Frozen Fish: Control of Glazing Operation

Tânia Manso, Luís Teixeira, and Paula M. Reis Correia

***Abstract*—**Glazing is a process used to reduce undesirable drying or dehydration of fish during frozen or cold storage. To evaluate the effect of the time/ temperature binomial of the cryogenic frozen tunnel in the amount of glazing watera Central Composite Rotatable Design was used, with application of the Response Surface Methodology. The results reveal that the time/ temperature obtained for pink cusk-eel in experimental conditions for glazing water are similar to the industrial process, but for red fish and merluza the industrial process needs some adjustments. Control charts were established and implementedto control the amount of glazing water on sardine and merluza. They show that the freezing process was statistically controlled but there were some tendencies that must be analyzed, since the trend of sample mean values approached either of the limits, mainly in merluza. Thus, appropriate actions must be taken, in order to improve the process.

***Keywords*—**Control charts, frozen fish, glazing, RSM.

I. Introduction

CONSUMERdemand for seafood has steadily grown over the last several decades. This evolution was accompanied by a growing importance of frozen as opposed to fresh fish[1]. In 2006, 54% of the 110 million tons of worldwide fish produced for human consumption underwent some form of processing. The share of frozen fish in the total quantity of fish being processed before consumption amounted to 42% in 2006 [1]. The success of this processing method may be explained by its efficacy with respect to the preservation of an otherwise highly perishable product [2].

One of the main preoccupations of seafood industry is to improve the conservation technologies of perishable foods to reach a final product with optimal quality. Freezing and cold storage is an efficient method which preserves taste and nutritional value [3], but does not improve product quality. The final quality depends on the quality of seafood at the time of freezing as well as other factors during freezing, cold storage and distribution [4]. One particular established technology generally applied during freezing and frozen storage of seafood is the application of a layer of ice on the surface of a frozen product, referred to as ice-glazing [2].

Ice-glazing is carried out by dipping or spaying the product in a water bath, to protect sea-products from dehydration and oxidation during long-term storage [5].Oxidation is an important cause of quality deterioration for frozen seafood, because fish meat is abundant in polyunsaturated fatty acids present in its flesh so it is more susceptible to oxidative degradation [6]-[8].During frozen or cold storage, seafood products may develop surface drying and dehydration, which may lead to freezer burn [2].

Statistical process control (SPC) is the application of statistical methods to the monitoring and controlling a process to ensure that it operates at its full potential to produce a product which conforms to the law. Statistical Process Control may be broadly broken down into three sets of activities: understanding the process, understanding the causes of variation, and eliminating of the sources of special cause variation. In understanding a process, the process is typically mapped out and the process is monitored using control charts. Control charts are used to identify variation that may be due to special causes, and to free the user from concern over variation due to common causes. This is an ongoing activity.

Glaze is typically applied from 4% to 10% depending on the product, although it should be noted that as a result of their high surface to volume ratios seafood products such as prawns and squid rings can have up to 25% unavoidable water-ice glaze [2].Thus, the ice-glaze up-take on a product is dominated by factors such us, surface area/volume ratio and residence time. In Portugal the glaze in fish products is regulated by Portuguese law, DL 37/2004. This law describes the procedure and the limit glaze limits.

In order to optimize glazing conditions, a Central Composite Rotatable Design (CCRD) of the experiment was used. In particular, this optimization step was carried out using Response Surface Methodology (RSM). This technique is a collection of mathematical and statistical techniques, that are useful for modeling and analysis in applications where a response of interest is influenced by several variables, and the objective is to optimize this response [9].It is a powerful technique for testing multiple process variables because fewer experimental trials are used, compared with the study of one variable at a time. Interactions between variables can also be identified and quantified [10]. This is probably the most widely used and successful optimization technique based on designed experiments [11].

The present work had two main objectives: the evaluation of the effect of the time/ temperature binomial in the total glazing water using a cryogenic freezing tunnel, in order to monitor the process and evaluate possible changes in the industrial processing of frozen to obtain the ideal amount of glazing water. Other objective was to study if the process was statistically controlled.

