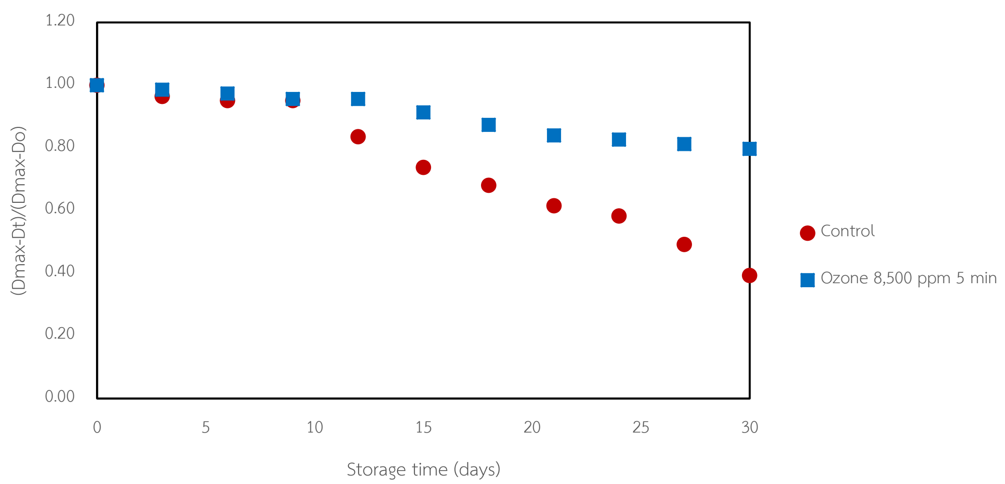


Figure 30 Correlation relationships between deterioration rate constants of longan fruit during storage.

Table 18 Kinetics parameters for the deterioration of the longan fruit during storage.

Treatment	k (day^{-1})	R^2
Non-treated ozone	2.45×10^{-2}	0.89
Treated ozone 8,500 ppm 5 min	0.74×10^{-2}	0.95

Kinetic curves of deterioration on untreated and treated HCO longan at 8,500 ppm for 5 mins of longan fruit at 2 °C based on modified Matar's model to experimental data were presented in Figure 30. Results indicated that the HCO treatment had an effect on deterioration rate constants in longan fruit. As the storage time increased, deterioration rate constants increased and followed the S-shaped curve. Deterioration kinetic parameters using the modified Matar's equation was shown in Table 18. All the R^2 of determination were more than 0.85, which indicated that the modified Matar's model could well-realize the simulation of deterioration condition in longan. The untreated and treated HCO longan showed deterioration rate constants (k) of 2.45×10^{-2} and 0.74×10^{-2} day^{-1}, respectively, meaning that the HCO treatment gave approximately 3 folds lower deterioration than the untreated longan. The greater deterioration rate constant indicated the faster deterioration of longan to decline. Similar to previous research by Pandiselvam et al. (2017) who reported that ozone fumigation is an alternative to conventional insecticides such as phosphine and methyl bromide for pest control treatments, which applied improve or maintain quality in grain. The reaction kinetics of ozone gas in grains used to the effect of ozone on stored grains, the total fumigation time of farm-level storage bin and optimize the design parameters of ozone fumigation bin. This was corresponded the study kinetic of deterioration in food such as frozen industrial burgers by Quevedo et al. (2018).

4.3.3 Quality parameter

1) Disease incidence

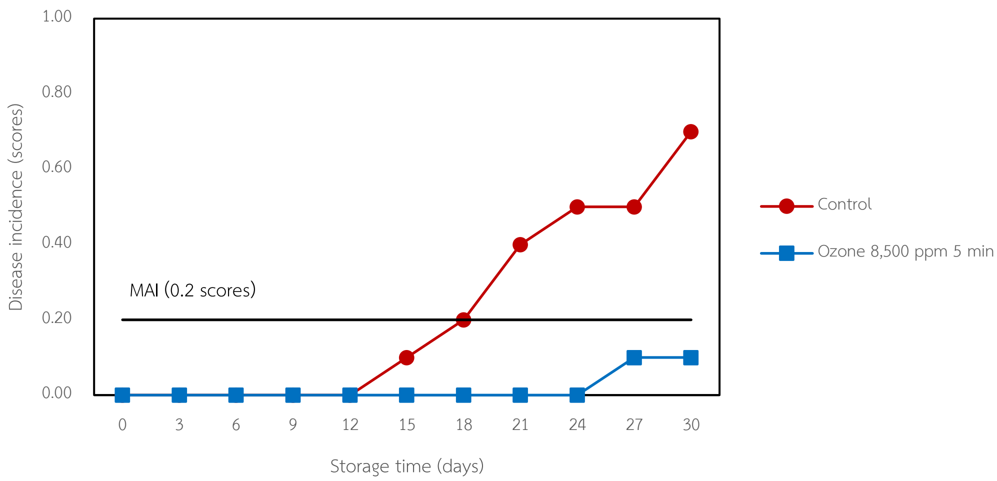


Figure 31 Disease incidence of longan fruit during storage.

Note: MAI = Maximum acceptable disease incidence at which ≥0.2 scores of consumers rejected the product.

In Figure 31, disease incidence of longan increased when storage time increased. The disease incidence of control sample emerged rapidly, up to 15 days and became unacceptable in 18 days. However, longans treated with HCO exhibited disease incidence in 27 days when stored at 2 °C. This was account for an extending 80% longer disease incidence as compared to the control. This is to confirm that ozone could destroy microorganisms by oxidizing the cellular components, which it affected to reduce the microorganism population in fruits (Victorin, 1992).

2) Pericarp browning

The pericarp browning of longans increased throughout its shelf-life (Figure 32). The longan fruit fumigated with gaseous ozone exhibited less pericarp browning than that of non-fumigated longan fruit. The HCO sample exhibited the pericarp browning score of 3.60, whereas the control sample exhibited the pericarp browning score of 5.00 at stored 2 °C in 30 days. Ozone may affect the inhibitory of polyphenol oxidase (PPO) enzymes as previously report on fruit and vegetables by Miller et al. (2013), which it caused of a slow pericarp browning of longan fruit.

