Osmotic drying kinetics of pineapple and papaya[1]

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ABSTRACT

Two osmotic dehydration processes were studied for pineapple and papaya: immersion in sucrose 70° Brix syrup; and in sucrose 70° Brix with 1000 p/m potassium sorbate and 150 p/m sodium metabisulfite syrup. The additives acted not only as preservatives but also in some way helped increase the driving force of the osmotic solutions, lowered the water activity of the final fruit products, and raised the final pH of the solutions, but did not affect that of the fruits. Pineapple had a greater tendency for absorbing sugar than papaya, and papaya induced fewer chemical changes in the osmotic solution than pineapple. Therefore, the immersing solutions can be recycled more times with papaya than with pineapple.

RESUMEN

Cinética del secado osmótico de la piña y la papaya

Se estudiaron dos procesos de deshidratación osmótica para piña y papaya: inmersión en sirop de sacarosa a 70° Brix y en sirop de sacarosa a 70° Brix con 1,000 p.p.m. de sorbato de potasio y 150 p.p.m. de metabisulfito de sodio. Los aditivos no sólo actuaron como preservativos sino que, de alguna manera, ayudaron a aumentar la fuerza motriz de las soluciones osmóticos, disminuyendo la actividad del agua de los productos finales a base de fruta y aumentando el pH final de las soluciones sin afectar el de las frutas. La piña mostró una tendencia mayor que la papaya hacia la absorción del azúcar y la papaya indujo menos cambios químicos en las soluciones osmóticos que la piña. Por lo tanto, las soluciones en que se sumergen las frutas pueden volverse a usar más veces con papaya que con piña.

INTRODUCTION

Intermediate moisture foods (IMF) are those sufficiently plastic to eat without further hydration and of sufficiently low water activity (a_w) to prevent bacterial growth. Human consumption of IMF has been known for centuries. Prunes, smoked meats, salted fish, and dates are some of the earlier examples of IMF which were processed through sun drying, smoking, salting, and freezing. More recently, spray, drum, foam, or freeze drying methods have been applied in the making of such products even including pet foods. Lately, the technique of osmotic drying has been the subject of great study as a new means of producing IMF (2, 5, 7, 10, 11, 12, 13).

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Osmosis is the process by which molecules from a certain solution pass through a semipermeable membrane to another solution which has a lesser concentration of the referred molecules. Osmotic drying is achieved by the immersion of foods in liquids with a lower water content than that of the food. In this scheme, the cellular structure of the food serves as the semipermeable membrane through which water flows from the food to the solution while solutes flow from the solution into the food. Some of the stated advantages of osmotic drying in comparison with other drying processes include minimization of heat damage to color and flavor, and less discoloration of the food by enzymatic oxidative browning (3, 9).

Osmotic solutions used in drying must have a low water content (hence a low a_w); moreover, the solutes used must be harmless and taste good. Concentrated sucrose solutions (50° to 70° Brix) have been the most commonly used osmotic solutions. Solute concentration of the osmotic solution, immersion time, temperature, solution/food ratio, specific surface area of the food, and low pressure are some of the factors that affect the amount of water lost by foods. The final product's a_w depends not only on the a_w of the osmotic solution but also on the gain of solids, which is determined by many other factors, such as chemical composition of the osmotic solution, nature of the sample, and sample shape (4,9).

The mechanisms through which osmotic drying of foods is achieved is not simple. Therefore, knowledge of the kinetics involved in the process is highly desirable, specially if we consider subjects such as osmotic solution recycling for the industrial production of IMF.

The widest known studies on osmotic drying kinetics have been performed on apple (4). The most important discoveries made on the subject are:

a. A rapid loss of water for 2 h followed by a rapid but decreasing rate of water loss for 2 to 6 h.
b. Initial rates of water loss were insensitive to rates of circulation of the solution, though at the intermediate times the circulation of the osmotic solution did give an improved water loss.
c. Blanched fruit lost water faster in the initial phases of the process, though ultimate water loss was not greatly different from that of the unblanched product.
d. The amount of sugar taken up for the blanched treatment was about twice as great as for the unblanched fruit (corrected for differences in water loss). The uptake was very rapid in both cases, reaching the ultimate level in 0.5 h of treatment, at which point it remained constant.
e. Organoleptic tests showed no difference between blanched and unblanched fruits.