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II.EXPERIMENTAL PROCEDURE

A.Materials

The red fish (*Sebastes marinus*), pink cusk-eel (*Genypterus blacodes*), and merlusa (*Merluccius hubbsi*) arrived at Beiragel enterprise frozen and after they were processed. Generally, fish could be processed whole or cut into slices. In this study we used the whole fish. After arriving, the fishis washed with water (T≤ 4ºC), and frozen in a nitrogen tunnel (T≤ -50ºC). Thenitis glazed by dipping the product in a water bath (T≤ 4ºC), and then it goes to the packaging lines. The fish products packed in bags are transferred to the cold store (T≤ -19±1ºC).

A MT 1250-8 (BOC, United Kingdom) cryogenic freezing tunnel was used.

Samples of 2kg were introduced in the processing line and the glazing percentage determined in order to study their behavior during continuous fish processing.

The four fishes were used for the experimental design, but just merlusa and sardines were used for statistic control process study.

B.Methods

The percentage of glazing was determined according to Portuguese law DL 37/2004, 26th February, similar to the procedure described in the Codex Alimentarius Committee for Fish and Fishery Products: CODEX STAN 190-1995. First, the frozen fish sample (at -19±1ºC) was removed from the freezer and its gross-weight (= W_1) determined on a PB 3003-5 scale (Mettler Toledo S.A., Greifensee, Switzerland). Subsequently, the frozen sample was immersed into a shaking water bath (SWB25, Thermo Scientific Haake, Geel, Belgium) and gently shaked for about 30s until all visible ice-glaze was removed. This was checked by carefully feeling the fish surface with the finger tips. When the smooth surface of the glaze disappeared and the rough surface of the fish itself could be felt, the deglazing procedure was stopped. The water bath contains an amount of fresh water equal to about 10 times the declared weight of the product; the temperature should be adjusted to about 20±2ºC. Finally, the sample was carefully dipped dry (without pressure) with a cotton rag and the non-glazed or net-weight (=W_2) determined. The percentage of glazing or glaze-weight relative to gross-weight was then calculated as follows (1):

$$\%\,Glazing = 100\,\frac{(W_1 - W_2)}{W_1} \qquad (1)$$

A Central Composite Rotatable Design (CCRD) of the experiment was applied, using the Response Surface Methodology (RSM). The experiments were performed with k = 2 for: temperature/ as independent variables. The upper and lower limits for these variables were established: temperature (-90ºC; -30ºC); time (3.5 – 10 minutes). Table I shows the coded and uncoded experimental design (Table I). The dependent variables included the percentage of glazing water.

Data was fitted to second-order polynomial (2) for each dependent Y variable, through a stepwise multiple regration analysis using Statistic® vs 6 software.

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_1x_2 + b_4x_1^2 + b_5x_2^2 \qquad (2)$$

where b_n are regression equation coefficients and x_n the independent variables [12].

Based on the predicted model equations surface plots were generated. The analysis of the variance was performed to determine the lack of fit and the significance of the effects of each of the two independent factors.

TABLE I
CODED AND ACTUAL VARIABLES FOR THE EXPERIMENTAL DESIGN OF THE OPTIMIZATION OF GLAZING CONSIDERING THE TEMPERATURE AND TIME VARIATION

Run number by order	Coded		Independentvariables	
	Temperature	Time	Temperature (T ºC)	Time (min)
1	0	-1.41421	-60	3.5
2	1.41421	0	-67	10
3	-1	-1	-30	4.0
4	0	0	-60	7.0
5	1	-1	-90	4.0
6	-1	1	-30	10.0
7	0	1.41421	-60	7.8
8	-1.41421	0	-25	7.0
9	0	0	-60	7.0
10	1	1	-90	10.0
11	0	0	-60	7.0
12	0	0	-60	7.0
13	0	0	-60	7.0

To establish of control charts25 batches, of each seafood products, with 5 samples of 1Kg were analyzed. The inspection procedure was the same for each sample and was carried out consistently from sample to sample. A $\bar{X}$ and *R*control chart was created in order to motorize the glazing. The glazing values presented a Normal distribution. The mean ($\bar{X}$) and range(*R*) of each sample were calculated as follow (3) and (4):

$$\bar{X} = \frac{X_1 + X_2 + X_3 + \cdots + X_n}{n} \qquad (3)$$

where X_1, X_2, X_3, … are the observed values for a sample of size *n*.