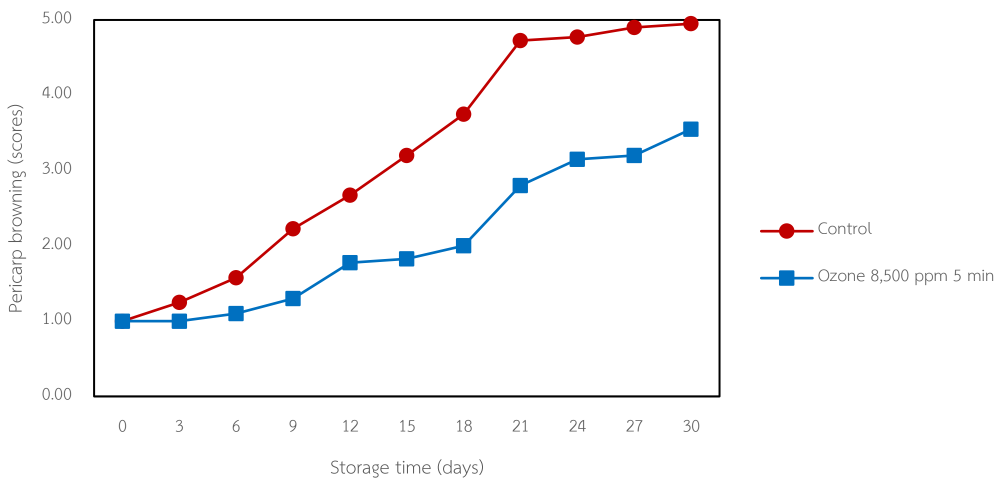


Figure 32 Pericarp browning of longan fruit during storage.

3) Weight loss

The weight loss (water loss) parameter is particularly interesting to evaluate the success of storage and affect the marketability of the fruits (Haffner et al., 2002). Weight loss of longan with and without HCO treatments were not different. When storage time increase, weight loss of longan increased. During a storage for 30 days, samples had weight loss in a range of 0-1.21% (Figure 33). Ozone had not much effect on weight loss of longan treatment, similar to the previous report by Giuggioli et al. (2015) who found that control and exposed with ozone concentration (500 ppb and between 50-200 ppb) samples had showed similar weight losses within range of 7.92-10.92% in raspberry fruits.

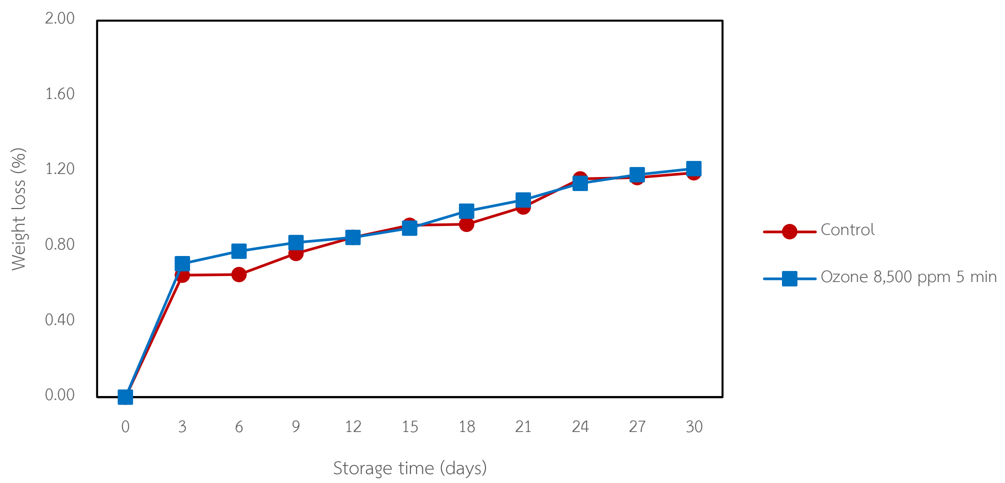
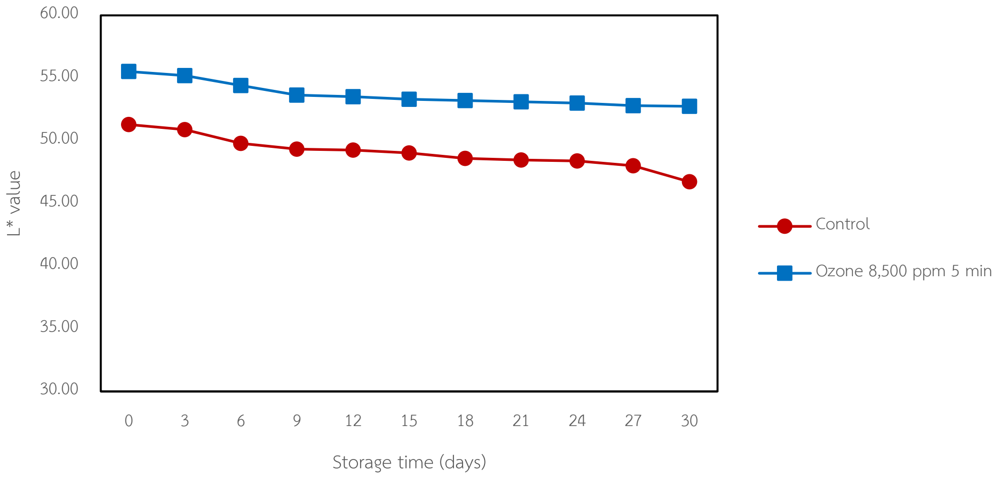


Figure 33 Weight loss of longan fruit during storage.

4) Color parameters

Color in the longan fruit at day 0, the L* value of longan fruit without and with HCO fumigation were 51.29 and 55.52, and the b* value were 27.24 and 29.91, respectively as shown in Figure 34 (A) and 34 (B). Color changes were affected by the HCO treatments because ozone could oxidize pigments and resulted in an increase in L* value of longan fruit (Taimaneerak et al., 2018) and raspberries (Giuggioli et al., 2015). When storage time increased, color parameters of both treatments tended to decrease, reflecting the darkening of fruits.

(A)



(B)

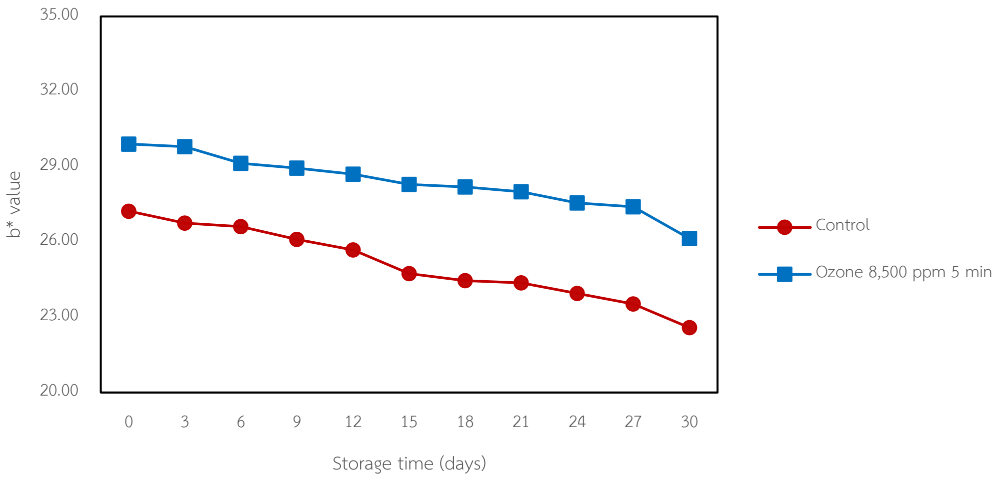


Figure 34 Color parameters

(A) L* value and (B) b* value of longan fruit during storage.

