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Effects of ozone fumigation on shelf life and sulfur dioxide residues of longan fruit

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Abstract The result of reducing SO_2 by O_3 fumigation found that O_3 fumigation for 120 min. before SO_2 fumigation at the concentrations of 1.2%, 1.0% and SO_2 commercial prevented pericarp browning for 42 days, while SO_2 commercial treatment was 35 days. The usages of O_3 prior to SO_2 or SO_2 prior to O_3 fumigation did not reflect significant differences from the SO_2 fumigation in commercial practice. For the prolonged shelf life, it was found that O_3 fumigation for 120 min. prior to SO_2 1.2% application extended shelf life for 28 days compared with commercial SO_2 fumigation of 21 days. This study showed that SO_2 at the concentration of 1.0 and 1.2% fumigation made the SO_2 residue in longan flesh lower than 50 mg/kg which it recommended that SO_2 residue was decreased by the storage time.

Keywords: Longan fruit, Ozone fumigation, Sulfur dioxide

Introduction

Longan (*Dimocarpus longan* Lour.) cv. Daw is an important economic exported fruit of Thailand. Longan is a non-climacteric fruit (Jiang *et al*., 2002). It has very short postharvest life of 3-4 days under ambient temperatures (Tongdee, 2001). The main factors that reduce the storage life and marketability of longan fruit are pericarp browning, fungal and microbial decay (Shi *et al*., 2013). Pericarp browning was associated with desiccation and/or heat stress, senescence, chilling injury and pest or pathogen attack. Although it is a visual symptom and has no effect on flavor, color deterioration causes the fruit to bring a low price in the market and even becomes unremarkable because of consumers preference for visual appearance (Jiang *et al*., 2002).

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Sulfur dioxide fumigation is used commercially to extend the shelf life of fresh longan at least 45 days at low temperature storage (Tongdee, 1994). However, there have been numerous reports on the negative effects of its use, such as residues in the fruit, asthmatics and reactions in sensitive individuals (Jiang *et al*., 2002). Apai (2010) reported that most Thai exporters were satisfied and confident in sulfur dioxide fumigation to extend longan shelf life. China is one of the importing countries of Thai longan. The bilateral agreement government permits a maximum concentration of sulfur dioxide residue levels of 50 ppm in aril. However, preventing or inhibiting enzymatic browning has become essential for improving fruit marketing (Duan *et al*., 2007). Moreover, food safety awareness gradually increases in the international market.

Ozone is preferred over most popular disinfectants, such as chlorine, because of the relatively low inactivation rate of chlorine at concentrations limited by regulation. The primary purposes of ozone application at the postharvest stage of fruit and vegetable processing are inactivation of pathogenic and spoilage microorganisms, and destruction of pesticide and chemical residues. US Food and Drug Administration (FDA) approval of ozone as Generally Recognised as Safe (GRAS) status and an antimicrobial agent for direct food contact (FDA, 2001) have allowed ozone to be used in food processing.

Application of ozone fumigation in longan is one of the most interesting safe methods for prolonged shelf life. Whangchai *et al*. (2006) found that using ozone in combination with some organic acids controlled the postharvest decay and pericarp browning of longan fruits. The effects of ozone fumigation on sulfur dioxide residue and postharvest disease control of fresh longan fruit were studied (Kankham, 2013) by a varying period of time for ozone fumigation at 200 ppm after SO_2. It was found that longan fruits after treated with ozone for 10 hrs showed the most effective SO_2 residue reduction at 93.05% in pericarp and 81.54% in the flesh. The ozone fumigation showed L* and b* values of pericarp color higher than the control group (SO_2 only). There are no data on the improvement by ozone fumigation before SO_2 in Thailand. The result of Hantawee *et al*. (2009) found that using ozone fumigation for 120 min helped bleach pericarp from dark skin color to an attractive brighter color, but it became brown and rotted by five days at ambient temperature. If it is fumigated with SO_2 with a low dose, its shelf life will be prolonged and high price value. SO_2 has been used to practice in longan for a long time, but one reason which limited this method was that it had found SO_2 residue in the flesh more than the limit standard between Thai and China (50 mg/kg). It was hypothesized that this was caused by the natural pericarp color of longan, which does not show beautiful color; thus, exporters have to treat them at a higher dose of SO_2 than Sulfur Table in GFP standard.