$$R = X_{max} - X_{min} \qquad (4)$$

Let $\bar{X}_1$, $\bar{X}_2$, $\bar{X}_3$,…,$\bar{X}_m$ be the average of each sample R_1, R_2, R_3,…, R_m the range of the *m* samples, the grand average and average range will respectively be (5) and (6):

$$\bar{\bar{X}} = \frac{\bar{X}_1 + \bar{X}_2 + \bar{X}_3 + \cdots + \bar{X}_n}{m} \qquad (5)$$

$$\bar{R} = \frac{R_1 + R_2 + R_3 + \cdots + R_n}{m} \qquad (6)$$

The $\bar{\bar{X}}$ and $\bar{R}$ are the center line of control charts.

The control limits for $\bar{X}$ control chart are (7) and (8):

$$UCL_{\bar{X}} = \bar{\bar{X}} + A_2\bar{R} \quad (7)$$

$$LCL_{\bar{X}} = \bar{\bar{X}} + A_2\bar{R} \quad (8)$$

where A_2 is defined as(9):

$$A_2 = \frac{\bar{R}}{d_2\sqrt{n}} \quad (9)$$

The control limits for R control chart are (10) and (11):

$$UCL_R = D_4\bar{R} \quad (10)$$

$$LCL_R = D_3\bar{R} \quad (11)$$

where D_3 and D_4 are defined as (12) and (13):

$$D_3 = 1 - 3\frac{d_3}{d_2} \quad (12)$$

$$D_4 = 1 + 3\frac{d_3}{d_2} \quad (13)$$

Factors d_2, d_3, A_2, D_3 and D_4 are tabulated for various sample sizes [9].

After the establishing the $\bar{X}$ and R control charts, 24 samples were taken from processing line and the glazing percentage determined in order to study their behavior during continuous fish processing.

III. Results and Discussion

The results of the analysis of variance obtained for red fish (*Sebastes marinus*), pink cusk-eel (*Genypterus blacodes*), and merlusa (*Merluccius hubbsi*) from dependent variables fit to (1) are summarized in Table II. Only parameters adjusted by the model (p≥0.05) are shown. It was found that the model did not fit adequately for sardine.

Considering the regression equation coefficients as response parameters of time/ temperature, the only equations adjusted from RSM were (15) and (16), with r^2 of 0.87 and 0.74 for red fish and pink cusk-eel, respectively (Table III). RSM regression equations did not adjust for merlusa, suggesting that higher order interaction and/or other variables not considered in the experimental design may have contributed to a better explanation of the data.

Fig. 1 shows that red fish presents high percentage of glazing water, about 18%, for temperatures of -70ºC and time in freezing between 7 and 9 minutes. This value of glazing water is excessively high. According to Vanhaecke et al. [2] this excessive glazing (>12%) may contribute to the ecological footprint of seafood production since unnecessary amounts of ice (water) are being cooled, stored, shipped and transported.In spite of the encountered high values of glazing found Beiragel always sold their fish considering the net weight, without taking the glazing percentage into account. Furthermore, the enterprise usually applies temperature of -60 ºC during 7 minutes, for these conditions the percentage of glazing is also higher than 12% (Fig. 1), which was also observed in previous studies [13]. This could be due to the morphology of the fish species, mainly related with the high surface to volume ratios [2]. The freezing process conditions for pink cusk-eel to obtain high percentage of glazingwater, about 16%, are 100ºC during 8 minutes. Beside the high glazing water content these conditions are extremely difficult to apply because the temperature has to drop down about -40 ºC the time has to be longer what is extremely expensive consider mainly the energy consumption. Usually the Beiragel enterprise glazes this fish with temperature of -60ºC during 5 minutes, which correspond to a percentage of glazing water around 12% (Fig. 1).

