The air drying behaviour of shark fillets

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Mujaffar, S. and Sankat, C.K. 2005. **The air drying behaviour of shark fillets**. Canadian Biosystems Engineering/Le génie des biosystèmes au Canada **47**: 3.11-3.21. A study was conducted to investigate the drying behaviour of salted shark fillets. To evaluate the effect of air temperature on drying behaviour, shark fillets (100 x 50 x 10 mm) were first osmotically treated in saturated salt (NaCl) solution for 4 h. The initial moisture content fell from 2.86 to 1.66 g H_2O/g DM (74.1 to 62.4% wet basis). The salt content of the fillets after salting was 0.40 g NaCl/g DM (16% salt, wet basis) and the water activity (a_w) fell from an initial value of 0.99 to 0.84. The fillets were dried in a cabinet type drier for 72 h to near equilibrium conditions at fixed temperatures of 40, 50, and 60°C at a constant air velocity of 1.5 m/s and also under ambient conditions (30°C, <0.5 m/s). Samples dried under ambient conditions and at 40°C showed both constant rate and falling rate periods. For samples dried at 50 and 60°C, drying was found to occur in the falling rate period only. The falling rate period for both unsalted and salted fish fillets occurred in two phases, each characterized by a drying rate constant (k_1 and k_2). Drying rate constants for the first phase (k_1) were always higher than those for the second phase (k_2). Increasing the drying temperature from 30 to 50°C significantly enhanced the drying rate of unsalted slabs with rate constants (k_1) increasing from 0.0879 to 0.2229 h^{-1} and diffusion coefficients (D_1) increasing from 2.5 x 10^{-6} to 6.3 x 10^{-6} cm^2/s. Increasing the drying temperature from 30 to 50°C also significantly enhanced the drying rate of salted slabs with rate constants (k_1) increasing from 0.0389 to 0.1660 h^{-1} and diffusion coefficients (D_1) increasing from 1.1 x 10^{-6} to 8.6 x 10^{-6} cm^2/s. Beyond 1.5 h of drying at 60°C, drying rates decreased dramatically possibly due to case hardening in salted fish. The temperature dependence of D_1-values was expressed by an Arrhenius equation. Varying the air speed did not affect drying behaviour of unsalted slabs, while there was a small increase in the drying rate of salted slabs as air speed increased. Salted fish took considerably longer to dry than unsalted (untreated) fish, and drying rates fell as salt content increased. The decline was evident in D_2-values as they decreased from 2.28 x 10^{-6} to 1.39 x 10^{-6} cm^2/s for slabs treated in 60 and 100° brine. For both unsalted and salted slabs, drying rate constants decreased as slab thickness increased and showed a thickness dependence with a power of less than 2. **Keywords:** shark, drying, Fick's law, rate constants, diffusion coefficients.

Les caractéristiques de séchage de filets de requin salés ont été étudiées. Pour évaluer les effets de la température de l'air sur le comportement de séchage, des filets de requin (100 x 50 x 10 mm) ont été premièrement traités par osmose dans une solution de sel saturée (NaCl) durant quatre heures. La teneur en eau initiale est passée de 2,86 à 1,66 g H2O/g MS (soit de 74,1 à 62,4% base humide (b.h.)). La teneur en sel des filets après la salaison était de 0,40 g NaCl/g MS (16% b.h.) et l'activité de l'eau (a_w) est passée de la valeur initiale de 0,99 à 0,84. Les filets étaient séchés dans des séchoirs de type armoire durant 72 heures jusqu'à l'atteinte de l'équilibre à des températures de séchage fixes de 40, 50 et 60ºC et à une vitesse d'air constante de 1,5 m/s ainsi que sous des conditions ambiantes (30ºC, <0,5 m/s). Les échantillons séchés sous les conditions ambiantes et à 40ºC ont tous deux présenté des phases de séchage à taux constants ainsi que des phases à taux de séchage décroissant. Pour les échantillons séchés à 50 et 60ºC, le séchage semblait survenir seulement dans la période de taux de séchage décroissant. La période de séchage décroissant pour les filets de poisson salés et non salés survenait en deux stades, chacun caractérisé par une constante de séchage différente (k_1 et k_2). Les constantes de séchage pour le premier stade (k_1) étaient toujours plus élevées que pour le second stade (k_2). Une augmentation de la température de séchage de 30 à 50ºC augmentait de manière significative le taux de séchage des filets non salés avec des constantes de séchage (k_1) augmentant de 0,0879 à 0,2229 h^{-1} et des coefficients de diffusion (D_1) augmentant de 2,5 x 10^{-6} à 6,3 x 10^{-6} cm^2s^{-1}. Une élévation de la température de séchage de 30 à 50ºC augmentait aussi de manière significative le taux de séchage des filets salés avec des constantes de séchage (k_1) augmentant de 0,0389 à 0,1660 h^{-1} et des coefficients de diffusion (D_1) augmentant de 1,1 x 10^{-6} à 8,6 x 10^{-6} cm^2s^{-1}. Au-delà de 1,5 h de séchage à 60ºC, les taux de séchage diminuaient dramatiquement, possiblement en raison du durcissement de la surface des filets de poisson salés. La dépendance de la température sur les valeurs de D_1 a été exprimée par une équation de séchage de type Arrhenius. Les variations de la vitesse d'air n'ont pas eu d'effet sur le comportement de séchage des filets non salés, cependant il y avait une légère augmentation du taux de séchage dans le cas des filets salés avec une augmentation de la vitesse d'air. Le poisson salé a pris un temps considérablement plus long à sécher que les filets non salés et les taux de séchage diminuaient avec une augmentation du contenu en sel. La diminution des valeurs D_2 était évidente passant de 2,28 x 10^{-6} à 1,39 x 10^{-6} cm^2s^{-1} pour les filets traités dans une saumure de 60 et 100%. Pour les filets non salés et salés, les constantes de taux de séchage diminuaient avec l'augmentation de l'épaisseur du filet et montraient une dépendance à l'épaisseur avec une puissance de moins de 2. **Mots clés**: requin, séchage, loi de Fick, constantes de séchage, coefficients de diffusion.

INTRODUCTION

Dried, salted fish is a very popular food item for West Indians in the Caribbean, Europe, and Canada, where the demand for dried salted fish is driven more for the flavour of the product than for preservation purposes. In an attempt to provide an acceptable alternative to the costly salted codfish, as well as to create an alternative outlet for the less popular species, various species of fish have been used with variable success in the production of dried salted fish. In Trinidad and Tobago, shark is commonly used for this purpose.

Dehydration and salt (sodium chloride) absorption are the fundamental processes contributing to the stability of dried salted fish. Preservation of fish by salting and drying is achieved by lowering the water activity (a_w) of the fish flesh. The addition of salt to the fish flesh also alters the state of proteins and enzymes, and reduces bacterial growth since most spoilage bacteria, with the exception of halophilic bacteria, cannot survive at salt concentrations above 12% wet basis (Ismail and Wooton 1992). Salting alone, however, does not stabilize fish products sufficiently to allow long-term storage. Thus, after salting most products are air-dried to reduce the moisture content to such a level that the water activity (a_w) is sufficiently lowered to prevent or retard spoilage. Most spoilage bacteria will cease to grow in foods whose a_w is below 0.9, mould growth is inhibited below 0.8, halophilic bacteria do not grow below 0.75, and almost all microorganisms are inhibited below 0.6 (Ismail and Wooton 1992).