Therefore, much restriction from the government are needed. Ozone was one of the interesting methods in combination with the other treatment to reduce the application dose (Kankham, 2013). The fumigation with ozone to bleach pericarp color to bright before or after SO_2 fumigation are increasingly interested to correct this solution and could increase the price as compared with SO_2 alone. The effects of this treatment on fruit residue and fruit quality are studied in order to correct SO_2 residue and benefit for consumer and exporter in supply chain in the future.

Materials and methods

Mature longan fruits of 11.5 kg for the commercial were loaded in the perforated plastic basket for export from the packing house in Chiang Mai province, Thailand. They were transferred to laboratory one day before testing and stored overnight at 5°C in 80-90% relative humidity (RH). On the next day, longan fruits were selected with uniformity shape, color size and without disease or insect infested. They were divided and put into 5 treatments in 3 replications with O_3 fumigation for 120 min before SO_2 fumigation at the concentration of 1.2% and 1.0%, SO_2 fumigation commercial practice (1.5%) before O_3 fumigation for 120 min., SO_2 fumigation commercial practice and untreated fruit. The fruits were stored at 5°C in 80-90% (RH) for 42 days. The samples were taken every 7 days for quality evaluation as the browning index, pericarp color, disease incidence, sensory evaluation and ClO_2 residue and storage life until day 42.

Browning index (BI)

Browning index was assessed visually by the total of the brown area on fruit surface using the following scale: 1= no browning, 2= slight browning, 3= less than 25% browning of the total surface, 4= 25-50% browning and 5= >50% browning. The browning index was calculated by Σ (browning scale × percentage of fruit on each scale). A browning index scale over 3.0 was considered as unacceptable marketability.

Pericarp color

Pericarp color was measured by chromameter (Model CR400, Minolta Japan). The results were expressed as L*, b* value and hue angle. L* value indicated lightness of color wheel, ranged from black = 0 to white = 100, b* value = (-) blue to yellow (+) and hue angle was true color. Two spots on opposite sides of the fruit were measured and the mean of the two measurements considered as one reading. The results were expressed as a mean value from three replications of the 5 measured samples.

Flesh discoloration

The following scale was used as follows 1 = normal (excellent quality); 2 = slight flesh discolored; 3 = less than 25% discolored of the total surface; 4 = 25-50% discolored and 5 = 50% discolored (poor quality). A flesh discoloration index was calculated using the following formula: ∑ (discolor scale x number of fruit in each class)/Total fruit. Fruits flesh having a discolor score above 3.0 were rated as unacceptable.

Disease incidence (DI)

Disease incidence was visually assessed by counting the fruits that showed lesions of mycelia or rot on the fruit surface.

Sensory evaluation

Sensory evaluation was evaluated during cold storage every 7 days. The in-house trained panel consisting of 10 members was assessed the samples. The acceptability of pericarp color, flesh quality, taste and overall quality was used a five-point hedonic scale where 5 = like extremely, 3 = neither like nor dislike and 1 = dislike extremely.

Storage life

Storage life was determined from 3 parameters of the quality of the longan fruit. Assessment by the unacceptable of BI was the score ≥ 3.0, flesh discoloration ≥ 2.0, DI ≥ 25% and sensory evaluation ≤ 3.0.

Sulfur dioxide residues

10 longan fruits were weighed on the whole fruits, peels, and flesh, then separated between peels and flesh and soak in 5% ethanol overnight, and extracted with heat and HCI acid solution for 60 minutes. The collected pink

solution and titration with standard solution NaOH 0.1 N for peel or 0.01 N for flesh were used methyl red as an indicator (AOAC, 2000).