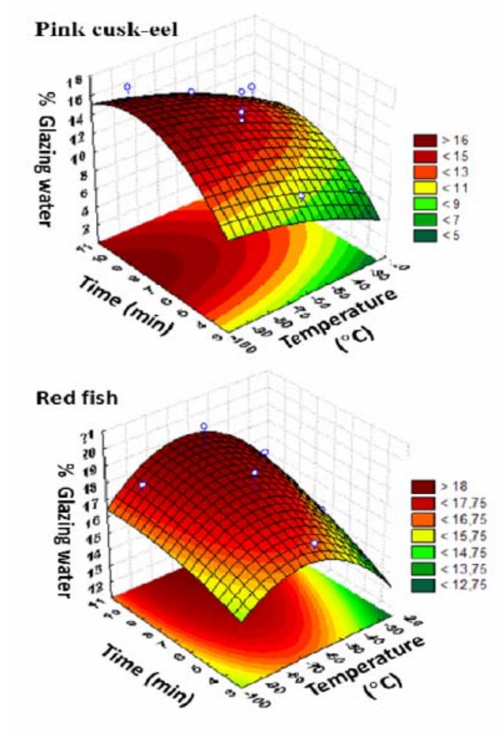

Fig. 1 Percentage of glazing water response surfaces for pink cusk-eel and red-fish

$\bar{X}$and$R$ control charts are determined and implemented. The results are presented in Fig. 2. When the preliminary samples averages were plotted on these charts, no indication of an out-of-control condition was observed. Therefore, since both charts exhibit control, the process was in control at the stated levels and the determined control limits were used in the on-line statistical process control. Fifteen additional samples from the glazing process were collected after the control charts were established. The control charts indicate that the process was in control. Generally, $\bar{X}$ and R control chats showed a mixture pattern, because the plotted points tended to fall near control limits indicating a great variance in the glazing process. There was a shift in the process level in the red fish $\bar{X}$ control chart probably due to raw materials [9].Thus, appropriate actions must be taken in order to improve the process.

Also for control charts, the merlusa presented some process values consecutively near the upper limit in the dispersion chart and lower limit in the average chart which may indicate some difficulties in controlling perfectly the process operations, as it is the case for example of the glazing tank considering the time/temperature parameters or temperature of the fish before glazing. In fact, due to the multiple variables related with the glazing process it is very difficult to find some correlation between them. Correia et al. [13] studied a possible correlation between the glazing water percentage and the line processing temperatures (product temperature, temperature of pre-washing tank, temperature of ozone tunnel, ramp temperature and glaze water temperature) and no correlation was found between them.

TABLE II
ANOVA OF THE PERCENTAGE OF GLAZING WATER IN SARDINE, RED-FISH, MERLUSA AND PINK CUSK-EEL

		Factor							
		T (ºC) (L)	T (ºC) (Q)	t (min) (L)	t (min) (Q)	T x t	Lack of Fit	Pure error	Total SS
	SS	13.86748	8.57061	4.78394	0.22546	0.36464	1.48789	2.66667	31.07692
	df	1	1	1	1	1	4	3	12
Red-fish	MS	13.86748	8.57061	4.78394	0.22546	0.36464	0.37197	0.88889	
	F	15.60092	9.64193	5.38194	0.25365	0.41022	0.41847		
	p	0.028948	0.053082	0.103094	0.649176	0.567421	0.79049		
	SS	8.91446	0.23392	2.66245	6.83936	2.03723	10.51616	2.66667	36.76923
	df	1	1	1	1	1	4	3	12
Merlusa	MS	8.914456	0.233922	2.662447	6.839356	2.037228	2.629041	0.888889	
	F	10.02876	0.26316	2.99525	7.69428	2.29188	2.95767		
	p	0.050604	0.643342	0.181942	0.069345	0.227275	0.199842		
	SS	23.2341	1.00811	32.39093	14.48143	0.04953	21.17332	4.66667	98.76923
	df	1	1	1	1	1	4	3	12
Pink cusk-eel	MS	23.2341	1.00811	32.39093	14.48143	0.04953	5.29333	1.55556	
	F	14.9362	0.64807	20.82274	9.30949	0.03184	3.40286		
	p	0.030635	0.479693	0.019736	0.055378	0.869747	1.171081		