5) Overall acceptance

Overall acceptance of longan fruit to determine the disease incidence, pericarp color, odor, flavor and firmness by train panelist. For Figure 35, the overall acceptance of longan fruit all treatments decreased when storage time increased, result like to previous report by Whangchai et al. (2006) who found that eating quality of longan fruit treated with ozone decreased gradually, when increased storage period. Overall acceptance of longan fruit without and with ozone fumigation was in a range of 25.00-63.54% and 57.29-71.88%, respectively during storage at 2 ^{o}C for 30 days. At 0 days, overall acceptance both of longan fruit were difference. The control sample had quite dark color and make it less pericarp color than HCO treatment. Since day 9th the overall acceptance of control sample rapidly decreased, while that of HCO treatment gradually decreased throughout the storage period.

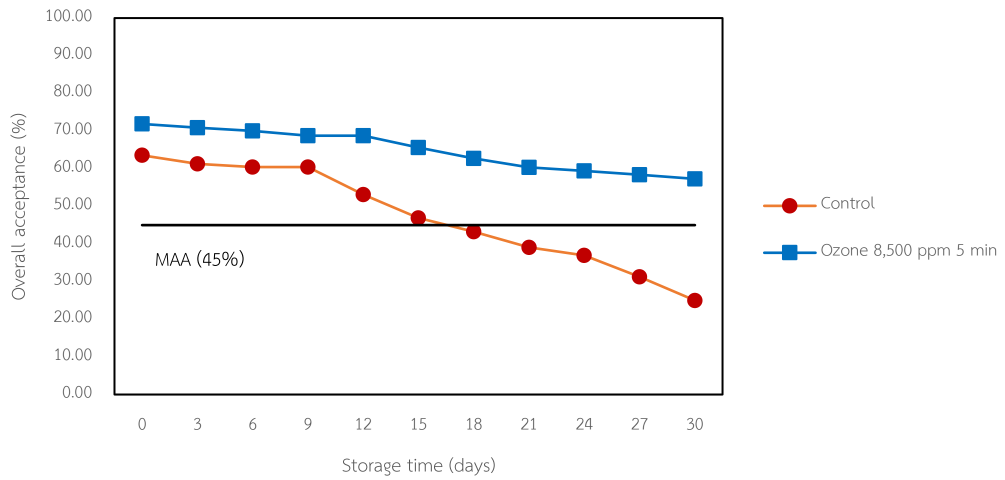


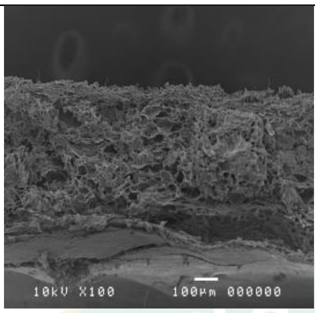
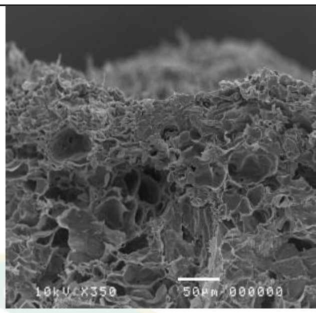
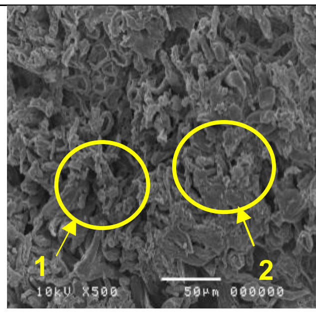
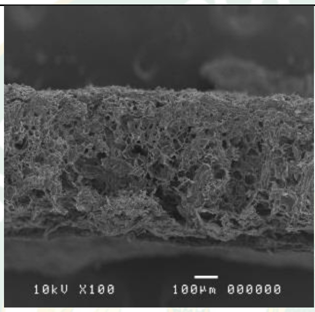
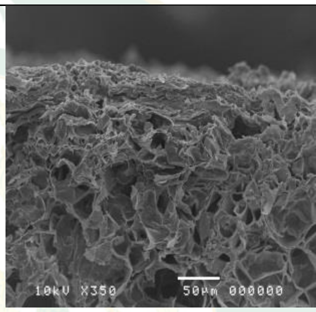
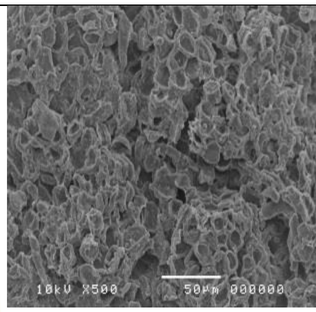
Figure 35 Overall acceptance of longan fruit during storage.

Note: MAA = Maximum acceptable overall acceptance at which less than 45% of consumers rejected the product.

6) Microstructure

The pericarp of longan consisted of three layers: epicarp, mesocarp and endocarp (Guo et al., 2010). In this work, the SEM images of longan epicarp illustrates a typical cross and surface morphology in comparison between HCO treatment and the control (Table 19). It was observed that surface of longan fruit epicarp had tumordial honeycomb-liked shape (1) on the bottom and epidermal hairs (2) on the top of surface epicarp longan fruit (Guo et al., 2010). The control sample had less honeycomb shape and more epidermal hairs than the HCO treatments on surface epicarp longan fruit. From cross section of epicarp longan fruit, the control had larger pore than the HCO-treated longan. The epidermal hairs inhabit the microorganism which cause fruit deterioration. For HCO treatments, when concentration of ozone gas increased, epidermal hairs of HCO treatments had more fallen off, therefore it is less susceptible to be inhabitant of microorganisms so that the deterioration occur slower than that of the control.

