“Emerging Challenges in Chemical Engineering Research, Education, and Industries”

PROCEEDINGS

Regional Symposium on Chemical Engineering (RSCE 2013)

Alona Kew White Beach Resort, Panglao Island, Bohol, Philippines
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Organized by the

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Kinetic Study on the Osmotic Dehydration of Anchovy Salted Fish in Binary and Ternary Solutions

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Most of the salted fish processing in Indonesia is still done traditionally by relying on sunlight. Although this method is cheap, it can decrease the quality of the product because the rate of dehydration cannot compete with the decay of the fish. The use of salt improves the speed of water extraction but to some extent it creates a problem with the texture and the taste. The goal of this study is to improve the anchovy preservation process, to maintain and standardize its quality during processing and to reduce the energy use, by studying the kinetics of osmotic dehydration of that fish. The variables used in this research are the variation of osmotic solutions (NaCl in water - binary solution and NaCl + sucrose - ternary solution), the concentration of the binary solution (15 %, 24 % - saturated, and 50 %), and process temperature (atmospheric temperature and 40 °C). The ternary solution was only applied at the concentration of 24 % NaCl. As a comparison the fish was also treated by salting directly with 10 and 35 %-wt. of food grade salt to the total weight of fish, the more usual preservation method. The results of this study indicate that the loss of water from and the diffusion of salt into the fish substrate increase in parallel with the increase of the osmotic solution concentration and temperature. The effect of temperature on very high NaCl concentration (50%) of the osmotic solution is not significant however. In addition, the use of ternary solution increases the loss of water and also reduces penetration of salt.

Keywords: Anchovy salted fish, Binary solution, Osmotic dehydration, Ternary solution.

INTRODUCTION

15 % of total Indonesian fish production ($5x10^6$ ton/year) is preserved by drying/salting (N.A., 2008). Most of the production is carried out in small-scale sites near the sea. A fresh fish is usually treated by spreading the salt (NaCl) granules on it and store it for uncertain time. Therefore, the quality of the final product is poor which is exhibited by high-salt content while dehydration is inefficient. This leads to more problems like, insect infestation, decay by microbial attack, the formation of toxic compounds and loss of the nutritional value (Yu, 1994).

Osmotic dehydration is a technique of water extraction from the material through immersion it in an osmotic solution. Then, simultaneous countercurrent flows occur: water flows from the material into the solution while solute is simultaneously transferred from the solution into the food material (Rahman, 2007). This method has been used widely especially in the preservation of fruits and vegetables. It has the advantage that fruit and vegetable characteristics and quality are retained while it is a simple process with relative low energy use (Chavan, 2012,).

The osmotic solutions that are widely used in the preservation of food are salt (NaCl) or sucrose ($C_{12}H_{22}O_{11}$) as a binary solution. Bohuon et al. (1998) reported some advantages of using a ternary solution (NaCl + sucrose + water), such as higher levels of dehydration without over-salting the product and the possibility to increase the total solute concentration without exceeding the saturation limits. However, a better understanding of the mechanisms involved in the three simultaneous flows (water flow, salt and sugar penetration) is still needed.

Many parameters have been reported that influence the osmotic dehydration, such as type of the osmotic solutions, the concentration of osmotic agents (Barat, 2001, Nguyen, 2012), process temperature, process time (Torezan, 2004), the geometry of food (Czerner, 2010) and the characteristic (composition) of the food.

