

## Optimization of freezing point regulator and its penetration dynamics on large yellow croaker

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### Abstract

Different kinds of freezing-point regulators were evaluated to expand the freezing point zone of large yellow croaker, and several treatment methods such as ordinary atmospheric pressure, vacuum environment and injection during the process of penetration were compared to reveal the relationship of diffusion velocities, diffusion time and freezing point of the large yellow croaker. Results obtained for ideal freezing-point regulators were as follows: Sodium chloride 2.5% (w/w), trehalose 2.5% (w/w) and edible alcohol 2.0% (w/w), which could decrease the freezing point from  $-1.5^{\circ}\text{C}$  to  $-4.2^{\circ}\text{C}$ . Comparing with atmospheric pressure or vacuum degrees treatment, using injection method to deal with the freezing-point regulators could decrease the freezing point in a short time and benefit the meat quality.

**Keywords:** Ice temperature preservation; Control the freezing point, Large yellow croaker

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## Introduction

Large yellow croaker, called “State Fish” in China, belongs to the family *Perciformes* and the genus *Sciaenidae*, and is regarded as mascot and longevity fish due to the daintiness of taste (Quan *et al.*, 2000). With the increase in the scale of processing of large yellow croaker, seeking an effective preservation method to prolong the shelf life of fish product was an important problem that needed to be solved. The researches during the past decade indicated that the Ice Temperature Preservation was an ideal storage method to preserve the large yellow croaker compared with the traditional freezing method (Ando *et al.*, 2004; Duun *et al.*, 2008; Lauzon *et al.*, 2009). It was reported that the freezing point of the large yellow croaker was around  $-1.5^{\circ}\text{C}$  and storing the fish samples in the temperature range of  $0^{\circ}\text{C} \sim 1.5^{\circ}\text{C}$  can inhibit the microbial activity and benefit fish quality as well (Xu *et al.*, 2005). This was probably due to the bound water existing in the fish muscle, which was unfrozen when storing the large yellow croaker above the freezing point. However, accuracy of temperature control in most factories is about  $\pm 2^{\circ}\text{C}$  in the current times, and the ice temperature zone of large yellow croaker was  $\pm 0.5^{\circ}\text{C}$  to around  $-1.5^{\circ}\text{C}$ , which was not eligible for storing the fish samples (Shi *et al.*, 2002; Erdogdu *et al.*, 2005; Dirita *et al.*, 2007). In this study,

large yellow croaker was used as raw material and several freezing point regulators such as sodium chloride, sucrose, edible alcohol, sodium alginate and trehalose were evaluated to expand the freezing point zone and different treatment methods of several freezing point regulators on influencing the diffusion velocity were studied to reduce the requirements of temperature control accuracy in ice temperature preservation, and to save the operating costs to be beneficial to popularize the application in ice temperature preservation.

## Materials and methods

Fresh samples of large yellow croaker were obtained from Zhoushan Marine Fisheries Aquaculture Companies of China, weighing  $280 \pm 10\text{g}$ , sodium chloride. Sodium alginate, trehalose, edible alcohol, sucrose and other reagents used were analytically pure and deionized water was used in this study.

### *Main equipment and apparatus*

AR224CN precision balance from Ohaus Co., Ltd.; JK-16U temperature recorder from Jking Co., Ltd.; BZF-50 vacuum drying oven from Boxun Co., Ltd.; 539-WT refrigerator from Haier Co., Ltd.; HD-108 ice crusher from Hongda Co., Ltd.; TMS-PRO food texture analyzer from FTC Co., Ltd.

### *Single factor experiment*

Different concentrations (1%, 1.5%, 2%,

2.5%, 3%, 4%, 6% and 9% w/w) of sodium alginate were added to the surface of the fish cakes (2cm\*2cm\*2cm) and these fish cakes were then putted into a salver and stored for three hours. After the designated period, the fish cakes were transferred to a refrigerator and the freezing point of each fish cake was observed at -18°C gas quick-frozen condition by using a temperature recorder. Sodium chloride, trehalose, edible alcohol and sucrose group were applied in the same way as sodium alginate.