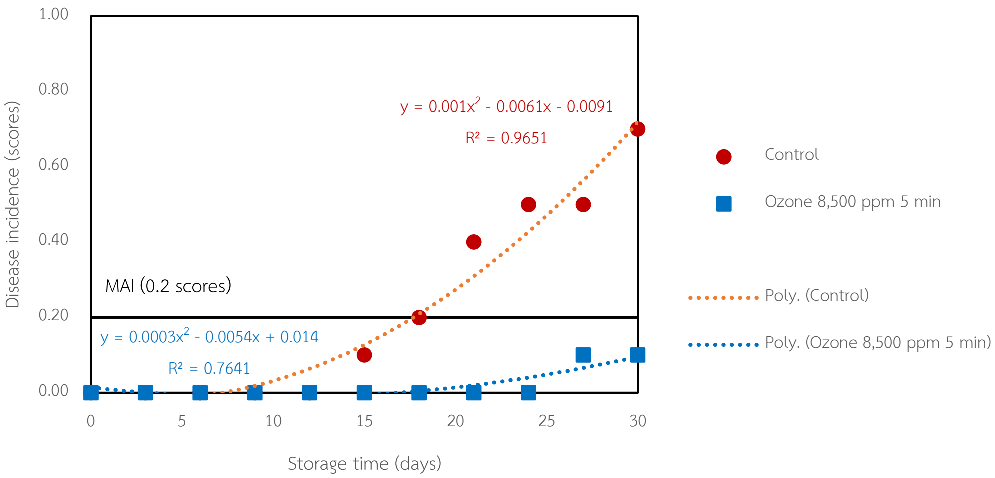
Table 19 SEM micrographs (50 μm) of the control and HCO treatment of longan epicarp cross and surface section.

Treatment	cross section 100X	cross section 350X	surface section 500X
Control			
HCO Treatment			

During our experiment, we also observed a smoother longan skin surface with bare-handed touch on the HCO longan than that on the control. This also confirmed the SEM analysis on the loss of epidermal hair loss due to the HCO treatment. Ozone could degrade cell walls in some other fruits such as kiwifruit (Minas et al., 2014) and reactive oxygen species (ROS) by necrotic damage or induce the process of programmed cell death in plant (KangasjÄRvi et al., 2005). Therefore, the used of suitable ozone condition (concentration and time, referred as dose) was necessary for maintain quality and extending shelf-life of longan. If ozone dose exceeds ozone tolerance of the fruit, it may cell walls causing degrading crack and subsequent penetration of microorganism into pericarp of longan fruit. If ozone dosage was too low, it may not be effective enough to destroy microorganism on longan, causing the high disease incidence of longan fruit.

7) Predict of shelf-life

(A)



(B)

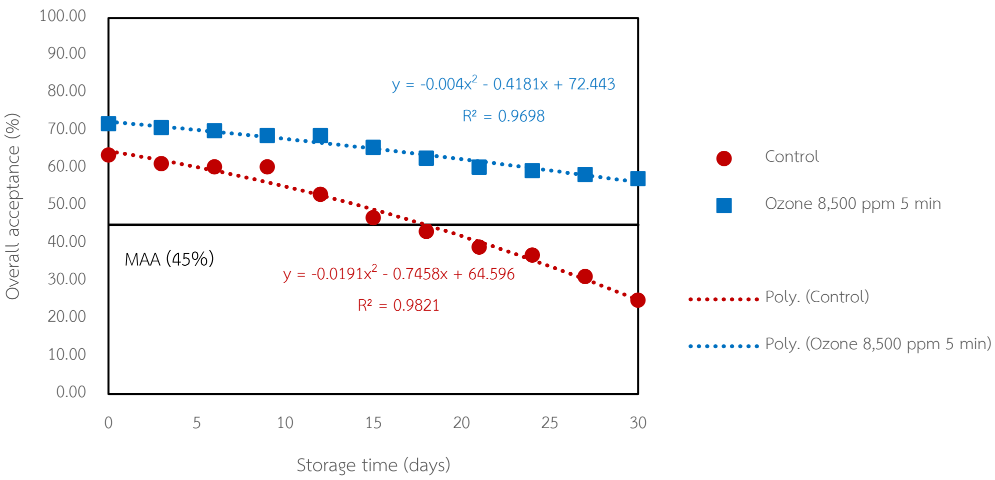


Figure 36 Prediction and experimental data of shelf-life;

(A) disease incidence and (B) overall acceptance of longan fruit during storage.

Note: MAI = Maximum acceptable disease incidence at which ≥0.2 scores

of consumers rejected the product.

MAA = Maximum acceptable overall acceptance at which less than 45%

of consumers rejected the product.

Figure 36 (A), also showed that the predicted disease incidence for the control was higher than HCO treatment during storage time for 30 days. The prediction of control follows equation $y = 0.001x^2 - 0.0061x - 0.0091$ with $R^2 = 0.9651$, while HCO treatment is $y = 0.0003x^2 - 0.0054x + 0.014$ with $R^2 = 0.7641$. Both of samples were polynomial equation. Based on Figure 36 (A) with a given MAI of 0.2 scores, the estimated HCO treatment laid above the MAI limit, but the control was 17.8 days of storage. Figure 36 (B), showed the predicted overall acceptance for the control and HCO treatment under 2 °C storage temperature. The overall acceptance in HCO longan was higher than that of the control throughout storage period. The prediction of acceptance of the control follows equation $y = -0.0191x^2 - 0.7458x + 64.596$ with $R^2 = 0.9821$, while that of the HCO longan follows equation $y = -0.004x^2 - 0.4181x + 72.443$ with $R^2 = 0.9698$. Overall acceptance limit needed to exceeded the MAA (45%). The control was 18.0 days, while HCO longan laid above the MAA limit. Therefore, the disease incidence and overall acceptance was dependent factor to predict the longan shelf-life.

The predicted shelf-life for longan during cold storage in transportation container, simulation (A) control and (B) ozone 8,500 ppm 5 min, is shown in Figure 37. This simulation showed that an increasing disease incidence and decreasing overall acceptance represented the overall extension of shelf-life. For longan shelf-life prediction, the disease incidence and overall acceptance based-lines were 17.8 and 18.0 days for control, as compared to 35.5 and 45.7 days for the HCO longan. When longan shelf-life prediction using combined disease incidence and overall acceptance the control and HCO longan had shelf-life of 17.8 and 35.5 days, respectively. This confirmed that disease incidence and overall acceptance were dependent factors to determine the shelf-life prediction of longan fruit. If we simulate the transportation of longan shipment from Thailand to China, the major part of disease incidence and overall acceptance occurred after the longan fruit reached to the China about 5-6 days; therefore, the longan fruit remained within acceptable quality for a period. Our results agreed with Zambre et al. (2010) who report that ozone concentration 35 ppm treated with tomatoes could enhanced shelf-life by 12 days when stored at 15 °C. The longer shelf-life was mainly due to a reduction in surface microbial count.