Models of the mass transfer during osmotic dehydration have been developed based either on the theoretical or the empirical approaches. Although empirical equations are preferred due to their simplicity in application, some reports showed that they only fitted for certain conditions (Berhimpon, 1990, Corzo, 2005b, Bellagha, 2007, Czerner, 2010). The approach in this study is to derive a mathematical model based on Fick's second law of diffusion, as it has reported before by others like (Azuara, 1992, Singh, 2008, Mundada, 2011). Due to the complex equations that govern the calculation of mass transfer by diffusion, it is common in the literature to make simplifying assumptions, for example, to assume certain food geometry as an infinite flat plate configuration and to neglect peripheral diffusion. The model used in this study was developed based on that assumption and the experiments were done during the dynamic process until the equilibrium condition was reached. The rate of moisture loss during the osmotic hydration using the Fick's second law for unsteady state can be described as follows:

$$\frac{\partial M}{\partial x} = D\frac{\partial^2 M}{\partial x^2} \qquad (1)$$

Where M = diffusing substance after time after t, t = time, x = thickness of the sample, D = diffusion coefficient for moisture in solid.

In the starting situation, one side (x = 0) of the plate is kept at a constant concentration of solute C_1 and the other side (x = l), at C_2 while the plate initially has a uniform concentration C_0. In a finite interval of time during the unsteady state condition, the concentration changes according to,

$$C = C_1 + (C_2 - C_1)\frac{x}{l} + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_2\cos n\pi - C_1}{n}\sin\frac{n\pi x}{l}\exp\left(\frac{-Dn^2\pi^2 t}{l^2}\right) + \frac{4C_0}{\pi}\sum_{m=0}^{\infty}\frac{1}{2m+1}\sin\frac{(2m+1)\pi x}{l}\exp\left(\frac{-D(2m+1)^2\pi^2 t}{l^2}\right) \qquad (2)$$

However, at infinite time ~ equilibrium condition, equation (2) can be simplified to a linear concentration distribution (Crank, 1975, Azoubel, 2000, Telis, 2004). Then, the respective rates of moisture loss and solid gain during osmotic dehydration are determined by equation (3) and (4),

$$\frac{x - x_{eq}}{x_0 - x_{eq}} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{l^2}\right) \qquad (3)$$

$$\frac{M_0 - M}{M_0 - M_{eq}} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{l^2}\right) \qquad \text{............(4)}$$

Where x and M are the moisture content and the NaCl or sucrose concentration, respectively at time t. X_0 and M_0 are the initial value of those variables and x_{eq} and M_{eq} are the corresponding equilibrium values.

The purpose of this study is to investigate the effect of solute concentration (in binary and ternary solution) below, above and at the saturation solution and of process temperature on the water loss, solute gain and to determine the respective diffusion coefficients during the process of osmotic dehydration of the whole anchovy fish. The results of the osmotic dehydration processes are compared with the traditional method of dry-salting.

MATERIALS AND METHOD

The anchovy fish (*Engraulidaei)* was obtained from a local market and has been fished out around 24 hours before. It was cleaned and test samples were selected of about 3.2 – 3.7 g and 0.7 cm thickness. The salt solution was composed by 15 %, 24 % (saturated), and 50 % of analytical grade NaCl. The ternary solution was prepared from 24 % NaCl and 30 % sucrose (food grade). All the experiments were done at room temperature c.a. 25 ^{0}C and

40 ^{0}C. As a comparison a salted-fish (spreaded with 10 % and 35 % of the weight of the complete fish) using a traditional treatment was also prepared. The fresh fish was analyzed for its moisture and salt content.

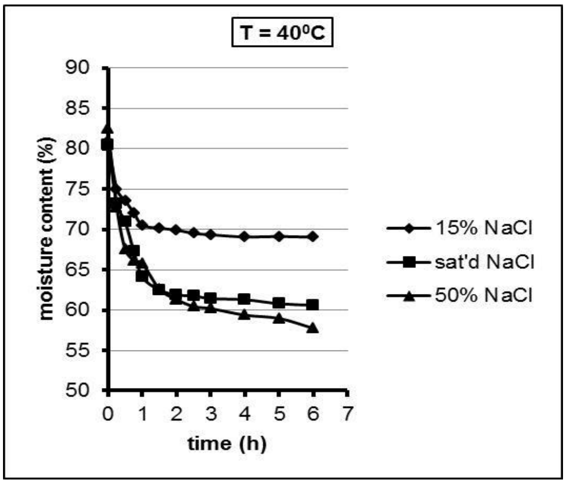
The osmotic dehydration of whole anchovy fish process was carried out in 500 mL Erlenmeyer filled with the required concentration of osmotic solution. The ratio between solution to fish was 10 : 1 (v/v), so the dilution effect can be ignored (Raoult-Wack, 1994). The fish was immersed in the solution and then the Erlenmeyer was placed in the thermostatic shaker.