#### *Sensory evaluation*

There were 7 trained panelists from the laboratory staff, who constituted the sensory evaluation group and the sensory evaluation test was applied by using sensory evaluation standards shown in Table1. The sensory evaluation scores were divided into 5 grades called good (7~8 points), slightly good (5~6 points), common (3~4 points) and bad (1~2 points). Each staff scored according to the appearance, meat quality and flavor. Scores of separate characteristics were summed to give a comprehensive sensory score.

#### *Penetration velocity of freezing-point regulator under different treatments*

Freezing-point regulator's penetration velocities were considered under different treatments. Fish samples were

randomly assigned into seven groups including the injection group (dealt with the freezing point regulators through the injection) and six groups as follows: Fish samples were given coating treatment with optimized freezing point regulators. After that, they were placed in a vacuum container separately under the pressure of 0.01Mpa, 0.03Mpa, 0.05Mpa, 0.07Mpa, 0.09Mpa and 0.1Mpa, respectively, then fish samples of each group were taken out in turns to observe the freezing point once an hour within a total of eight hours at temperature -18°C.

#### *Test of Large yellow croaker quality and structure*

Textural parameters such as hardness, brittleness, viscosity, cohesion, elasticity, tackiness and chewiness were being tested to assess the quality of fish samples after adding the freezing-point regulators through different methods. Fish samples were randomly assigned into four groups including the control (untreated) group and three groups treated with the freezing-point regulator under different pressure as follows. First samples were given coating treatment with optimized freezing point regulators under 0.1Mpa. The second group was taken to the same treatment under 0.05Mpa, and the third group was treated with the freezing point regulators through the method of injection. After three hours, quality and structure of fish

samples were tested by using texture analyzer. The parameters of the apparatus were set as follows: A flat-ended cylindrical probe was used with a constant speed of 40 mm/min, and the deformation of the fish samples was set at 40%.

#### *Statistical treatment*

SPSS17.0 were used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained according to the comprehensive score, which was calculated as follows:

Comprehensive score = (|Freezing point | + Sensory score)/2

## **Results**

### *Result of single factor experiment*

The effects of different freezing point regulators on decreasing the freezing point are shown in Table 2. Almost each freezing point regulator has the ability to decrease the freezing point. This is probably caused by the increase in non-freezable water after adding the freezing regulators, which lead to a decrease in the freezing point (Zhang *et al.*, 2010; Tao *et al.*, 1999). Sodium chloride had a large impact on decreasing the freezing point, which was benefiting from the small molecules (Bili *et al.*, 2007; Li *et al.*, 2012). It was easy to penetrate into the muscle cell and lead to an increase in intracellular osmotic pressure and prompt

the free water to transform into a lot of bound water (Liu *et al.*, 2005). When the additive concentration of sodium chloride increased from 1% to 9%, the freezing point decreased from -1.8°C to -5.5°C. Other substances such as edible alcohol and trehalose had the same effect. It ranged from -3.4°C to -5.7°C when the additive concentration increased to 9%. The ability of sucrose and sodium alginate to regulate the freezing point was less than that of sodium chloride. When the additive concentration rose to 9%, they only decreased the freezing point from -1.5°C to -2.4°C and -2.3°C, respectively.

The relationship between the sensory evaluation score and the additive concentration was similar to a parabolic, and there was a highest point. When the sodium chloride concentration was 2.5%, fish samples achieved the highest score 6. This phenomenon also existed in other freezing point regulators such as edible alcohol, trehalose, sucrose and sodium alginate. When the additive concentration rose to 2%, 2.5%, 2% and 2.5%, the highest sensory score was 7, 6.5, 6.5 and 6, correspondingly. A certain additive concentration of the freezing point regulators could slow the progress of the fish changing yellow.

**Table 1: Sensory evaluation standards.**

Project	Good (7~8 points)	Slightly good (5~6 points)	Common (3~4points)	Bad (1~2points)
Appearance	Very bright	Bright	Slightly dull	Dull
Meat quality	High muscle elasticity	Slightly muscle elasticity	Low Muscle elasticity, a slight taste of chewing additives	No muscle elasticity, a intense taste of chewing additives
Flavor	Neutral	Fishy	Stale	Spoiled

But if the additive concentration increased further, the meat quality traits of the large yellow croaker will become worse, and finally affect the quality of processed products.