Results

Pericarp browning

The O_3 fumigation for 120 min+SO_2 1.2% reduced pericarp browning for 42 days (BI = 1.00–2.07) (Figure 1 and 2) during storage at 5°C in 60-70% RH. The BI was 1.07 on day 42nd after storage, which was the lowest BI among the O_3 fumigation for 120 min+SO_2 1.0%, SO_2 commercial+O_3 fumigation for 120 min and SO_2 commercial practice treatments. The BI of these three treatments was 1.87, 2.07 and 3.00, respectively. For the untreated fruits, the BI was over the limit acceptant of BI which rated as 3.0 on the day 21st after storage.

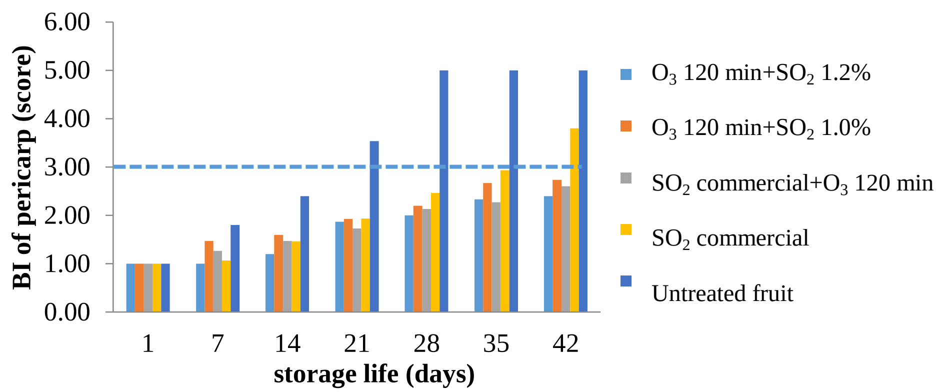

Figure 1. Browning index of longan pericarp during storage at 5°C for 42 days (Dot line represents the limit of acceptance, acceptance ≤ 3.00)

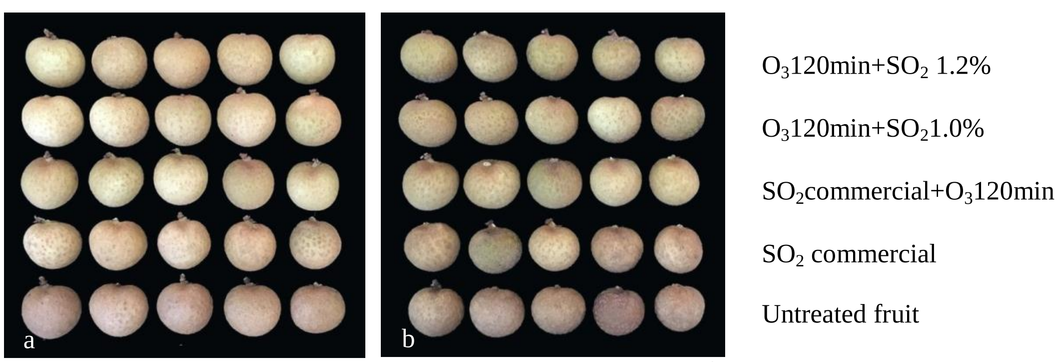

Figure 2. Pericarp color of longan during storage at 5°C for 42 days, day 1 (a) and day 42 (b)

Pericarp color

The pericarp color, L*, c*values and hue angle of the fruit in O_3 fumigation for 120 min+SO_2 1.2% tended to be higher than other treatments during the storage time (Figure 3).