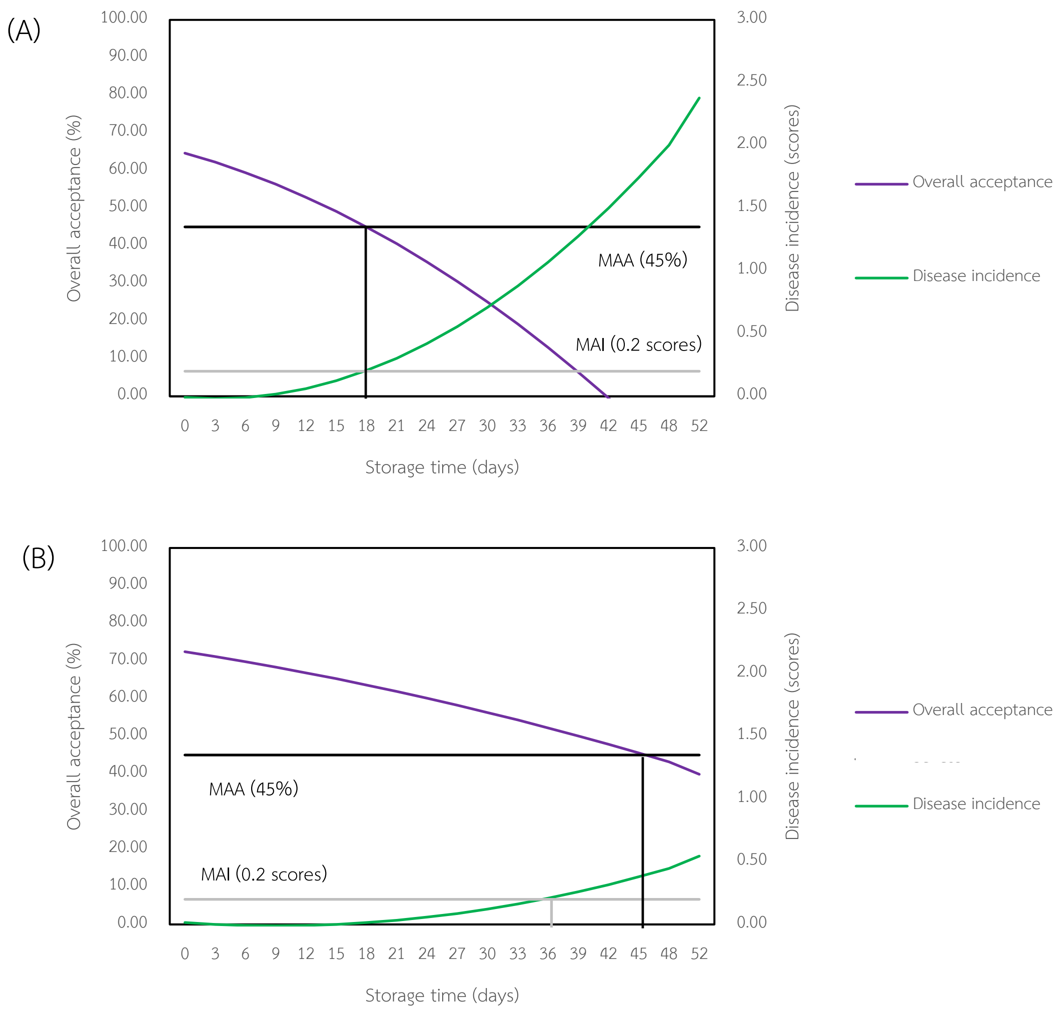


Figure 37 Predict shelf-life

(A) control and (B) ozone 8,500 ppm 5 min of longan fruit during storage.

Note: MAI = Maximum acceptable disease incidence at which ≥0.2 scores of consumers rejected the product.

MAA = Maximum acceptable overall acceptance at which less than 45% of consumers rejected the product.

In addition, ozone concentrations 0.075 and 0.15 ppm could extend the shelf-life of strawberries by at least 3 weeks under refrigerated conditions (Aday et al., 2014). Thus, our proposed model would enable optimize the shelf-life of longan during cold storage for the oversea shipment. Further study are needed to confirmed the actual shipment with HCO condition to extend the shelf-life of longan fruit during oversea transportation.

To conclude the results in Part 3, we found the kinetic study of deterioration on ozone fumigation longan at 2 ^{o}C showed deterioration rate constants (k) of $0.74x10^{-2}$ day^{-1}, which was 3 folds smaller than that of the controls. The SEM images on epicarp longan revealed that the control had less honeycomb shape of cell, more epidermal hairs and larger pore than those of HCO treatments. The ozone fumigation inhibits the growth of microorganism causing slower deterioration of longan. Prediction of longan shelf-life was developed following the polynomial equation. The simulation of longan shipment transportation showed that the control had less shelf-life than HCO longan by 17.7 days.

CHAPTER 5
CONCLUSION

This dissertation presents a study of pressurized ozone fumigation process for extending shelf-life on longan fruit. It consists of 3 objectives and experiments accordingly, as follows:

1. To determine the suitable packaging for HCO longan during storage
2. To determine the ozone fumigation conditions to achieve the good quality of longan fruit
3. To investigate the kinetics of deterioration of HCO longan during cold storage

In the first part, it was found that longan without HCO treatment had more incidences of disease, pericarp browning, and weight loss in storage for 15 days than that of those HCO longan. With ozone fumigation, the disease incidences, weight loss and shelf-life of the longan fruit yielded positive result, depending upon on the type of packaging materials. Using ozone fumigation combined with PE packaging was the optimum treatment, resulting in a storage shelf-life of longan up to 36 days.

In the second part, we found that the HCO treatments affected the fresh quality of longan fruit. The optimum HCO fumigation and storage condition in this study was optimized with ozone concentration of 8,500 ppm treated for 5 min and stored at 5 ^{o}C. This results in storage shelf-life up to 35 days.

In the third part, the kinetic study indicated that deterioration on ozone fumigation longan at 2 ^{o}C showed deterioration rate constants (k) of 0.74×10^{-2} day^{-1}, which was 3 folds smaller than that of the control. When storage time increased, carbon dioxide, weight loss, pericarp browning and disease incidence increased, while oxygen, pericarp color (L* and b*) and overall acceptance decreased. The SEM images revealed that the control had less honeycomb shape of cell, more epidermal hairs and larger pore than those of HCO treatments on epicarp longan fruit. The ozone fumigation may inhibit the growth of microorganisms causing slower deterioration of longan. Predicting model follows the polynomial equation where the HCO longan had shelf-life of 35.5 days, which was 2 folds more shelf-life than the control. Simulation Ozone fumigation can be an alternative to the Sulphur Dioxide to effectively reduce deterioration of longan and to improve food safety of longan in future.

Novelty of this research

- HCO treatment was found to be a new method, it can be an alternative to effectively reduce deterioration, improve or maintain qualities and safety of longan and other agricultural fruit. This could be proposed as the food processing innovation of longan fruit.
- HCO treatment exhibits a great potential to be further developed as a rapid method of longan in the industrial scale. This method could be further applied in other agricultural fruit or techniques.
- The modified correlation was established to predict the shelf-life of longan fruit. This correlation provides the varied characteristic such as disease incidence and overall acceptance, and can simulate the shelf-life of longan during oversea transportation.