TABLE III
MASS TRANSFER PROPERTIES OF PEARS CALCULATED FOR THE TWO TEMPERATURES STUDIED

Dependent variable	Equation	R^2	R_{adj}	Eq. number
Red-fish	4.925396-0.268726*T-0.0018459*T^2+0.945567*t-0.03000*t^2+0.003337*T*t	0.87	0.77	(14)
Pink cusk-eel	8.203885-0.144735*T-0.000633*T^2+3.895574*t-0.240433*t^2-0.001230*T*t	0.74	0.65	(15)
Merlusa	0.793303-0.039148*T-0.000305*T^2+1.887724*t-0.165233*t^2-0.007888*T*t	0.64	0.0.39	(16)

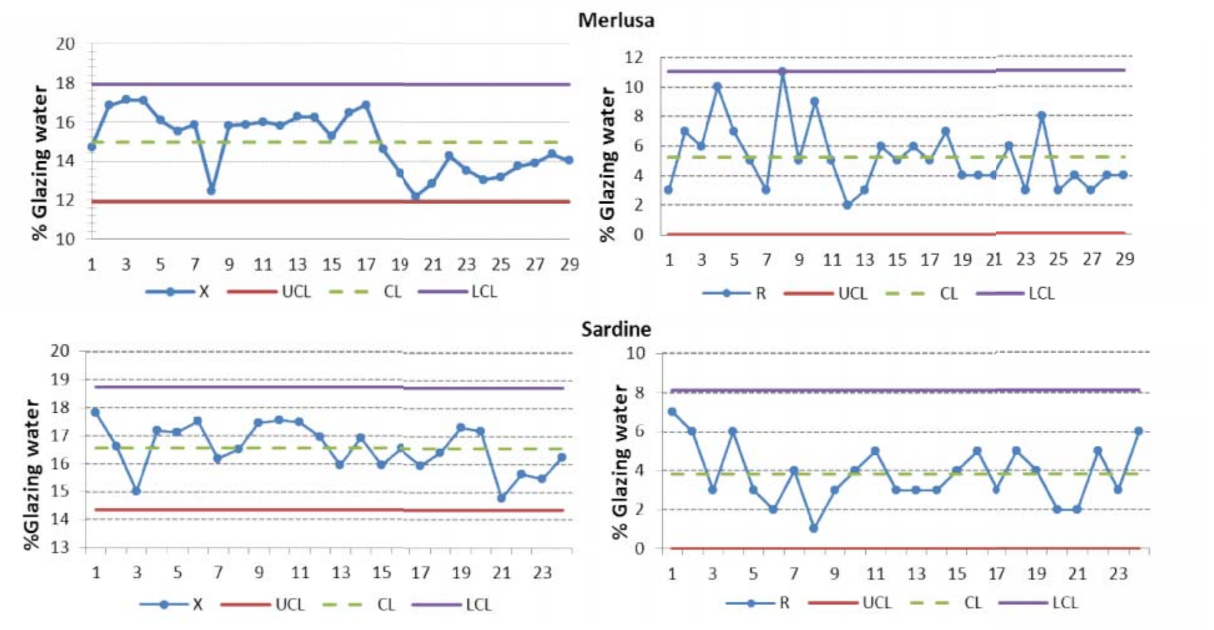

Fig. 2 $\overline{X}$ and R control charts for merluza and sardine

IV. Conclusion

One of the main preoccupations of seafood industry is to improve the conservation technologies of perishable foods to reach a final product with optimal quality. Glazing is a process used to reduce undesirable drying or dehydration of fish during frozen or cold storage. Excessive drying during frozen storage results in freezer burn and a decrease in fish quality.Temporal variations of the ice-glaze uptake on fish during regular production in a plant were monitored by DL 37/2004 and Codex procedure methods. The control of glazing is very important to the quality of fish. Moreover, it is compulsory by Portuguese law. The glazing percentages are generally high, and dependent of fish product.The time/ temperature obtained for pink cusk-eel are closed to the ones used usually in the cryogenic freezing tunnel, -60ºC during 5 minutes. For red fish and for merluza the percentage of glazing water was high and the maximum in the maximum point of RSM the amount of glazing water is too much. More over when the model was applied to sardines did not fit. The results of control charts revealed that the process for sardine and merluza was statistically controlled but presented some random variation causes that must be analyzed and controlled, mainly for merluza. The *R* control chart patterns of the plotted points provide some useful information about the process, generally showing points near the upper and lower limits indicating a great variance in the glazing process.

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