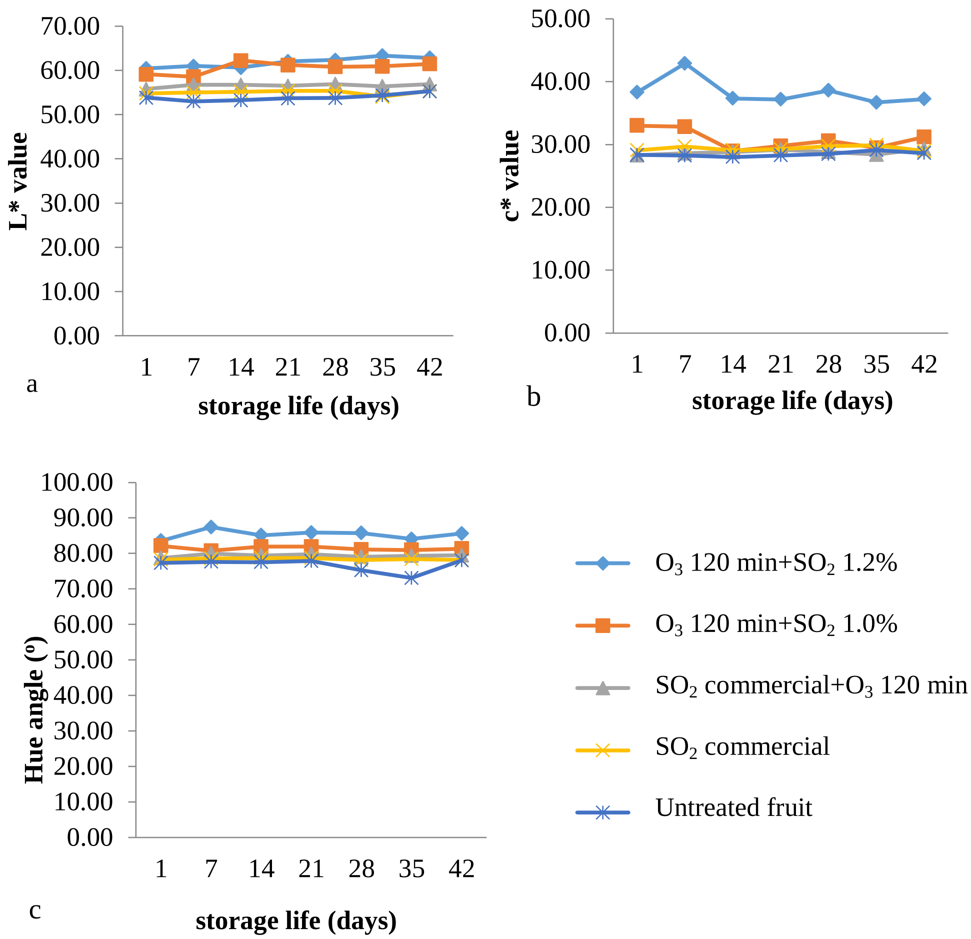

Figure 3. Pericarp color as L*value (a), c* value (b) and Hue angle (c) of longan pericarp during storage at 5°C for 42 days

Flesh discoloration

For the flesh color, all treatments delayed the flesh color changes better than the untreated fruits (Figure 4 and 5).

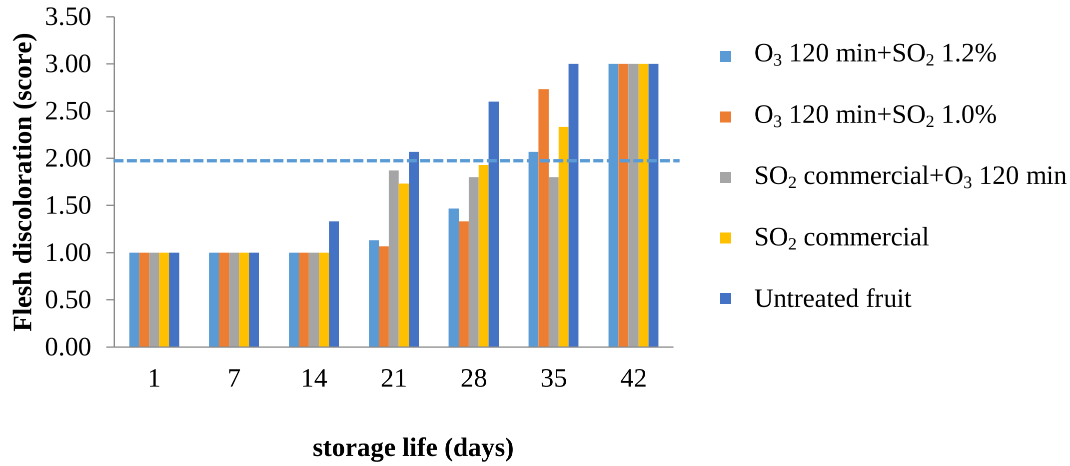

Figure 4. Flesh discoloration of longan during storage at 5^{o}C for 42 days (Dot line represents the limit of acceptance, acceptance ≤ 2.00)