The comprehensive scores are shown in Table 2. Regardless of decreasing the freezing point or protecting the food sensory, good performance was achieved with sodium chloride, edible alcohol and trehalose, and sodium chloride 2.5% (w/w), trehalose 2.5% (w/w) and edible alcohol 2% (w/w) were considered as the ideal freezing point regulators to decrease the freezing point of large yellow croaker. Three parallel verifications showed that it could decrease the freezing point from -1.5°C to -4.2°C. However, large yellow croaker was more than a fish cake in industrial processing and the diffusion velocity of freezing regulators was one of the most important factors that needed to be considered. Effect of penetration conditions of freezing point regulators was finally evaluated to let the freezing

point penetrate into the fish muscle quickly.

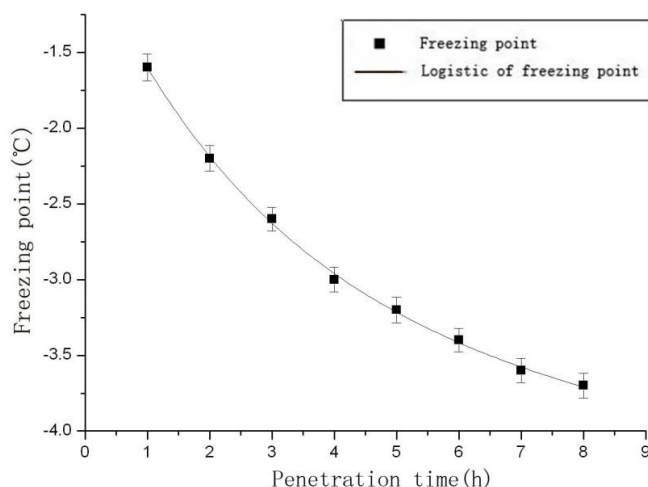
#### *Dynamics of freezing point regulator penetration into large yellow croaker*

The dynamics of freezing point regulator penetration into large yellow croaker were taken into consideration. Changes of the freezing point during the frozen storage are shown in Fig. 1. The freezing point was decreased from -1.7°C to -3.6°C gradually in tandem with the penetration time increasing from 1 hour to 8 hours. Correlative analysis, obtained by the experiment, showed that there was a positive correlation between penetration time and freezing point. The formula (Eq.1) founded based on the freezing point indicated the whole penetration process takes 4.6 hours to hasten the freezing point regulators penetration into fish samples completely, which was long and not effective in the industrial production.

$$y = -3.87 + \frac{2.5}{1 + \left(\frac{X}{2.69}\right)^{1.89}} \quad (1)$$

**Table 2** Effect of different freezing point regulator on the freezing point and Sensory Evaluation of Large Yellow Croaker.

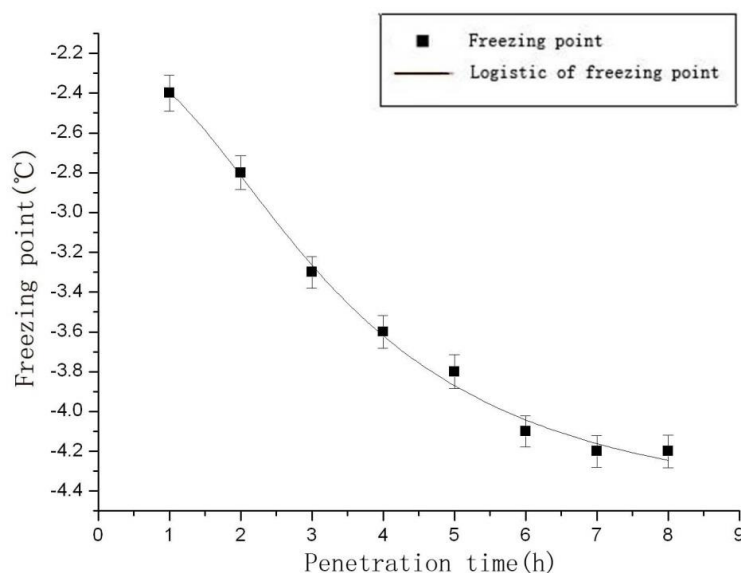
Coating		1%	1.5%	2%	2.5%	3%	4%	6%	9%
Sodium chloride	Freezing point(°C)	-1.8	-2	-2.3	-2.6	-2.9	-3.4	-4.3	-5.5
	Sensory score	4.5	4.5	5	6	5.5	5	4	3
	Comprehensive score	3.15	3.25	3.65	4.3	4.2	4.2	4.15	4.25
Sucrose	Freezing point(°C)	-1.6	-1.6	-1.7	-1.9	-2.1	-2.2	-2.3	-2.4
	Sensory score	5	6.5	6.5	6	5	5	4.5	4
	Comprehensive score	3.3	4.05	4.1	3.95	3.55	3.6	3.4	3.2
Edible alcohol	Freezing point(°C)	-1.7	-2	-2.6	-2.8	-3	-3.4	-4.6	-5.7
	Sensory score	5.5	6	7	6	5	5	4.5	3
	Comprehensive score	3.6	4	4.8	4.4	4	4.2	4.55	4.35
Sodium alginate	Freezing point(°C)	-1.5	-1.5	-1.5	-1.6	-1.7	-1.9	-2.1	-2.3
	Sensory score	5	5.5	6	6	6	5.5	5.5	5
	Comprehensive score	3.25	3.5	3.75	3.8	3.85	3.7	3.8	3.65
Trehalose	Freezing point(°C)	-1.6	-1.8	-2	-2.3	-2.6	-2.9	-3.2	-3.4
	Sensory score	5.5	5.5	6	6.5	6	5.5	5.5	5
	Comprehensive score	3.55	3.65	4	4.4	4.3	4.2	4.35	4.2