Drying techniques for salted fish are often haphazard and weather dependent as drying is most commonly carried out in direct sunlight. This contributes to the production of salted fish with inferior sensory characteristics and keeping quality. Rapid drying of salted fish at high temperature results in cooking and burning of the fish or case hardening due to the formation of a salt crust at the surface. Too low a drying rate increases the risk of product deterioration due to bacteria and moulds. Because of the problems associated with sun drying, consideration is now being given to the mechanical dehydration of fish. Generally, drying conditions for various types of salted fish are optimized to give a high quality product in the shortest time. Air at a temperature of 27°C, 45-55% relative humidity (RH), and 1-2 m/s velocity has been recommended for the optimum drying of fish from temperate waters (Beatty and Fougere 1957; Waterman 1976). The optimal drying conditions for tropical species do not appear to be well established (FAO 1981). Higher temperatures (40-50°C) and relative humidities (50-65%) have been used for tropical species (Chakraborty 1978; Prabhu and Balachandran 1981; Shah et al. 1983).

Moisture is removed from fish in the falling rate period with the movement of water within the sample occurring by diffusion (Jason 1958; Wheaton and Lawson 1985; Ismail and Wooton 1992). Fick's second law of diffusion has been widely used to estimate moisture diffusivities (D) of fruits and vegetables (Chirife 1983). The analytical solution of Fick's Law for an infinite slab and which assumes a uniform initial moisture distribution and negligible external resistances, reduces to the straight-line equation for long drying times (Perry et al. 1984):

$$M_r = \frac{M - M_e}{M_0 - M_e} = \frac{8}{\pi^2} \exp\left[-\frac{\pi^2 D t}{4L^2} \right] \tag{1}$$

where:

M_r = removable moisture ratio,
M = moisture content (g H_2O/g DM),
M_e = equilibrium moisture content (g H_2O/g DM),
M_o = initial moisture content (g H_2O/g DM),
L = half-thickness of slab (cm),
D = diffusion coefficient ($cm^{2/}s$),
t = drying time (s)

Equation 1 is frequently written (Henderson and Perry 1976) as:

$$M_r = \frac{M - M_e}{M_0 - M_e} = A \exp(-kt) \tag{2}$$

where: k = rate constant or drying constant (h^{-1}) obtained from the slope of the plot of ln M_r versus t (in hours):

$$k = \frac{\pi^2 D}{4L^2} \tag{3}$$

While drying rate is a parameter of fundamental importance in the production of dried salted fish, limited information is available on the kinetics of water removal from salted shark fish fillets. Any improvement in the methods for the drying of shark would require a better understanding of the drying mechanism and how this is affected by various controllable factors. Consequently, the objective of this research was to investigate and mathematically model the mass transfer changes during the air drying of unsalted and salted shark fillets. The variables to be investigated in this study are drying air temperature, drying air velocity, osmotic solute concentration, and slab thickness.

MATERIALS and METHODS

Raw material handling

Shark was obtained from a local supplier. Upon capture, fish were cleaned, gutted, and skinned before being split in half and filleted (Riley 1973). The fillets were transported to the Processing Laboratory (University of the West Indies, St. Augustine) in an iced box, where they were immediately cut into rectangular slabs (100 mm long x 50 mm wide). These pieces were then carefully placed in reclosable plastic freezer bags and stored overnight in a freezer. The following day, fillets were allowed to thaw partially to allow for easy cutting and then accurately sliced into thin slabs using a food slicer (Model 1612E, Hobart Corporation, Troy, OH).

Osmotic dehydration (salting)

Brine salting of fish (immersing fish in a solution of salt in water) allows for a uniform uptake of salt and close control of the process. In fish processing, a brine strength of between 80-100% saturation is usually recommended (270-360g salt/L) for salting to be effective. The period of immersion is usually determined by trial and error for particular fish species. The fish are maintained in the brine at least until they have absorbed enough salt throughout the depth of the flesh to stop normal bacterial spoilage, usually 8-12% salt (Wheaton and Lawson 1985).

Saturated brine made from food-grade sodium chloride dissolved in distilled water was used as the osmotic medium. The brine solution and the samples were contained in temperature-controlled, stainless-steel water baths with water circulators (Model WB1110A, BlueM Constant Temperature Waterbath, Asheville, NC). The solution (11 L) was constantly recirculated at an average flow rate of 200 mL/s. Preliminary experiments revealed that salt gain and water removal both occurred at acceptable rates at ambient temperature (30°C) so this temperature was selected as a matter of convenience (Burgess et al. 1967; Torrey 1974). Prior to osmotic dehydration, fillets were immersed for 5 min in a 5% citric acid solution. This procedure is recommended as a bleaching step as well as to inhibit the conversion of urea to ammonia in shark. Fillets of 10 mm thickness were salted for a period of 4 h. A 4-h immersion time was sufficient to allow adequate salt absorption to stop normal bacterial spoilage (at least 12% salt, wet basis). After brining, samples were quickly rinsed with water to remove any surface salt to reduce the appearance of white salt crystals on the surface during subsequent drying (Clucas and Sutcliffe 1981).

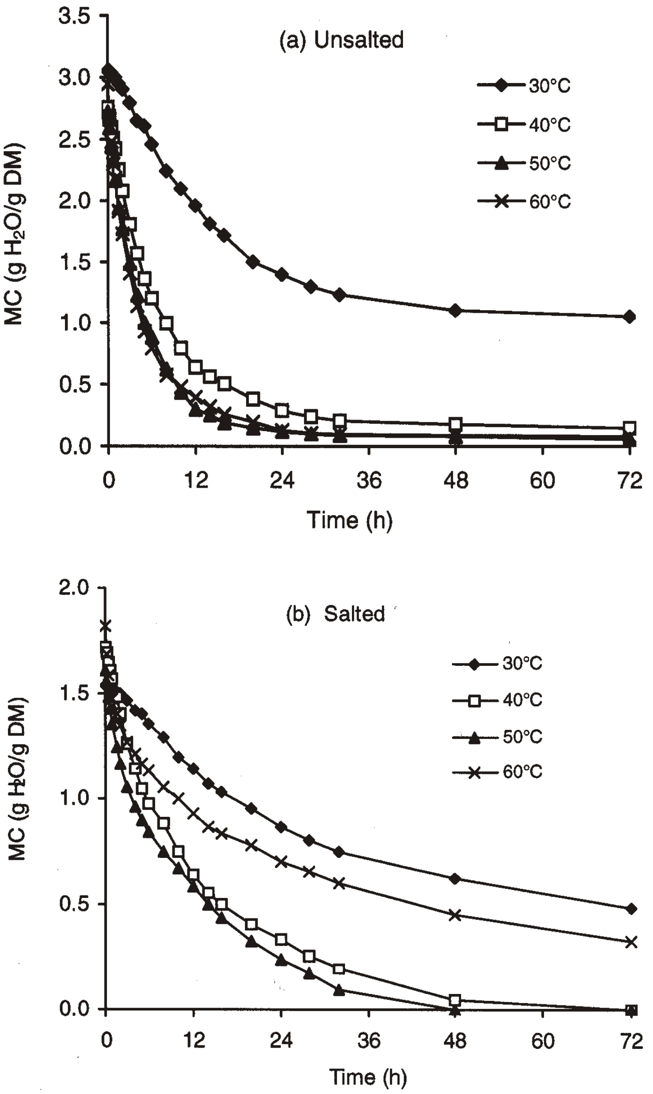


Fig. 1. The effect of temperature on the moisture changes in unsalted and salted shark slabs (100x50x10 mm) during air drying.

Air (oven) drying

Drying of fillets was carried out in a constant temperature, horizontal air flow cabinet oven (BlueM Electric Company, Watertown, WI). The dryer speed in this oven was fixed at 1.5 m/s. Fillets were also dried in a Cole Parmer Oven (Cole Parmer Instrument Company, Vernon Hills, IL) in which the air speed could be controlled via a dial and a slide valve (0 – 1 m/s). Air velocity of the drying air was measured using a digital thermo-anemometer (EXTECH Instruments, Waltham, MA) and relative humidity measured using a Humitemp monitor (Phys-Chem Scientific Corp, New York, NY). Fillets were spread in single layers on pre-weighed, shallow wire mesh trays. Five samples were placed on each tray, and two trays were used for each drying run. At regular intervals, the samples were taken out, quickly weighed and returned to the dryer. Drying was continued for a maximum of 72 h and after that samples were dried in an oven at 105°C for 24 h to determine dry mass. From this data, the average values of moisture content as a function of time were determined and used to construct the drying curves (Sankat et al. 1996).