The water loss during the dynamic process until equilibrium was observed by gravimetry: every 15 minutes during 1 h, 30 min during 2 h and the rest at 1 h intervals until equilibrium was reached (after up to 7 h). Salt gain inside the fish substrate was analyzed by a Volhard titration method at the same moments of the water loss measurements.

RESULTS AND DISCUSSION

Effect of solute concentration during osmotic dehydration

In the first period of process, the high salt concentration between the fish and the solution generates a high driving force. It is logical that the amount of water released was higher when the salt concentration in the solution was higher. From Figure 1 it can be seen that the over-saturated NaCl solution (50 % NaCl) produced the lowest moisture content inside the fish at the equilibrium condition.



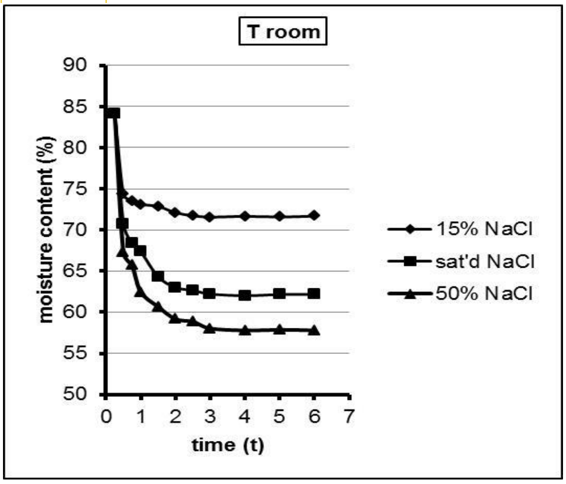
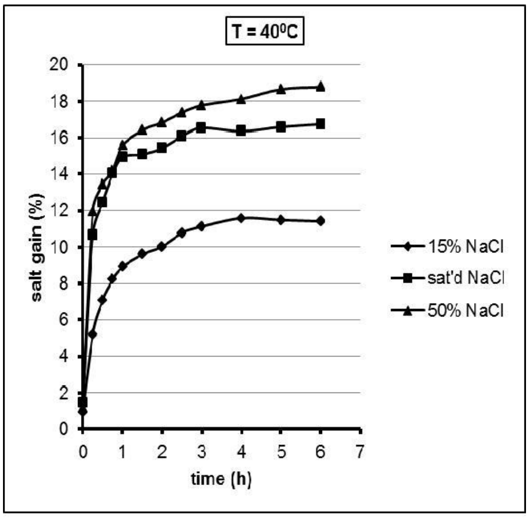


Figure1: Kinetics of water removal from anchovy fish at different concentration of binary solution (NaCl) and at different process temperatures

Generally the reduction of moisture content inside the fish increases with the higher NaCl concentrations. As consequence the salt concentration in the substrate increases as well. For cod brine-salting in varied NaCl concentrations, the average amount of salt in the fish product is 16 % – 20 % as (Oliveira, 2012) reported in a review of the processing of salted cod. This work confirms that report since our results are in the range 11 % – 19 %. But due to of the unpalatable high salt concentration in the fish product, sometimes it should be desalted before consumption. The 10 % dry-salting produced a low salt gain (showed in figure 2), but the dry-salting process tends to leave to much an unevenly distributed water inside giving rise to a spoilage of the fish because of microbial growth.