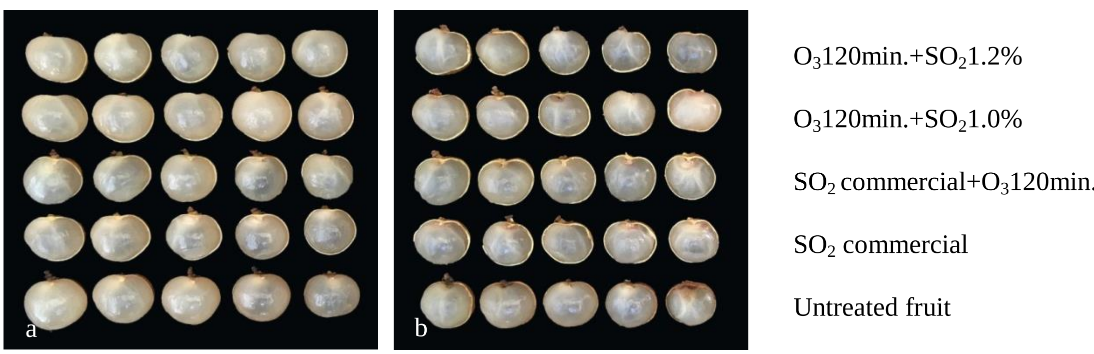

Figure 5. Flesh discoloration of longan during storage at 5^{o}C for 42 days, day 1 (a) and day 42 (b)

Disease incidence (DI)

O_3 fumigation for 120 min+SO_2 1.2%, O_3 fumigation for 120 min+SO_2 1.0%, SO_2 commercial+O_3 fumigation for 120 min showed the fruit rot symptoms after storage for 42, 42, and 35 days, respectively (Table 1). However, SO_2 commercial practice did not show the fruit rot symptom during the 42 days storage, but for the untreated fruits showed rotten fruits on day 14th after storage.

Table 1. Disease incidence(%) of longan during store at 5°C for 42 days (acceptance ≤ 25%)

treatment	Storage life (day)						
	1	**7**	**14**	**21**	**28**	**35**	**42**
O_3 120 min+SO_2 1.2%	0.00a	0.00a	0.00a	0.00a	0.00a	0.00a	3.33b
O_3 120 min+SO_2 1.0%	0.00a	0.00a	0.00a	0.00a	0.00a	0.00a	3.33b
SO_2 commercial+O_3 120 min	0.00a	0.00a	0.00a	0.00a	0.00a	3.33a	10.00b
SO_2 commercial	0.00a	0.00a	0.00a	0.00a	0.00a	0.00a	0.00b
Untreated fruit	0.00a	0.00a	3.33a	13.33a	16.67a	23.33a	66.67a

Means within the same column followed by the same letters were not significant at α=95% by LSD

Sensory evaluation

For the sensory evaluation, the acceptance scores of pericarp color for all treatments of the panels were reduced when the storage time increased. In all treatments which contained SO_2, O_3 fumigation for 120 min+SO_2 1.0%, O_3 120 min+SO_2 1.2%, SO_2 commercial and SO_2 commercial+O_3 fumigation for 120 min, the acceptance scores at the day 42th after storage were 3.06-3.78 (Figure 6a) whereas the untreated fruits received the acceptance scores 1.67-2.94 after stored for 1 day, which was lower than the limit of the acceptance score = 3.0.

The acceptance scores of flesh color were also reduced when storage time increased. The O_3 fumigation for 120 min+SO_2 1.0%, O_3 fumigation for 120 min+SO_2 1.2%, SO_2 commercial, SO_2 commercial+O_3 fumigation for 120 min and the untreated fruits still had acceptance scores over 3.0 after stored for 42, 35, 35, 35 and 28 days, respectively (Figure 6b).