To evaluate the effect of air temperature on the drying process, salted fillets (10 mm thick) were dried under ambient laboratory conditions (30°C), and at three oven temperatures, 40, 50, and 60°C. The air speed in the dryer was fixed at 1.5 m/s and under ambient conditions, less than 0.5 m/s. Fresh (unsalted) fillets were also dried at each temperature.

To evaluate the effect of air velocity on the drying process, 10 mm thick fillets (unsalted and salted) were dried at 50°C and at air velocities of 0 (natural convection), 0.60, 0.91, and 1.0 m/s. Drying was carried out at 50°C since shark fillets previously dried at this temperature dried quickly while maintaining good colour and texture.

To evaluate the effect of osmotic solute concentration on the drying process, 10 mm thick fillets were salted for a period of 4 h in three different brine solutions: 60, 80, and 100° brine. Fillets were dried at 50°C and at an air speed of 1.5 m/s. A similar set of untreated (unsalted) fillets were also dried.

To evaluate the effect of fillet thickness on the drying process, slabs 5, 10, and 20 mm thick were dried at 50°C (1.5 m/s). To ensure an initial uniform salt concentration in fillets of such varying thicknesses, these fillets were salted for a longer period of 24 h prior to drying. A control set of untreated (unsalted) fillets was also dried.

Analytical methods

Mass was measured using an Ohaus Electronic Balance (Ohaus Scale Europe Ltd., Cambridge, England). Moisture content, expressed both on a percentage wet mass basis (g H_2O/100g fresh mass) and on a dry mass basis (g H_2O/g DM) was determined by an oven-drying method (FAO 1981). Samples were dried for 24 h at 105°C in a Gallenkamp Size One BS Oven (SANYO Gallenkamp PLC, Loughborough, Leicestershire, England). Salt (NaCl) content of the fillets was determined titrimetrically using silver nitrate solution (FAO 1981) and expressed both as percentage salt on a wet mass basis (g NaCl/100g fresh weight) as well as on a dry mass basis (g NaCl/g DM). Water activity (a_w) was measured using a water activity meter (Rotronic Hygroskop DT, Rotronic Instrument Corp., Huntington, NY) and calculated as the equilibrium relative humidity divided by 100 (Gould and Gould 1988).

Data analysis

Data analysis consisted of simple regression analysis using Microsoft Excel 97 to examine the data for goodness of fit. Further Regression Analysis and ANOVA were carried out using GENSTAT Statistical Software (Lawes Agricultural Trust 1996).

RESULTS and DISCUSSION

Effect of air temperature

Air drying curves Air drying curves for unsalted and salted fish fillets at 30 to 60°C are shown in Figs. 1a and 1b, respectively. Moisture content was significantly affected by drying time, dry bulb temperature, treatment, and a time-temperature-treatment interaction ($p \leq 0.001$). The moisture content of unsalted slabs prior to air drying averaged 2.86 g H_2O/g DM (74.1% wet basis). The moisture and salt content of salted slabs prior to air drying averaged 1.66 g H_2O/g DM (62.4% wet basis), and 0.40 g NaCl/g DM (16% salt, wet basis), respectively. The difference in initial moisture content reflects

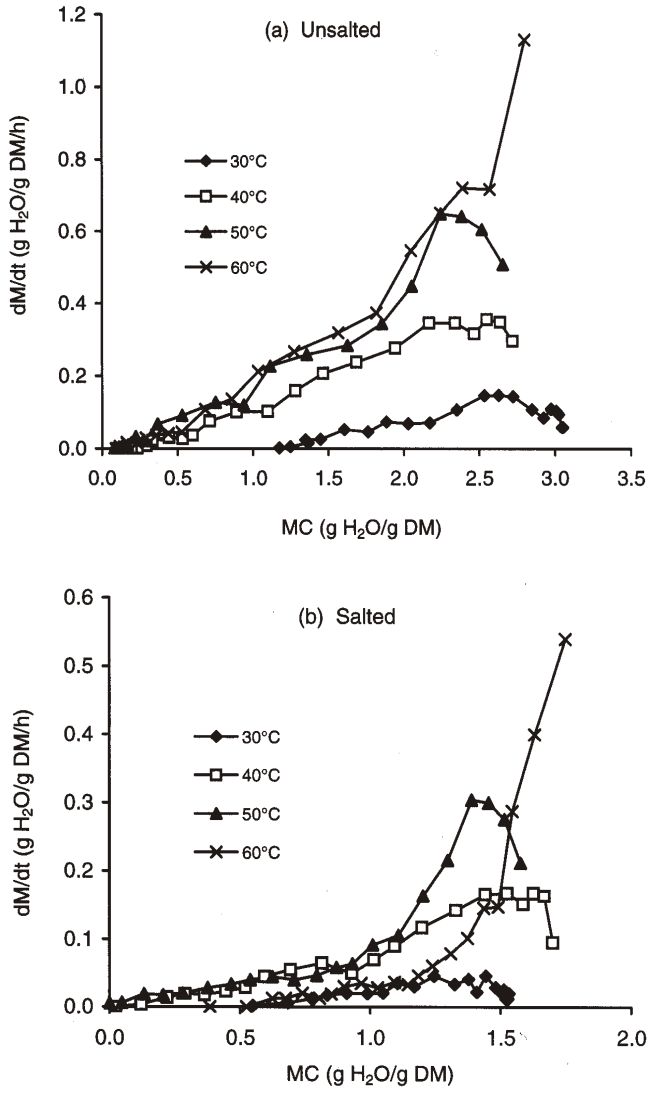


Fig. 2. Drying rate (dM/dt) versus average moisture content for shark slabs dried at different temperatures.

the degree of water loss during salting. During drying, moisture content decreased logarithmically with drying time, which means that the slabs suffered greater moisture loss at the initial stage of drying.

For unsalted slabs, the greatest decrease in moisture content occurred during the first 8 h of drying. Unsalted slabs dried under ambient conditions appeared moist and developed off-odours after 16 h, indicating spoilage. In the hot ambient temperatures of the tropics, fish can spoil within 12 hours (Maas-van Berkel et al. 1994). Increasing the temperature to 40 and 50°C resulted in a noticeable increase in moisture loss. Slabs at 60°C dried marginally faster than those at 50°C during the first 8 h, beyond which the decline in moisture content became more gradual, with the moisture values of these slabs being a little higher than those at 50°C. Slabs dried at 60°C developed the aroma of cooked fish. Moisture content values after 48 h of drying at 30, 40, 50, and 60°C averaged 1.10, 0.18, 0.08, and 0.09, respectively. Curves for unsalted oven-dried slabs showed some convergence after 32 h of drying.

Sankat et al. (1996) reported that equilibrium moisture values of fresh and osmosed banana slabs are dependent upon the drying conditions, falling as the air dry bulb temperature is increased and the relative humidity decreased. This was found to be true in the present study as the temperature increased from 30 to 50°C. Equilibrium moisture contents for unsalted slabs dried at 30, 40, and 50°C averaged 1.05, 0.15, and 0.06 g H_2O/g DM, respectively. The equilibrium moisture content for unsalted slabs dried at 60°C was marginally higher than that of slabs dried at 50°C, and averaged 0.08 g H_2O/g DM. Water activity values after 32 h drying also reflected this trend averaging 0.996, 0.657, 0.384, and 0.393 for slabs at 30, 40, 50, and 60°C, respectively.