Effect of process temperature during osmotic dehydration

From the figure 1 can be seen that the fastest moisture transfer occurs in the first period of process both at the process temperature 40^{0}C and at room temperature, and then it gradually slows down until the equilibrium state is achieved. The application of higher temperature reduces the equilibrium time, because at the increasing of temperature the solute molecules will have more energy to move, so the diffusion time of water and salt will be shorter. Only in the over-saturated NaCl solution, the equilibrium moisture content is reached after 6 h and is almost the same at process temperature 40 ^{0}C and at room temperature. But with NaCl concentrations below and until saturation, the effect of process temperature is significant. In this range, an increase of temperature gives a higher with the amount of moisture release from the foodstuff. This result is similar to the observations of osmotic dehydration of sardine (Corzo, 2005a), catfish (Ribeiro, 2004) and shark (Mujaffar, 2006). It is reported however by Kahn et al (Khan, 2012), that the sensorial and nutritional quality of fruits and vegetables is much better persevered when the treatment is done at room temperature. Therefore we would prefer room temperature also for fish preservation treatment.



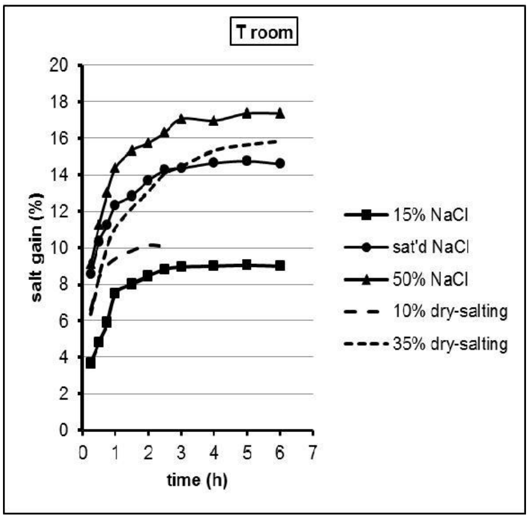


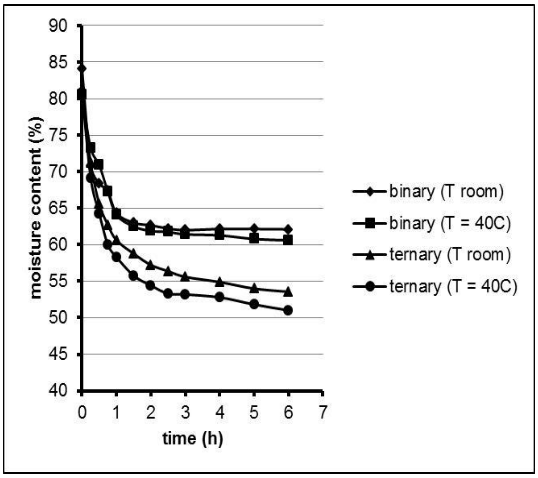
Figure 2: Kinetics of salt penetration in anchovy fish for different concentrations of the binary solution (NaCl) and with dry-salting, at different process temperatures

Effect of the binary and ternary osmotic solution

From figure 3 can be seen that with the addition of sucrose to the osmotic solution, water extraction is larger by 8.9 % at room temperature and 10.3 % at T = 40 ^{0}C. According to the literature, sucrose is a good dehydration agent. Because of its high molecular weight (MW=342), it diffuses only slowly into the fish muscle which means that a high concentration difference between substrate and solution is maintained much longer. So, both the rate and the total amount water release will be higher. The time to reach the equilibrium will reduce as well. Based on the salt gain graph in Figure 3 it can be seen that the presence of sucrose reduces the level of salt gain with 5.08 % at room temperature and with 5.60 % at T = 40 ^{0}C. Similar results were reported by Collignan (1994): for the same amount of water released, the addition of higher molecular weight solute to the treatment fluid can reduce the other solute gain. The addition of sucrose in osmotic solution creates a competition between 2 solutes, since the large molecule of sucrose tend to block diffusion porous, penetration of NaCl will be delayed.