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APPENDIX

APPENDIX A

Longan picture

Table 20 General characteristics of longan all treatment in 0 days (Part 2).

Exposure time (min)	Ozone gas concentration (ppm)			
	0	4,000	8,500	13,000
0		-	-	-
5	-			
10	-			
15	-			

APPENDIX B

Quality analysis

Table 21 Disease incidence level of longan fruit.

Level	**0**	**1**	**2**	**3**	**4**	**5**
Picture						
Meaning	No disease	Lesion area of fungal infection on each fruit surface 1-20%	Lesion area of fungal infection on each fruit surface 21-40%	Lesion area of fungal infection on each fruit surface 41-60%	Lesion area of fungal infection on each fruit surface 61-80%	Lesion area of fungal infection on each fruit surface 81-100%

Table 22 Pericarp browning level of longan fruit.

Level	**1**	**2**	**3**	**4**	**5**
Picture					
Meaning	Browning area appeared on each fruit pericarp 0-20%	Browning area appeared on each fruit pericarp 21-40%	Browning area appeared on each fruit pericarp 41-60%	Browning area appeared on each fruit pericarp 61-80%	Browning area appeared on each fruit pericarp 81-100%

APPENDIX C

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The Effect of Packaging Materials on the Quality of Freshness of Longan Fumigated with Medium Concentration-ozone Gas

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ABSTRACT

The objective of this research was to evaluate the performance of a medium concentration-ozone treatment in maintaining the quality of freshness of "Daw" longan packed in different types of packaging materials. For fumigation with ozone gas, a batch size of 3 kg of longan fruit was fumigated for 5 minutes at a concentration of 4,000 ppm. The longan was then packed in three different types of packaging- polyethylene (PE), polypropylene (PP) and wrap film (WF), and was then stored at 5°C for a shelf life of up to 36 days. Non-ozonated longan was kept as a control. The results showed that as storage time lengthened, the longan became more susceptible to disease incidences, pericarp browning, and weight loss under all treatments. During storage, the longan slightly changed in its firmness although there was no significant difference ($p \geq 0.05$) among the three different types of packaging. The ozonated longan stored in PE, PP, WF, and those with no-packaging had more L* and b* values and a longer shelf life, than those of the control. Among the three different types of packaging, the ozone fumigated longan stored in PE yielded the longest storage time with a shelf life of up to 36 days; an extended 140% longer shelf life as compared to the control.

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INTRODUCTION

One of the economically important fruits in the north of Thailand is longan (*Dimocarpus longan* Lour). China, Indonesia, Vietnam, Hong Kong and Malaysia are important trading countries of fresh longan fruit with Thailand (Department of International Trade Promotion, 2017). Unfortunately, longan rots easily in nature, rendering it susceptible to various postharvest pathogens intrusion which shortens the longan's shelf life at room temperature (Saengnil et al., 2014). This main problem results in restrictions on the export of longan to long distant markets due to rapid pericarp browning during storage (Sardsud et al., 1994).

Ozone is one of the powerful oxidants and has the strong capacity of disinfection and sterilization. It is a powerful germicide which destroys bacteria and fungi. Ozone gas has a longer half-life than in aqueous ozone solution (Gonçalves & Kechinski, 2011). Ozone has been confirmed as GRAS status, as a food processing aid and is compliant with the Environmental Protection Agency Disinfection by Products Rule (Ong et al., 2014). Ozone is an effective treatment for increasing shelf life and in decreasing fungal deterioration in the postharvest treatment of fresh vegetables and fruits such as tomatoes where its shelf life can be extended from 16 to 48 days (Zambre et al., 2010) as compared with control. Other fruits that yielded positive results after ozone treatment include stone fruit (Palou et al., 2002), strawberry (Thaer et al., 2013) and the papaya fruit (Ong et al., 2014), have been well documented.

Materials used for food packaging are essential to prevent physical damage to the product in order to obtain optimal shelf life. In addition, proper packaging has the proper characteristic of permeability, where a desirable equilibrium could modify the atmosphere when the rate of gas (oxygen and carbon dioxide) transmission permeating the packaging and thus balancing the respiration rate of the fruit (Kartal et al., 2012). Most packaging of fresh fruit uses polyethylene (PE) and polypropylene (PP) bags because of low water vapour permeability (Ščetar et al., 2010). Similarly, Sahoo et al. (2015) reported that the shelf life of pointed gourds packed in PP film and under refrigerated condition lasted for up to 16 days, while the shelf life of pointed gourds packed in LDPE film under ambient conditions could extend up to 4 days. The packaging of pointed gourds created a suitable headspace environment with low oxygen and high carbon dioxide concentrations. Chillies packed in microporous, PE-LD, polyolefin and anti-fog films had a shelf life of 16, 18, 22 and 28 days, respectively. In addition, control samples had shelf life of 15 days (Chitravathi et al., 2015).

Since ozone exhibits a high potential to extend shelf life of agricultural products, it can be used in combination with the proper packing material to prolong the shelf life of longan.

Thus, the objective of this study is to evaluate the effectiveness of fumigation with gaseous ozone, and the suitability in packaging, on the quality of freshness of longan during cold storage which could prevent desiccation, and which prolongs the shelf life of longan fruit.

MATERIALS AND METHODS

Longan Fruit Sample

Longan (*Dimocarpus longan* Lour.) cv. "Daw", harvested in less than 3 days from the orchards in Chiang Mai, Thailand, was used in this study. The fruit was graded for uniformity of size (grade AA with a size of 30 mm. in diameter), color and non-disease appearance.

Ozone Fumigation System

The ozone fumigation system consisted of a corona discharge ozone generator from purified oxygen gas. The generator connected with the control system using a Labview™ program access through a wireless network. The system connected to a fumigation chamber of $0.4 \times 0.4 \times 1.2$ m^3. The system conveyed ozone gas by silicone tube. The optimum flow rate of ozone gas was 7.5 L/min and back pressure 12 kPa. The output of generating ozone gas was 5.5 g/h (Changchai et al., 2015). Ozone concentration was measured by an ozone gas sensor connected with a data logger. This data logger was calibrated by an ozone gas-sampling pump with a detector tube (Gastec Model GV-100, Japan).