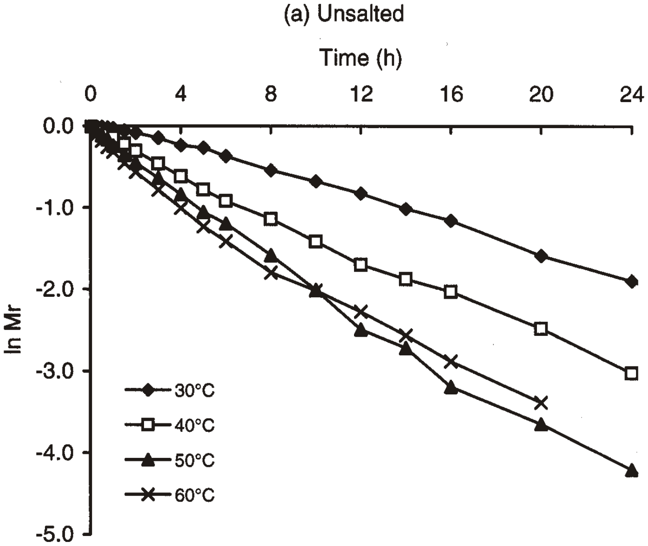
The decline in moisture content was considerably less for salted slabs compared with unsalted samples. Increasing the temperature from 30 to 50°C did result in a higher decline in moisture content, however further increasing the temperature to 60°C reversed this trend. Salted slabs dried at 60°C showed high moisture loss only during the first 1.5 h of drying and during this time slabs developed a white, crusty surface. After this time, these slabs lost moisture much more gradually. As a result, the moisture content values of these slabs beyond 3 h of drying were higher than for slabs dried at 40 and 50°C. By the fifth hour of drying, these slabs were very brittle and easy to break, but the insides of the pieces were still moist.

Equilibrium moisture values were again dependent on the drying air conditions, decreasing dramatically from 0.48 g H_2O/g DM for salted slabs dried at 30°C to near zero for slabs dried at 40 and 50°C. Water activity values for salted slabs dried at 30, 40, 50, and 60°C for 32 h averaged 0.794, 0.772, 0.436, and 0.782, respectively.

In this study, the relative humidity of the drying air was not maintained at a steady, controlled value. Increasing the oven temperature resulted in a decrease in humidity (sensible heating). The relative humidity of the drying air under ambient conditions and at each of the three oven temperatures (40, 50, and 60°C) was measured and found to be 60, 40, 25, and 15%, respectively. Drying fish with too low a humidity can lead to toughening of the surface and reduced drying rate during the falling rate period (Wheaton and Lawson 1985).

Salted slabs at 60°C appeared dried on the outside, but were still moist on the inside, a classic example of case hardening. Case hardening is the progressive formation of a thick crust of salt and protein at the surface. Surface layers dry quickly, producing a hard layer which is impervious to the passage of water. This layer then prevents the migration of water and the centre of the fish can become spoiled although it looks well dried (Wheaton and Lawson 1985).

Rate curves Moisture content data were used to calculate the rate of change in moisture with drying time. This was done by calculating the difference in moisture content (g H_2O/g DM) between consecutive sampling times and dividing this value by the time interval (h). The drying rate curves (rate versus average moisture content) for the air drying of unsalted and salted fish slabs are shown in Figs. 2a and 2b, respectively. The rate of change in moisture content was significantly affected by moisture content and moisture content-temperature interaction ($p \leq 0.001$). After an initial warm-up period in some instances, drying at 30 and 40°C occurred both in the constant rate and falling rate periods, while drying at 50 and 60°C occurred in the falling rate period only.


(a) Unsalted

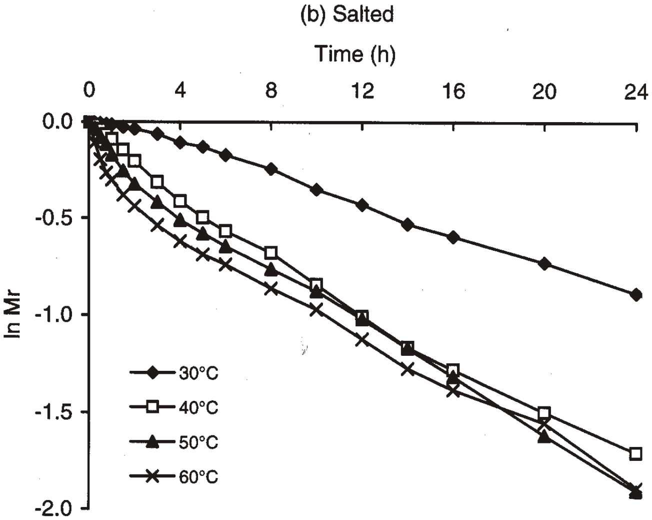

(b) Salted

Fig. 3. Free moisture (moisture ratio) for shark slabs dried at different temperatures.

For unsalted slabs at 30 and 40°C, there was a period of constant rate drying. As also reported by Jason (1958) for the air drying of unsalted cod muscle, there is an initial period of variable duration during which the drying rate is controlled by the rate at which water can evaporate at the surfaces and is essentially constant. After a certain critical moisture content (approximately 2.30 g H_2O/g DM), the drying rate curves began to decline. For unsalted slabs at 50 and 60°C, there was an initial rapid decline in rate, followed by a more gradual decline to equilibrium conditions in one or more linear portions. This implies that internal water movement was controlling from the beginning of the drying process at these temperatures.

This trend was similar for salted slabs, with two exceptions. Firstly, the rates for salted slabs were lower since the moisture content of these slabs were lower. Secondly, after the initial rapid drying rate at 60°C, there was a drastic decline in rate. As noted previously, excessive rapid drying results in a poorer quality and a lower drying rate during the falling rate period as the formation of a crust retards the diffusion of water from the deeper layers to the surface.

The constant rate drying observed under ambient conditions (30°C) and at 40°C was most likely due to the low drying rate potential of air and the formation of a saturated layer of air above the sample surface (Chirife 1983). Jason (1958) found that for fish muscle the constant rate period was a significant portion of the total drying time. This has been attributed both to the low temperature (30°C) and air velocity (0.3 m/s) employed in his drying experiments.

Drying constants When the experimental data for unsalted and salted slabs were plotted as free moisture versus time based on Eq. 1, Figs. 3a and 3b were obtained. After an initial constant rate drying period, a straight line was obtained for unsalted slabs dried at 30°C, which means that the falling rate period for unsalted slabs at this temperature occurred in one phase. Following the brief initial constant rate period for unsalted slabs at 40°C, the plot was broken into two linear portions representing two falling rate periods. For unsalted slabs dried at 50 and 60°C the plots were each broken into two linear portions again representing two falling rate periods. The first linear portion ended after 12 h (0.64 g H_2O/g DM), 12 h (0.30 g H_2O/g DM) and 6 h (0.79 g H_2O/g DM) for unsalted slabs dried at 40, 50, and 60°C, respectively. A drying behaviour similar to that shown in this study was found by other authors during dehydration of biological materials, including fish muscle (Del Valle and Nickerson 1968; Jason and Peters 1973) where the falling rate is divisible into two distinct phases, the first and the second falling rate periods.

With the exception of slabs dried at 30°C, plots for salted slabs were divisible into two linear portions, the first linear portion ending after 6 h (0.98 g H_2O/g DM), 2 h (1.16 g H_2O/g DM), and 1.5 h (1.40 g H_2O/g DM) for slabs dried at 40, 50, and 60°C, respectively.

Linear regression was employed to obtain values of rate constants for different dry bulb temperatures. The data for unsalted slabs dried at 30˚C were successfully fitted with a single straight line representing the first falling rate period with rate constant, k_1. The data for unsalted slabs dried at 40-60°C could not be fitted with a single straight line but with two segments of straight lines corresponding to the first and second falling rate periods with rate constants k_1 and k_2, respectively. Drying constants are given in Table 1. For unsalted slabs, increasing the drying temperature from 30 to 50°C significantly enhanced the drying rate and the k_1-values. Values increased approximately 2.3 times from 0.0879 h^{-1} for slabs dried at 30°C, to 0.2015 h^{-1} for slabs at 50°C. While further increasing the temperature to 60°C resulted in an increase in k_1-value, the duration of the first falling rate period was shorter (6 h) compared with slabs at 50°C (12 h). Beyond 6 h, the drying rate constant for slabs at 60°C declined to 0.1408 h^{-1} (Table 1). An increase in rate constant with increasing drying air temperature has been shown for the drying of many biological materials (Chiang and Petersen 1985; Yusheng and Poulsen 1988; Sankat et al. 1996). The k-values for the first falling rate phase were higher than those for the second phase.