Diffusion coefficients

The diffusion coefficient was calculated based on equation (3) and (4) using a Matlab 7.1 program. The results are shown in Table 1.



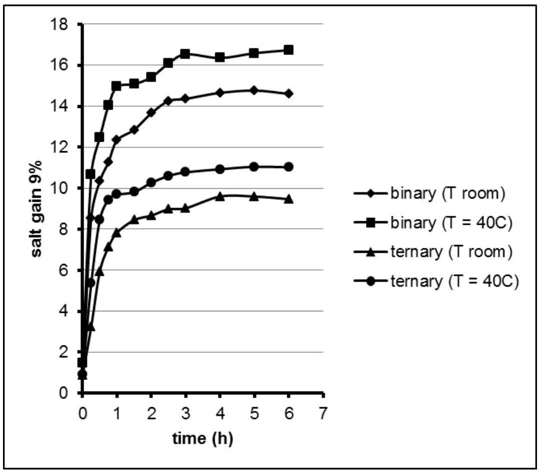


Figure 3: The water loss and salt gain in binary and ternary solution at different temperature

Table 1: Calculated diffusion coefficient of water and salt

No.	Osmotic solution	D_{water} ($cm^2.s^{-1}$)	D_{NaCl} ($cm^2.s^{-1}$)
1	15% NaCl, T= 40^oC	4.30E-05	1.56E-05
2	Sat'd NaCl, T= 40^oC	1.00E-05	1.25E-04
3	50% NaCl, T= 40^oC	1.18E-05	1.56E-04
4	15% NaCl, T room	4.90E-05	1.37E-05
5	Sat'd NaCl, T room	4.74E-05	2.83E-05
6	50% NaCl, T room	7.13E-05	2.05E-05
7	10% dry-salting	2,10E-03	3,32E-05
8	35% dry-salting	8,54E-06	1,07E-05

The diffusion coefficients of water and of salt for the whole anchovy in the brine-salting and dry-salting methods are in the range $1.0x10^{-5}$ – $8.5x10^{-5}$ cm^2 s^{-1} and $1.3x10^{-5}$ – $3.3x10^{-4}$ cm^2 s^{-1}. There are few reports on the calculation of diffusion coefficients during osmotic dehydration of fish. One of them which can be used as a comparison is the observation of Mujaffar and Sankat (Mujaffar, 2006) on shark filets. They obtained D_{water} in the range of $0.73x10^{-5}$ – $2.35x10^{-5}$ cm^2 s^{-1} and D_{NaCl} at $1.5x10^{-5}$ – $2.5x10^{-5}$ cm^2 s^{-1}, in a range of NaCl concentrations and temperature similar to our conditions. The lower value of D obtained in that work can be explained by a difference in the composition of the fish. The presence of lipids in shark may reduce the extraction of water and the penetration of salt (Mujaffar, 2006). Also, there are effects of size and geometry as observed by (Czerner, 2010) with different cuts of anchovies.

The high diffusion coefficient of water in 50% NaCl solution at room temperature and also at 35% dry-salting are conform the high rate of water moving out. To extract water is beneficial as such, however, according to (Martínez-Alvarez, 2005) and (Heredia, 2007) who worked on cod, the high NaCl concentration also leads to the extraction of water-soluble protein from the fish muscle. Also (Ishida, 1994) observed that the increase of brine-salting temperature, also increased the proteolytic activity that digested myosin heavy chain *in vitro* in muscle extracts from salted fillet of anchovy. These factors were not yet taken into account in the present investigation will be addressed in future publication.

CONCLUSIONS

The wet-drying is better than dry-salting in terms of the relation between water loss and salt gained. The distribution of salt inside the fish substrate is more uniform which reduces the risk of microbial growth. The use of ternary solution increases the water loss with a lower increase of the salt content. The higher process temperature to faster equilibrium and more water removal, but it also promotes decay leading to a reduction of the overall fish quality.

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