Ozone Fumigation Treatment and Quality Evaluation

Longan fruit with a batch size of 3 kg was filled in a polycarbonate container. For fumigation process, the longan sample was fumigated with ozone gas at a concentration of 4,000ppm and held under pressure for 5 minutes. Longan fruit with and without fumigation were of packed size of 200g per pack. Accordingly, the longans were packed using 3 different types of packaging, namely, polyethylene (PE), polypropylene (PP) and foam tray wrap with film (WF), and stored at 5°C 95% RH until the end of shelf life. Treatments according to packaging type were defined by codenames as follows:

Untreated with gaseous ozone:

NC = control without packaging　　NE = packed with PE

NP = packed with PP　　NF = packed with WF

Treated with ozone gas:

OC = control without packaging　　OE = packed with PE

OP = packed with PP　　OF = packed with WF

The properties of these films used for packaging experiments are given in Table 1. The fruit was determined for its quality analysis immediately after fumigation and every three days for disease incidence, pericarp browning, weight loss, firmness, color and shelf life evaluation.

Table 1

Permeability of gas through plastic films (Hernandez, 1997)

Permeability	PE	PP	WF
Water (g μm/m² d kPa) at 37.8°C	66-99	16.5-26	330-2,000
Oxygen (cc(STP)·μm/m²·d·kPa) at 25°C	1,940	622	389-3,900
Carbon dioxide (cc(STP)·μm/m²·d·kPa) at 25°C	10,490	2,100	1,170-2,330

Determination of Disease Incidence

Disease incidence was assessed by measuring lesion area of fungal infection on each fruit's surface. Disease incidence was scored into levels as: Level 0 = no disease; Level 1 = 1-20%; Level 2 = 21-40%; Level 3 = 41-60%; Level 4 = 61-80%; and Level 5 = 81-100%. Longan fruit evaluated at a score > 0.20 were considered unacceptable for marketing.

Determination of Pericarp Browning

Pericarp browning was determined by estimating the browning area that appeared on each fruit's pericarp due to deterioration of the longan's shelf life during storage. The measurement was scored into 5 levels with respect to it browning area as Level 1 (0 - 20%), Level 2 (21 - 40%), Level 3 (41 – 60%), Level 4 (61- 80%) and Level 5 (81- 100%)

Determination of Weight Loss

Two batches of 200g treated samples were weighed for weight loss using 2 digits digital balance with ± 0.01 g accuracy (model CP3202S, Sartorius, Germany). After weighing, the fruit was returned to storage cabinet at 5°C and 95%RH. The same batch of treated fruit was repeatedly weighed throughout storage time. Weight loss was expressed as Equation 1.

$$\text{Weight loss (\%)} = \frac{\text{(initial weight - final weight)}}{\text{initial weight}} \times 100 \qquad (1)$$

Determination of Firmness

Firmness analysis of 5 longan fruits from each treatment was selected at random where each fruit was penetrated on one side using a Texture Analyzer with ±0.1 g accuracy (model TA.XT-PLUS, Stable Micro Systems, UK). The firmness test applied a cylinder plunger SMS-P/2 probe (2 mm diameter), compressed by 20%strain using cross-head speed of pre-test, test, and post-test speed of 3 mm/s, 1 mm/s and 10 mm/s, respectively.

Determination of Color

The color of longan fruits was measured on the surface using a spectrophotometer with ±5 nm accuracy (model Mini Scan XE PLUS 45/0-S, Hunter Lab, USA). The means of L* (lightness) and b* (yellowness and blueness) were reported according to the consumer preference on visual appearance of longan fruit with a yellow to light brown color (Jiang et al., 2002).

Determination of Shelf Life Evaluation

The shelf life of longan fruit was determined by disease incidence, immediately after fumigation and every 3 day-intervals during storage. The fruit was considered to be at the end of its shelf life when disease incidence of the fruit was evaluated with score > 0.20.

Experimental Design and Statistical Analysis

The experiment was designed using factorial experimental design in a randomized complete block design (RCBD). Data were statistically analyzed by analysis of variance (ANOVA), and was carried out using SPSS 16.0. Duncan's Multiple Range Tests (DMRT) at a significance level of 0.05. Among the various treatments, the p-value less than 0.05 was considered as a significant difference.

RESULTS AND DISCUSSION

Effects on Disease Incidence

The first parameter related with the shelf life of the fruit can be defined as disease incidence. For Figure 1A, disease incidence of longan all treatments increased when storage time increased. The disease incidence of NC sample increased rapidly in 18 days. Longan treated with gaseous ozone exhibited less disease incidence than those of untreated samples when stored at 5°C. This corresponds with Ong et al. (2013) who found that ozone treatment reduced disease incidence up to 40% in papaya fruit. Other researchers also reported that ozone fumigation reduced the microorganism population in fruits such as longan fruit (Whangchai et al., 2006), date fruit (Habibi & Haddad, 2009), strawberry (Aday & Caner, 2014) and table grapes (Gabler et al., 2010) because it destroyed microorganisms by oxidizing the cellular components of cell fruit (Victorin, 1992). In our study, longan fruit packed in PE exhibited the least disease incidence when compared to PP, WF and without packaging. Since PE had more carbon dioxide (CO_2) permeability than other films (Table 1), it is possible that CO_2 might permeate to environment easier than those packed in other packaging. As a result, the ozonated longan packed in PE emerged less disease incidence than the others. The low percentages of diseases incidence in PE also slow down the rate of pathological disorder in PE films as well.

Effects on Pericarp Browning

The pericarp browning of longans under all treatments increased throughout shelf life (Figure 1B). At day 0, the longan fruit fumigated with gaseous ozone significantly exhibited less pericarp browning than that of non-fumigate longan fruit ($p<0.05$). When stored for 15 days, the OE sample exhibited the least pericarp browning score of 1.80, whereas the NC sample exhibited the highest pericarp browning score of 4.40. Correspondingly, Whangchai et al. (2006) reported that with the increase of storage time, longan fruit treated with low concentration ozone showed an increase in pericarp browning because of the time limit in ozone efficiency to inhibit browning of longan fruit.

Effects on Weight Loss

Gaseous ozone treatments did not significantly affect ($p\geq0.05$) the weight loss of longan fruit, however, type of packaging significantly did ($p<0.05$). During 15 days in storage, longan fruits with no packaging gained more weight loss than those packed in WF, PE, and PP, respectively. The NC sample had the highest weight loss of 9.39% in 15 days. These results agreed with Mistriotis et al. (2016) who suggested that unwrapped samples (cherry tomatoes and peaches) had more weight loss than samples packed in PLA and OPP film. When storage time lengthened, longan fruit under all treatments was susceptible to weight loss. The OE sample had the highest weight loss of 13.42% in 36 days, as shown in Figure 1C. An increase in weight loss of longan is normally due to evaporation and respiration (water and heat production), but under different packaging types, it yielded different responses (Chitravathi et al., 2015).