With the exception of slabs dried under ambient conditions (30°C), the data for salted slabs were fitted with two straight lines, again each characterized by a drying constant, k_1 and k_2 (Table 1). For salted slabs k_1-values were generally lower than those for unsalted slabs but showed a similar trend, increasing

Table 1. The effect of drying temperature on the drying rate constants of shark slabs (100 x 50 x 10 mm).

Temperature (°C)	rh (%)	Drying rate constants (h^{-1})							
		Unsalted				Salted			
		k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2
30	60	0.0879	0.9970	-	-	0.0389	0.9982	-	-
40	30	0.1429	0.9978	0.1146	0.9970	0.0993	0.9961	0.0645	0.9906
50	25	0.2015	0.9987	0.1431	0.9953	0.1660	0.9972	0.0715	0.9979
60	10	0.2396	0.9959	0.1408	0.9966	0.2486	0.9438	0.0637	0.9970

with increasing temperature. However, for slabs dried at 60°C the first falling rate period was very short (1.5 h), during which time there was very rapid drying and the k_1-value was high (0.2486 h^{-1}).

Cooking of meat tissues has a pronounced effect on its drying behaviour. Jason (1958) found that cooking of fish increased 2.7 times the diffusivity of water in the falling rate period, compared with an uncooked sample. Jason attributed this effect to the introduction of porosity in the muscle as a result of cooking. For the shark slabs dried at 60°C, k_2-values were considerably lower than the k_1-values, a reflection of the drastic decrease in drying rate due to case hardening during the initial stages of drying.

According to Peters (1971), the transition from the first to the second falling rate phase corresponds with the uncovering of the monomolecular inner layer of water molecules after the multiple-molecule outer layer is removed. Uddin et al. (1998) reported that for the drying of unsalted *Alute mate* fish samples (40 x 40 x 12 mm) at 40 to 70°C, no constant rate period was observed, and a second falling rate period was present in all cases. The second falling rate period started at a moisture content of approximately 210% (db).

Diffusion Coefficients The drying rate constants for unsalted and salted slabs were used to calculate diffusion coefficients according to Eq. 3. Diffusion coefficients for the first falling rate period (D_1) for all slabs increased with increasing drying temperature. These values were always higher than D_2-values at each temperature.

For unsalted slabs, D_1-values averaged 2.47 x 10^{-6}, 4.38 x 10^{-6}, 5.88 x 10^{-6}, and 6.75 x 10^{-6} cm^2/s for slabs dried at 30, 40, 50, and 60°C, respectively. D_2-values were lower and averaged 3.23 x 10^{-6}, 4.52 x 10^{-6}, and 3.97 x 10^{-6} cm^2/s for slabs dried at 40, 50 and 60°C, respectively. For salted slabs, D_1-values averaged 1.09 x 10^{-6}, 2.81 x 10^{-6}, 4.67 x 10^{-6}, and 7.00 x 10^{-6} cm^2/s for slabs dried at 30, 40, 50, and 60°C, respectively. D_2-values for salted slabs dried at 40, 50, and 60°C averaged 1.81 x 10^{-1}, 2.01 x 10^{-6}, and 1.80 x 10^{-6} cm^2/s, respectively.

These values compare reasonably well with the results of other researchers. Jason (1958) found that D_1-values for various fish including herring, whiting, halibut, haddock, and cod dried at 30°C ranged from 1.9 to 3.5 x 10^{-6} cm^2/s. Del Valle and Nickerson (1968) investigated the drying of swordfish slices (40 mm diameter x 50 mm thickness) and found that D_1-values increased from 3.0 x 10^{-6} to 3.9 x 10^{-6} cm^2s^{-1} as drying temperature increased from 40 to 55°C. Diffusion coefficients reported by Uddin et al. (1998) for the drying of a South-East Asian fish (*Alute mate*) at 40 to 70°C at an air velocity of 1.2 m/s averaged 6.3 x 10^{-7} to 1.2 x 10^{-6} cm^2/s. Del Valle and Nickerson (1968) reported D_1-values of 2.6 x 10^{-6} and 3.3 x 10^{-6} cm^2/s and D_2-values of 1.0 x 10^{-6} and 0.9 x 10^{-6} cm^2/s for salted swordfish slices dried at 40 and 55°C, respectively. The lower diffusivities for salted slices compared with unsalted slices reflect the lower rate of moisture loss experienced by salted slabs during drying.

According to Jason (1980), the rate of diffusion is always lower for the second falling rate period because the activation energy at this stage is higher (Ismail and Wooton 1992). Jason (1958) found that D_2-values for various fish averaged between 3.5 – 8.1 x 10^{-7} cm^2/s. Peters (1971) found that the second diffusion coefficient is invariant in the temperature range 15 to 30°C.

Differences in the values of the diffusion coefficients obtained in this study and those cited in the literature may be attributed to the small uniform slab size employed. Many researchers use cross-sectional slices of the fish, or in cases where fillets are used, the thickness of each fillet varies due to the curved shape of the fish.

The increase in D-values for unsalted and salted slabs with increasing temperature was described using an Arrhenius type equation:

$$\ln D = -\frac{E_a}{RT} \tag{4}$$

where:

E_a = activation energy (kJ/mol),
R = gas constant (8.314 kJ K^{-1} mol^{-1}), and
T = process temperature (K).

The activation energy determined from the slope of a plot of ln D versus $1/T$ was calculated to be 28.2 kJ/mol (R^2 = 0.9616) for unsalted slabs and 51.1 kJ/mol (R^2 = 0.9729) for salted slabs, respectively. This value compares well with E_a value cited by Jason (1958) for water diffusion in cod muscle during the first falling rate period (29.7 kJ/mol). A lower activation energy was given by Del Valle and Nickerson (1968) for the drying of swordfish (15.1 kJ/mol). The higher activation energy for salted fish corresponds to the tighter binding of water molecules in the protein structure at lower moisture levels (Jason 1958). It therefore takes longer to dry the same amount of water in the second phase of drying than in the first phase.

Effect of air velocity

The initial moisture content of shark fillets averaged 2.73 g H_2O/g DM (73.2% wb). After 4 h of brining, moisture content decreased to 1.47 g H_2O/g DM (59.5% wb) and salt content