**Figure 1:** Effect of ordinary atmospheric pressure (0.1Mp) on penetration velocity of freezing point regulator.

The effects of different pressures in promoting the penetration are presented in Fig.2 and Table 2. The initial freezing point was  $-1.8^{\circ}\text{C}$  placed under  $0.09\text{Mpa}$  for 1 hour. Meanwhile, the freezing point of the fish samples treated under other pressures ranged from  $-2.1^{\circ}\text{C}$  to  $-2.7^{\circ}\text{C}$ . It can be seen in the forepart of penetration time from Fig. 2, the freezing point regulator could quickly penetrate into the muscle and decrease the freezing point and these groups placed under  $0.05\text{Mpa}$ ,

$0.03\text{Mpa}$  and  $0.01\text{Mpa}$  had already reached the lowest temperature  $-4.2^{\circ}\text{C}$  four hours later. The formula (Eq.2) founded based on the method of Non-linear fitting revealed the relationship between freezing point and penetration time under  $0.05\text{Mpa}$ . It takes 2.9 hours for the whole penetration process to decrease the freezing point from  $-1.5^{\circ}\text{C}$  to  $-3.2^{\circ}\text{C}$ . The time did not meet the requirements of industrial production.

$$y = -4.58 + \frac{2.83}{1 + \left(\frac{X}{2.81}\right)^{1.92}} \quad (2)$$



**Figure 2: Effect of atmospheric pressure ( $0.05\text{Mpa}$ ) on penetration velocity of freezing point regulator**

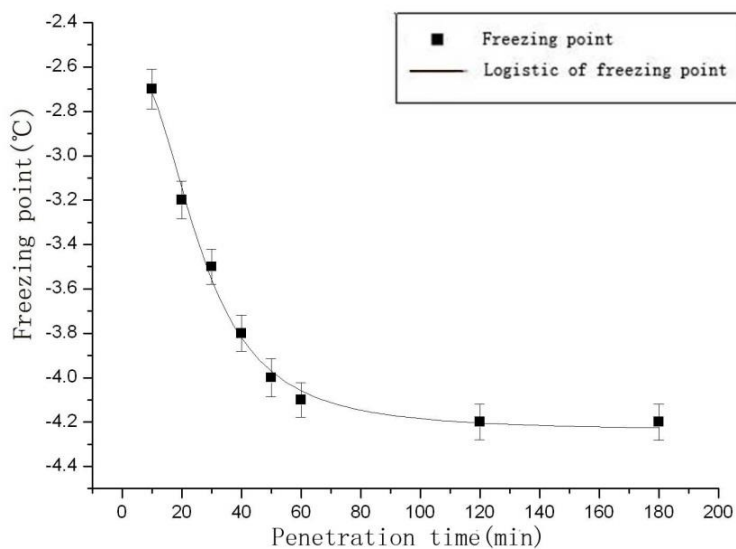
**Table 2: Effect of different atmospheric pressure on decrease in freezing point.**