Effects on Firmness

Firmness can be defined as the parameter which is related to cell wall strength and intercellular adhesion (Toivonen & Brummell, 2008). In Figure 1D, gaseous ozone treatments and packaging types did not significantly affect ($p\geq0.05$) the firmness of the longan fruit. During storage at 5°C, the firmness of longan was within a range of 9.98 to 10.04 N. Longan fruit changed slightly in firmness but with no significant difference ($p\geq0.05$). The firmness did not change. This may be due to lesser loss of moisture from the surface of longan fruit. In contrast to other fruits, Aday and Caner (2014) reported that significant difference in firmness values was observed between ozone treated and ozone untreated strawberries. All treated strawberries had higher firmness values than the control group. Pointed gourd in all packaging types had peak force decreased during storage under ambient and refrigerated storage condition (Sahoo et al., 2015).

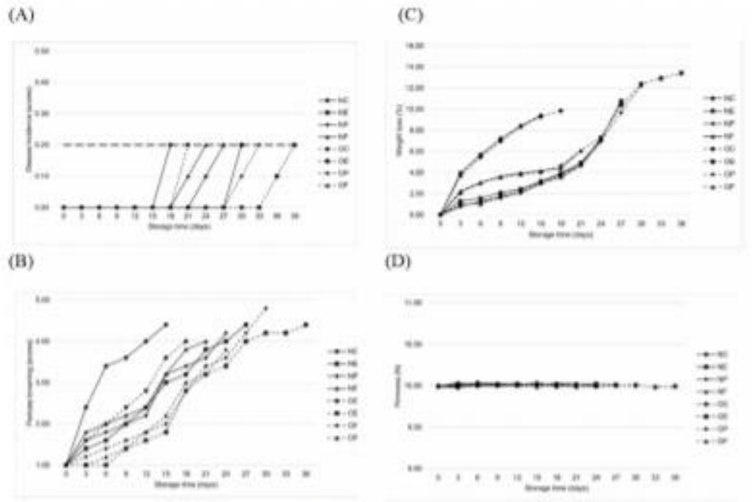

Figure 1. Effect of ozone fumigation and packaging materials on physicochemical properties of longan fruit during storage at 5°C: (A) disease incidence, (B) pericarp browning, (C) weight loss, and (D) firmness. Each data point represents a mean of three replicates (n=3)

Effects on Color

Color is the one factor in deciding visual attributes for buying and selling of longan fruit (Apai, 2010). At day 0, longan fruit without ozone fumigation possessed the L* and b* of 49.80 and 28.64. When fumigated with ozone gas, the longan had increased in L* and b* to 52.64 and 30.29, respectively. Ozone may cause an increase in L* of longan due to the bleaching effect (Forney, 2003). During storage at 5°C, the ozonated longan stored in PE, PP, WF and without packaging had more L* and b* (light yellow-brown color) as well as a longer shelf life than those of the untreated longan (dark brown color), as shown in Figure 2A and 2B. Similar trend was also observed by Aday and Caner (2014) who suggested that strawberries with ozone treatments and storage times were significant factors affecting the L*.

Effects on Shelf Life

The shelf life of longan fruit due to effects of ozone treatment and storage packaging type was determined by disease incidence, as shown in Figure 1A and Table 2. Longan fumigated with ozone gas had a longer shelf life than untreated samples. The ozonated longan packed in PE had a longer shelf life than that of PP, WF and those with no packaging when stored at 5°C. Among three different types of packaging, the ozone fumigated longan stored in PE yielded the longest storage time up to 36 days, equivalent to 140% longer shelf life than that of the control. According to Zambre et al. (2010), tomatoes treated with ozone gas and stored at 15°C had a prolonged shelf life of tomato by 22 days. The longer shelf life of longan was possibly due to a reduction in the surface microbial count in combination with proper modified atmosphere effect inside the package. The modified gaseous composition in the different packaging created a suitable headspace with low oxygen and high carbon dioxide, which resulted in maintaining the quality and marketability of vegetables (Sahoo et al., 2015). Our results also agreed with that of Mangaraj et al. (2012) who found that the modified atmosphere packaging extended shelf life of the litchi fruit from 100 to 150% compared with unpackaged fruits.

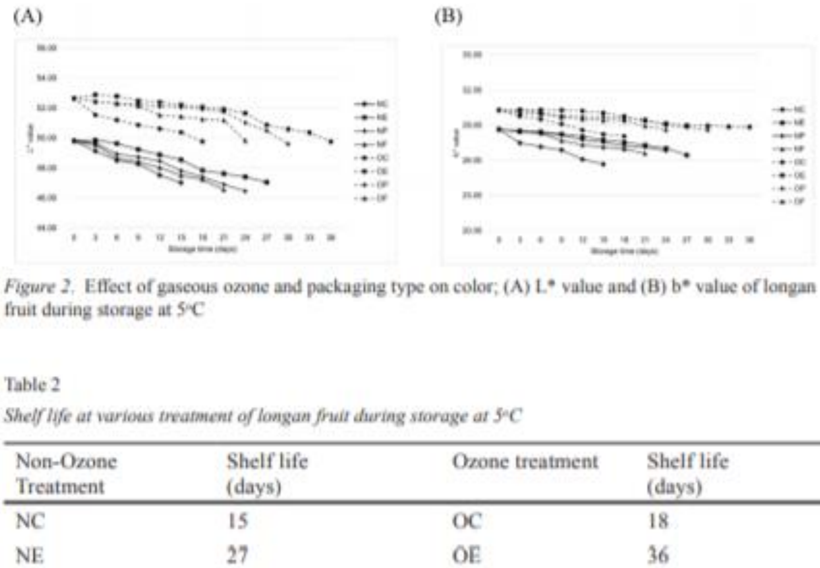

Figure 2. Effect of gaseous ozone and packaging type on color; (A) L* value and (B) b* value of longan fruit during storage at 5°C

Table 2

Shelf life at various treatment of longan fruit during storage at 5°C

Non-Ozone Treatment	Shelf life (days)	Ozone treatment	Shelf life (days)
NC	15	OC	18
NE	27	OE	36
NP	24	OP	30
NF	21	OF	24

CONCLUSION

Gaseous ozone treatment and the type of storage packaging materials are two important factors affecting the quality of freshness of the longan fruit. Without ozone fumigation, longan fruit had more incidences of disease, pericarp browning, and weight loss, with less L* and b* in storage for 15 days. With ozone fumigation, the disease incidences, weight loss and shelf life of the longan fruit yielded positive effects, depending upon on the type of packaging materials. Using ozone fumigation combined with PE packaging was the optimum treatment that resulted in a storage shelf life up to 36 days. It is suggested that a combined treatment of a varied concentration of ozone fumigation, with more variety of packaging materials and storage conditions, can be further studied to improve the shelf life of fresh longan.

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