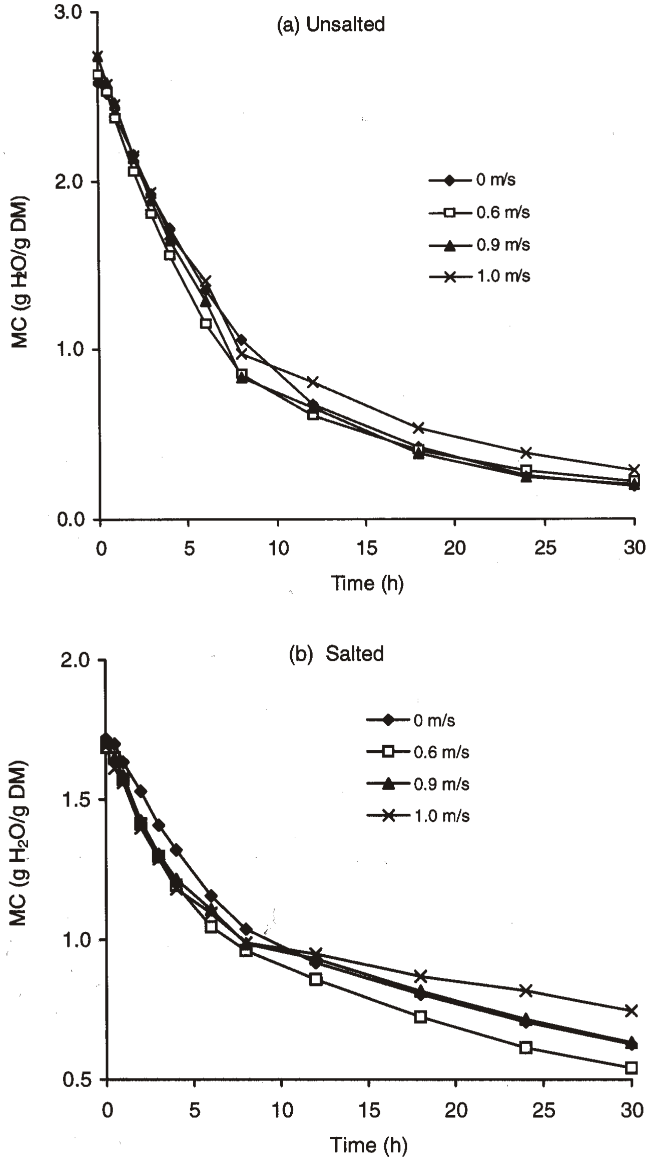


Fig. 4. The effect of air velocity on the moisture changes in unsalted and salted shark slabs dried at 50°C.

increased to 0.40 g NaCl/g DM (16.0% salt, wb). The drying curves for unsalted and salted slabs dried at different air velocities at 50°C (Figs. 4a and 4b) are not very different from each other and the slopes of the lines are almost identical. The diffusion coefficients (D_1) for unsalted and salted slabs appeared to be independent of air velocity, averaging 3.37 x 10^{-6} and 3.02 x 10^{-6} cm^2/s, respectively.

It has been established that drying at 50°C occurs only in the falling rate period. A number of workers have studied how the air flow rate affects the drying rate (Saravacos and Charm 1962; Vaccarezza et al. 1974; Jason 1980; Chiang and Peterson 1985; Yousheng and Poulsen 1988), and have found that either air velocity did not influence the drying rate during the falling rate period or that its influence can be neglected. Sankat et al. (1996) noted that at lower air velocities (0.62 to 1.03 m/s) a small improvement in drying rate was observed in banana slabs dried at 60°C. Uddin et al. (1998) found that at temperatures of 40 to 70°C, an increase in air velocity from 0.60 to 1.20 m/s resulted in an increase in first and second diffusion coefficients in unsalted *Alute mate* fish.

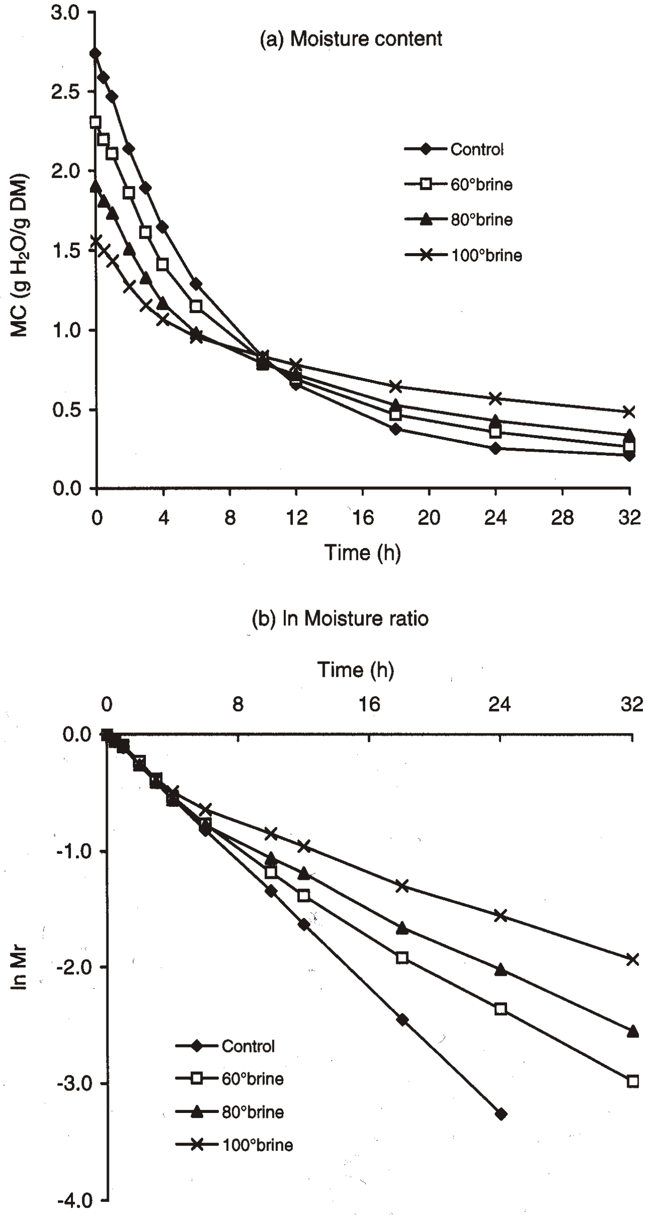


Fig. 5. Drying data for shark slabs osmotically pretreated in brines of different concentrations.

Effect of osmotic solute concentration

To further evaluate the effect of osmotic solute concentration on the drying rate, fillets which were salted for 4 h in 60, 80, and 100°brine, as well as unsalted fillets (control) were dried at 50°C and at an air speed of 1.5 m/s. The initial moisture content and water activity of slabs averaged 2.73 g H_2O/g DM (73.2% wb) and 0.998, respectively. The characteristics of fillets after 4 h salting using different brine concentrations are summarised in Table 2.

As shown in Fig. 5a, the higher the salt concentration used to osmotically treat the fish prior to drying, the lower the decline in moisture ($p \leq 0.001$). This was caused by higher moisture

Table 2. The characteristics of shark slabs after 4 h brining in a saturated (100° brine) solution.

Brine concentration	Mass reduction (%)	Moisture content ($g\ H_2O/g$ DM)	Salt content (g NaCl/g DM)	a_w
60° brine	0	2.29 (69.6% wb)	0.35 (10.5% salt wb)	0.933
80° brine	5.9	1.82 (64.5% wb)	0.43 (15.2% salt wb)	0.924
100° brine	9.4	1.47 (59.5% wb)	0.46 (18.7% salt wb)	0.832

Table 3. The effect of salt concentration used in osmotic pre-treatment on the drying rate constants and diffusion coefficients of shark slabs (100 x 50 x 10 mm) dried at 50°C.

Salt concentration	Drying constants (h^{-1})				Diffusion coefficients* (cm^2/s)	
	k_1	R^2	k_2	R^2	D_1	D_2
Control	0.1361	0.9999	-	-	3.83×10^{-6}	-
60° brine	0.1327	0.9968	0.0812	0.9978	3.72×10^{-6}	2.28×10^{-6}
80° brine	0.1349	0.9957	0.0682	0.9988	3.81×10^{-6}	1.92×10^{-6}
100° brine	0.1278	0.9968	0.0494	0.9982	3.58×10^{-6}	1.39×10^{-6}

* $D = 4kL^2/\pi^2$

contents and lower salt contents produced by salting in lower brine concentrations, thus allowing faster removal of water (Jason and Peters 1973; Wuttijumnong et al. 1985; Poernomo et al. 1992). The higher the salt, the lower the initial moisture of the slabs and therefore the faster to reach equilibrium (Yu et al. 1982). As seen in this study, the equilibrium values for slabs salted at higher brine concentrations were higher then for slabs salted at the lower concentrations. Moisture values after 32 h of air drying averaged 0.206, 0.260, 0.333, and 0.482 $g\ H_2O/g$ DM for control (untreated) slabs, and slabs dehydrated in 60, 80, and 100° brine, respectively. Plots of free moisture versus time (Fig. 5b) were divisible into 2 linear portions from which the rate constants k_1 and k_2 were obtained (Table 3). There was a small decline in k_1-values as the salt content of the slabs increased. This decline was more evident in k_2-values as they decreased from 0.0812 to 0.0494 h^{-1} for slabs treated in 60 and 100°brine respectively. A decline in D_2-values from 2.28×10^{-6} to 1.39×10^{-6} cm^2/s as brine concentration increased from 60 to 100° brine further showed this trend.