Atmospheric pressure	1h	2 h	3 h	4 h	5 h	6 h	7 h	8 h
<b>0.09 Mpa</b>	-1.8°C	-2.4°C	-2.8°C	-3.2°C	-3.5°C	-3.7°C	-3.8°C	-3.9°C
<b>0.07 Mpa</b>	-2.1°C	-2.5°C	-3.0°C	-3.2°C	-3.6°C	-3.8°C	-4.0°C	-4.2°C
<b>0.05 Mpa</b>	-2.4°C	-2.8°C	-3.3°C	-3.6°C	-3.8°C	-4.2°C	-4.2°C	-4.2°C
<b>0.03 Mpa</b>	-2.5°C	-3.3°C	-3.9°C	-4.2°C	-4.2°C	4.2°C	-4.2°C	-4.2°C
<b>0.01 Mpa</b>	-2.7°C	-3.5°C	-3.9°C	-4.2°C	-4.2°C	4.2°C	-4.2°C	-4.2°C

The effects of injection on penetration velocity of the freezing point regulators are presented in Fig.3. The freezing point decreased progressively from an initial value  $-2.7^{\circ}\text{C}$  to the ultimate value  $-4.2^{\circ}\text{C}$ . It could be noticeably observed from the forepart of the cooling curve that the use of injection had significantly impacted the freezing point. The penetration

process takes 22 minutes to impel the freezing point decrease from  $-1.5$  to  $-3.2^{\circ}\text{C}$  according to Eq.3, which was beneficial to the quality of Large Yellow Croaker and good for the industrial production as well.

$$y = -4.24 + \frac{1.67}{1 + \left(\frac{X}{25.75}\right)^{2.49}} \quad (3)$$

**Figure 3: Effect of injection on penetration velocity of freezing point regulator .**



**Table 3: Texture analysis results of Large Yellow Croaker.**

	Hardness (N)	Brittleness (N)	Viscosity (mj)	Cohesion (P)	Elasticity (mm)	Tackiness (N)	Chewiness (mj)
Control group	22	22	0.18	18	1.65	7.60	12.56
Treated under 0.1Mpa	16	15	0.11	12	0.58	6.75	8.71
Treated under 0.05Mpa	18	17	0.14	15	1	7.60	10.25
Treated by injection	21.5	22	0.17	18	1.62	7.58	12.32

The variation in textural parameters of the fish sample treated with different methods is presented in Table 3. The hardness of the fish varied slightly between the control group and the injection group, which was 22N for the control group and 21.5N for the injection group. But when these groups were placed under 0.1Mpa and 0.05Mpa the hardness reduced drastically to the value of 16N and 18N, respectively. Brittleness of the fish sample was 22N for the control group and the injection group. But it was reduced to 15~17N for the groups placed under 0.1Mpa and 0.05Mpa. Other texture indices were the same as that of hardness and brittleness, which indicated that the injection method was advantageous to fish quality.

### Discussion

Using ice temperature preservation to prolong the shelf life of food had been reported. Lu studied the technique of keeping beef fresh under ice-temperature conditions, and the results showed that beef could be kept

fresh for 28 days under these conditions, and its pH value was 6.09, TVB-N value 14.634 mg/100g, the total number of colonies was  $3.7 \times 10^4$  cfu / g, and it had purplish red color (Lu *et al.*, 2008). Jiang observed the changes of strawberries during ice temperature preservation and the results showed that the changes of strawberries during 50d of ice temperature preservation were small and there is not any distinct difference in texture and flavor between tested strawberries and fresh ones (Jing *et al.*, 2004). However, using freezing point regulators to expand the freezing zone of the fish samples to meet the standards of industry production is less reported. In this study, the effects of several freezing point regulators on decreasing the freezing point of large yellow croaker were evaluated and optimized. The optimal conditions obtained are as follows: Sodium chloride 2.04 % (w/w), trehalose 2.54% (w/w) and edible alcohol 2.58% (w/w), which can decrease the freezing point from -1.5°C to -4.2°C compared to the control group. The

dynamics test indicated that using the injection method can accelerate the penetration velocity and benefit fish quality as well.

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