For the taste acceptance scores, it was found that SO_2 commercial+O_3 fumigation for 120 min, O_3 fumigation for 120 min+SO_2 1.0%, O_3 fumigation for 120 min+SO_2 1.2%, SO_2 commercial and untreated fruits still had the taste acceptance scores over the limit acceptance score (3.0) after stored for 42, 35, 35, 28 and 28 days, respectively (Figure 6c).

Storage life

After stored the fruits at 5°C in RH 75%, they were found that O_3 fumigation for 120 min+SO_2 1.2% had 28 days of storage life. The O_3 fumigation for 120 min+SO_2 1.0%, SO_2 commercial+O_3 fumigation for 120 min. and SO_2 commercial had 21 days of storage life while the untreated fruit had 14 days of storage life.

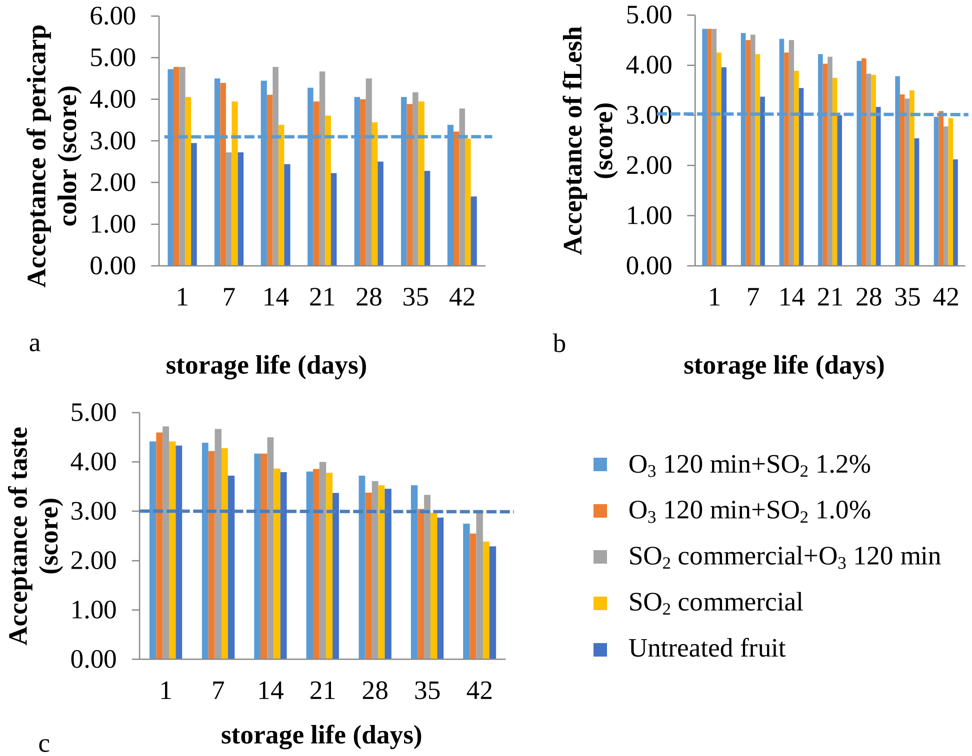

Figure 6. Sensory evaluation of pericarp color (a), flesh color (b) and taste (c) acceptance of longan during storage at 5^{o}C for 42 days (Dot line represents the limit of acceptance, acceptance ≥3)

Sulfur dioxide residues

On the first day of the storage, the SO_2 residues on pericarp were reduced by the storage time. Ozone treatments could not reduce the SO_2 residues. The SO_2 residual on pericarp of O_3 fumigation for 120 min+SO_2 1.2% and O_3 fumigation for 120 min+SO_2 1.0% were 2,308.10 and 2,619.80 mg/kg, respectively (Table 2) which were higher than SO_2 commercial and SO_2 commercial+O_3 fumigation for 120 min (1,720.50 and 1,770.40 mg/kg, respectively) at the first of storage then the SO_2 residues reduced continuously to 1,111.50-1,437.30 mg/kg after stored for 42 days.