Similar results were obtained by Jason (1958) for the drying of codfish at 30°C. Initially, moisture ratio curves for unsalted and salted slabs were characterized by almost the same slope, the effective diffusion coefficients being 3.09×10^{-6} and 3.23×10^{-6} cm^2/s. Jason (1958) found that D_2-values for unbrined samples averaged 0.61×10^{-6} cm^2/s while D_2-values for brined fish averaged 1.35×10^{-6} cm^2/s. As also found in this study, the drying curve for salted slabs entered the falling rate period considerably sooner (4 h) than for unsalted slabs (24 h). According to Jason (1958) the two factors which appear to contribute to the retardation in drying rate in salted fish slabs are (i) an early entry into the falling rate period, and (ii) a smaller D-value. He added that the physical changes in the fish muscle which give rise to the retardation in drying rate after the fish muscle has been brined are different from those changes which brought about either by cooking or by previous osmotic drying.

The drying rate of fish salted in higher brine concentrations was lower than that of fish salted in lower brine concentrations. This was caused by higher moisture contents and lower salt contents produced by salting in lower brine concentrations, thus allowing faster removal of water (Jason and Peters 1973; Yu et al. 1982; Wuttijumnong et al. 1985; Poernomo et al. 1992). Del Valle and Nickerson (1968) found that the diffusion coefficient for the first falling rate period was a function of the degree of salting of the fish muscle, increasing initially, passing through a maximum, and subsequently decreasing with the degree of salting. The second diffusion coefficient was found to decrease as the degree of salting increased.

Rahaman and Lamb (1991) found that for the air drying of osmotically treated pineapple slices, effective diffusivities decreased (or water removal resistance increased) with the increase of solid (in this case sucrose) in the slices prior to drying at the same drying conditions. Sankat et al. (1996) showed decreasing k_1 and k_2-values as sugar content of bananas increased. Lower drying rates of osmosed fruits have been attributed to higher initial solid content and/or the action of solute on the water sorption behaviour (Rahman and Lamb 1991).

Effect of sample thickness

The initial moisture content of shark fillets averaged 2.83 $g\ H_2O/g$ DM (73.9% wb). The moisture content of fillets 5, 10, and 20 mm thick decreased to an average of 1.45 $g\ H_2O/g$ DM (58.4% wb) and salt content increased to 0.46 g NaCl/g DM (18.7% salt, wb). Figures 6a and 6b show the drying curves for unsalted and salted slabs of varying thickness dried at 50°C. It is immediately apparent that slab thickness affects the decline in moisture content of both unsalted and salted samples ($p \leq 0.001$), with the 5 mm thick slabs showing the fastest decline in moisture content. The effect of slab thickness is made even clearer from the rate curves (Figs. 7a and 7b), and from evaluation of the rate constants (Table 4) which show a clear dependence on thickness. Lower drying rate corresponded to a lower k-value, with values decreasing from 0.4862 to 0.0626 h^{-1} for unsalted slabs, and 0.3332 to 0.0757h^{-1} for salted slabs. As explained by Uretir et al. (1996) for the drying of apples, it is expected that the drying rate constant for the falling rate will increase with surface area. The surface area of shark slabs 5, 10, and 20 mm thick averaged 115, 130, and 160 cm^2, respectively. The ratio of the surface area to volume of the slabs averaged 4.6, 2.6, and 1.6 cm^{-1} for slabs 5, 10, and 20 mm thick. Therefore, the higher this ratio, the higher the expected drying rate. However, as also shown by Uretir et al. (1996), increasing the thickness of the slab slowed the drying process which means that thickness effects suppressed the surface area effect. These results further support that drying at 50°C is controlled by

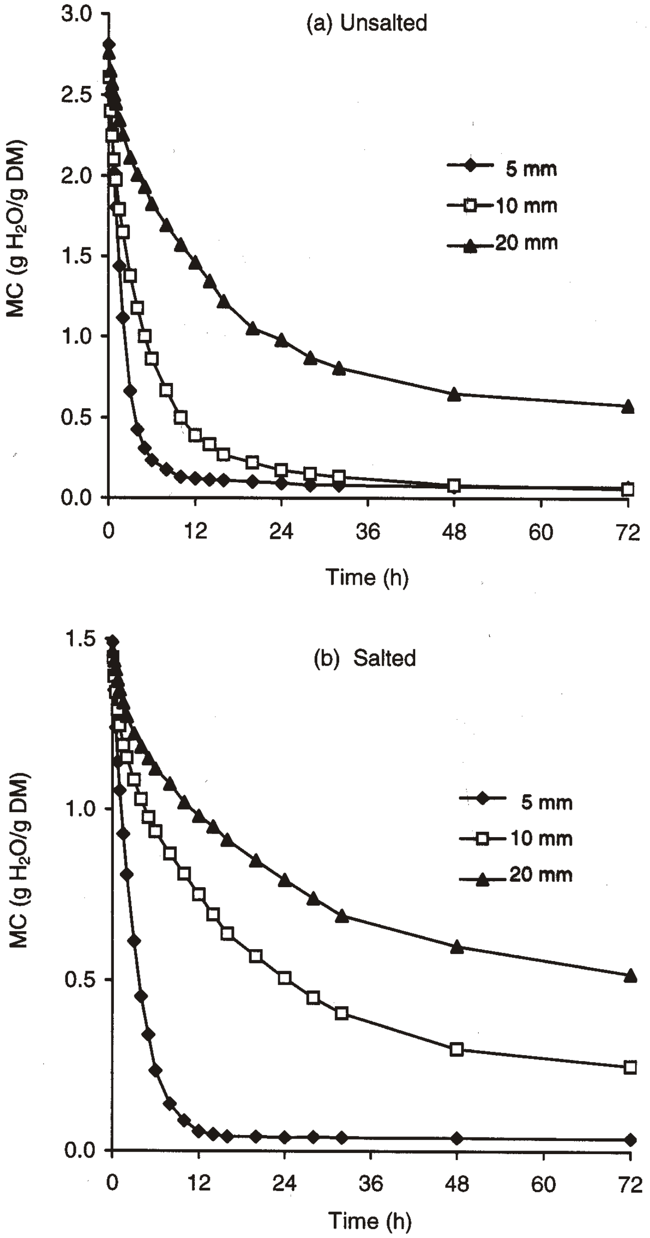


Fig. 6. The effect of slab thickness on the moisture changes in unsalted and slated shark slabs dried at 50°C.