The SO_2 residual in the flesh of all treatments was 4.94-34.90 mg/kg (Table 3). The SO_2 residue was reduced rapidly during the first week of the storage to 1.31-20.19 mg/kg, whereas SO_2 residual of O_3 fumigation for 120 min+SO_2 1.2% reduced from 34.90 mg/kg to 9.50 mg/kg. After stored the fruits for 42 days, the SO_2 residual of all treatments was 1.43-2.21 mg/kg.

Table 2. SO_2 residues on pericarp of longan during store at 5^oC for 42 days

Treatment	Storage life (day)						
	1	**7**	**14**	**21**	**28**	**35**	**42**
$O_3$120 min+ $SO_2$1.2%	2,308.10ab	2,120.30a	1,168.10a	1,378.60a	1,410.90a	1,689.30a	1,437.30a
$O_3$120 min+ $SO_2$1.0%	2,619.80a	1,970.70ab	1,779.20a	1,406.10a	1,353.90a	1,662.30a	1,194.30ab
SO_2 commercial+ O_3 120 min	1,770.40bc	1,963.60ab	1,843.90a	1,344.50a	1,334.00a	1,568.50a	1,323.70ab
SO_2 commercial	1,720.50c	1,611.90b	1,753.50a	1,406.50a	1,196.70b	1,522.10a	1,111.50b
Untreated fruit	25.00d	30.04c	31.50b	13.62b	10.42c	13.30b	11.96c

Means within the same column followed by the same letters were not significant at α=95% by LSD

Table 3. SO_2 residues on the flesh of longan during store at 5^oC for 42 days

Treatment	Storage life (day)						
	1	**7**	**14**	**21**	**28**	**35**	**42**
$O_3$120 min+$SO_2$1.2%	34.90a	9.50a	6.87a	1.20a	1.29a	1.27a	2.21a
$O_3$120 min+$SO_2$1.0%	21.80ab	20.19a	3.85a	1.13a	1.30a	1.58a	1.43b
SO_2commercial+$O_3$120 min	20.60ab	6.85a	1.47a	2.06a	1.27a	1.62a	2.03a
SO_2 commercial	17.31ab	3.09a	1.25a	1.46a	1.42a	1.38a	1.81ab
Untreated fruit	4.94b	1.31a	1.20a	0.83a	1.14a	1.48a	1.95a

Means within the same column followed by the same letters were not significant at α=95% by LSD

Discussion

The reduction of SO_2 usage by O_3 fumigation for 120 min before SO_2 fumigation at the concentrations of 1.0 and 1.2%, O_3 fumigation for 120 min+SO_2 1.2%, O_3 fumigation for 120 min+SO_2 1.0% and SO_2 commercial+ O_3 fumigation for 120 min prevented pericarp browning for 42 days, while SO_2 commercial treatment was 35 days. The usages of O_3 prior to SO_2 or SO_2 prior to O_3 did not make significant differences from the SO_2 fumigation in commercial practice. O_3 has efficacy against a wide range of microorganisms, including bacteria, fungi, viruses, protozoa and bacterial fungal spores (Restaino *et al*., 1995; Khadre *et al*., 2001; and Cullen *et al*., 2009). Such advantages make ozone attractive to the food industry, and consequently, it has been affirmed as Generally Recognized as Safe (GRAS) to use in food processing (Graham, 1997) and was approved as an antimicrobial food additive in 2001 (FDA, 2001). Coke (2012) reported that using ozone as a sanitizer in food surface hygiene and to extend the shelf life of many postharvest agricultural products.

The MRL for SO_2 residue in the flesh of longan, exported to China was 50 mg/kg. This study showed that SO_2 at the concentration of 1.0% and 1.2% fumigation made the SO_2 residue in logan flesh not exceeding 50 mg/kg, which agrees with the recommendation of TAS 1004-2014. The SO_2 residue was decreased by the storage time in the negative exponential pattern (Tongdee, 1994). Carletti (2013) suggested that ozone degrades quickly into oxygen and leaves no residues after application. Ozone is environmental friendly confirmed as a Generally Recognized As Safe (GRAS) for food contact application. Ozone is a powerful oxidant with a wide range of sanitizing applications due to its instability with a half-life of 20-30 minutes in distilled water at 20^{o}C (Chelme, 2010).

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