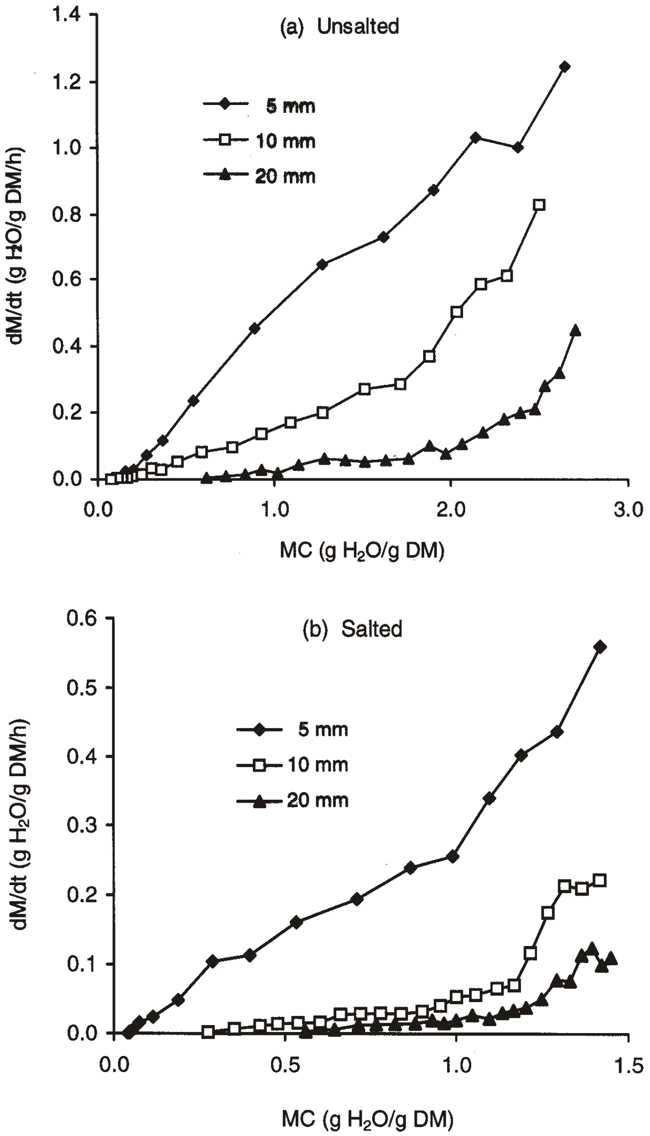


Fig. 7. Drying rate (dM/dt) versus average moisture content for shark slabs of varying thickness dried at 50° C.

Table 4. The effect of slab thickness on the drying rate constants of shark slabs dried at 50°C.

Thickness (mm)	Drying rate constants (h^{-1})							
	Unsalted				Salted			
	k_1	R^2	k_2	R^2	k_1	R^2	k_2	R^2
5	0.4862	0.9972	0.0692	0.9941	0.3332	0.9983	-	-
10	0.1578	0.9921	0.0933	0.9921	0.1604	0.9994	0.0402	0.9960
20	0.0626	0.9939	-	-	0.0757	0.9944	0.0214	0.9965

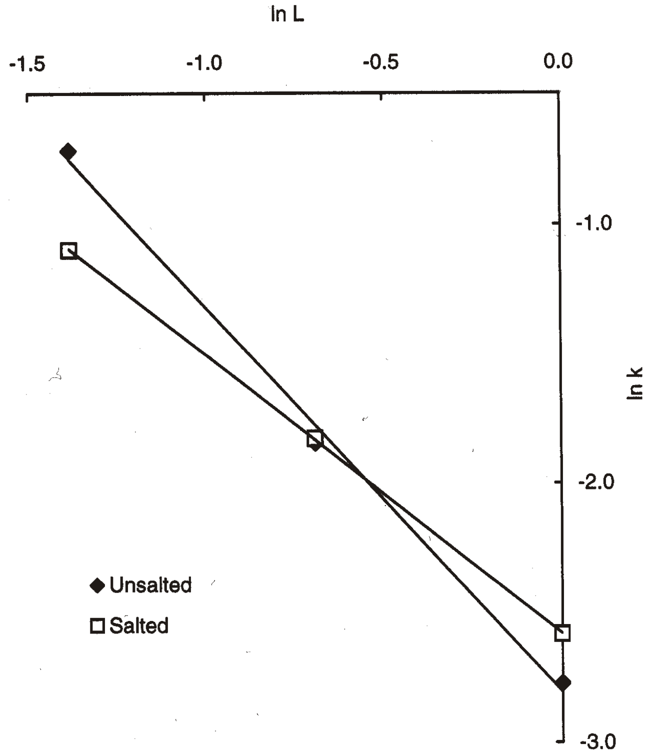


Fig. 8. Plots used to determine the dependence of the rate constant (*k*) on thickness (*L*) for unsalted and salted shark slabs.

internal diffusion. In the falling rate period, the thickness of the slab through which water must diffuse will become the rate-determining factor. Diffusion is therefore a function of thickness, and thicker slabs will require longer drying times.

Interestingly, D_1-values for both unsalted and salted slabs calculated using the rate constants were found to increase with increasing slab thickness and increasing L values ($^1/_2$ thickness of slab). For unsalted slabs, D_1-values increased from 3.42 x 10^{-6} to 7.06 x 10^{-6} cm^2/s as slab thickness increased from 5 to 20 mm. For salted slabs, D_1-values increased from 2.33 x 10^{-6} to 8.53 x 10^{-6} cm^2/s as slab thickness increased from 5 to 20 mm. In a study on the effect of geometry on the moisture transfer diffusion coefficient, Tutuncu and Labuza (1996) noted that many researchers do not investigate the effect of sample thickness on the diffusion coefficient. It is generally expected that when thickness increases, slopes will decrease while effective diffusivity is assumed to be the same. For example, Yusheng and Poulsen (1988) showed a decrease in rate constant with increasing potato slab thickness, but did not calculate D-values. The study by Tutuncu and Labuza (1996) showed an increase in D-values with increasing bed depth of breakfast cereals. This was attributed to a possible increase in captured air allowing for an increase in moisture flow through the drying bed to the surface.

Classical drying theory (Fick's Law) predicts that drying rate will vary inversely with the square of the piece thickness (L), and an L^2 dependence is very often assumed. Del Valle and Nickerson (1968) and Jason (1958) calculated the diffusion coefficients for fish muscle during drying assuming a $k \propto L^2$ relationship. To determine the actual experimental thickness dependence in this study, a thickness dependence of the type $k \propto L^x$ was assumed by plotting ln k versus ln L (Yusheng and Poulsen 1988). A straight line was found for both unsalted and salted shark slabs (Fig. 8) and x-values (slopes) were found to be 1.48 ($R^2 = 0.9968$) and 1.07 ($R^2 = 0.9999$) for unsalted and salted slabs, respectively. Diffusion coefficients calculated using an L^x dependence instead of an L^2 dependence were found to remain constant with slab thickness, averaging 7.06 x 10^{-6} cm^2/s for unsalted slabs and 8.53 x 10^{-6} cm^2/s for salted slabs. Yusheng and Poulsen (1988) added that the most usual reason for x-values being less than 2 is the existence of an external mass transfer resistance. Islam and Flink (1982) suggested that values of between 1 and 2 demonstrate resistance changing from totally externally controlled to totally internally controlled. External mass-transfer resistances may be due to different factors such as low air velocities and particle shape and size. However, the absence of external resistances was theoretically and experimentally verified for sugar beet and avocado (Chirife 1983).

CONCLUSIONS

Shark fillets (unsalted and salted) dried at 30-60°C showed the typical decline in moisture content with drying time, with the greatest decline occurring during the initial stages of drying. The decline in moisture content is considerably less for salted slabs compared with unsalted samples. For unsalted slabs, further increasing the temperature to 60°C does not increase the drying rate, while case hardening occurs in salted slabs. Drying at ambient temperature (30°C) and at 40°C occur in both the constant rate and falling rate periods. Drying at 50 and 60°C occurs in the falling rate period only. The drying data can be modelled using the analytical solution for Fick's Law for an infinite slab assuming uniform initial moisture distribution and negligible external resistances. The falling rate period for both unsalted and salted fish fillets occurs in two phases, each characterized by a drying rate constant (k_1 and k_2). Drying rate constants for the first phase (k_1) are higher than those for the second phase (k_2). Both the drying rate constants and diffusion coefficients increase with increasing temperature. Varying the air speed does not affect drying behaviour of unsalted and salted slabs. Drying rates and D_2-values decrease as the salt content of the slab increases. For both unsalted and salted slabs, drying rate constants decrease as slab thickness increase, and show a thickness dependence with a power of less than 2.

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