Studies such as the above for the improvement of osmotic drying processes are vital for the eventual commercial success of these foods. In the present study, the osmotic drying kinetics as applied to pineapple and papaya were examined. The observations obtained will reveal the optimization of osmotic drying methods while applying them to locally harvested fruits.

MATERIALS AND METHODS

Red Spanish pineapple and Solo papaya varieties were obtained locally. Once the fruits were ripe, they were peeled and cut into pieces of approximately 7 g each. Each individual fruit piece was submerged in 40 g of a 70° Brix sucrose solution. The mixture was agitated mechanically at room temperature for the duration of the experiments. Each sample consisted of a vial which contained a 7-g fruit piece immersed in 40 g of solution. As mentioned in one of our earlier reports, the behavior of the osmotic drying system depends on the fruit/syrup weight ratio (14). Therefore, the experiments were set so that each sample was independent in its results from the behavior of other samples. Three samples were collected at 10-min intervals during the first 2 h of the experiment, at 20-min intervals during the third hour, and at 30-min intervals thereafter. For collection, the fruit pieces were taken out of the osmotic solution and the excess syrup wiped out of the fruit with a previously weighed paper towel. The weight of the fruit, syrup and paper towel was recorded. The final syrup weight was taken to be that of the remaining syrup plus the syrup absorbed by the paper towel.

The syrup was analyzed for water activity, pH, Brix, and weight change; the fruit pieces were analyzed for water activity, Brix, humidity, and weight change. Water activity was analyzed with a Decagon CX-1 a_w meter (Decagon Devices, Inc., Pullman, Washington)[4], pH with a Beckman ϕ71 pH meter (Beckman Instruments, Inc. Fullerton, CA) and Brix with a Reichart ABBE II digital refractometer (Cambridge Instruments, Optical Systems Division). Humidity was analyzed according to the standard AOAC method (1).

The experiments with pineapple and papaya were repeated with a second 70° Brix sucrose osmotic solution which contained in addition 1000 p/m potassium sorbate (Pfizer Inc., New York, NY), and 150 p/m sodium metabisulfite (Fisher Scientific Co., Fair Lawn, New Jersey). All the experiments were done in triplicate.

Data obtained from a set of the analyses chosen at random from all the experiments were submitted to the statistical F test to verify the

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[4] Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico, nor is this mention a statement of preference over other equipment or materials.

reproducibility of the experiments by comparing the standard deviations of the sample triplicates of each analysis. The analyses tested for reproducibility:

Experiment	*Analysis*
Pineapple/solution with additives	Weight lost percent of solution Fruit water activity
Pineapple/solution without additives	Solution water activity Fruit Brix Weight lost percent of fruit
Papaya/solution with additives	Weight lost percent of solution Solution water activity
Papaya/solution without additives	Solution pH Solution Brix

RESULTS AND DISCUSSION

Figure 1 shows the loss of humidity with syrup immersion time for both papaya and pineapple. Papaya loses water at a steady slow rate, which is not affected by the addition of preservatives. This finding contrasts with what was observed for pineapple. When the osmotic solution does not contain preservatives, a rapid loss of water in the fruits is observed immediately after immersion. After the first hour, however, humidity fluctuates. This pattern may be due to the speed at which the water molecules travel through the osmotic solution.

In the initial phases of the process the water molecule migration is limited to the fruit body's outer layer and the layers of syrup that are near the fruit. This is the initial humidity drop viewed in the process (time = 0 to 60 min in diagram 1).

DIAGRAM 1

FRUIT				OSMOTIC SOLUTION		time min.
inner layer		outer layer		inner layer	outer layer	
H20	H20	H20	H20			
H20	H20	H20	H20			00
H20	H20	H20 >>>>		>>>> H20		
H20	H20	>>>>>>>		>H20 > H20		60
H20	>>	>H20	H20>		>>>>H20	
H20	H20		H20<	< H20 >>>		120
		>H20	H20>	>H20	H20	
H20	H20			>H20	>H20	220

This causes the fruit to be "dryer" on its surface than inside. To compensate for the lack of humidity uniformity two things happen: first, the water molecules from the fruit's interior will migrate to the fruit's outer

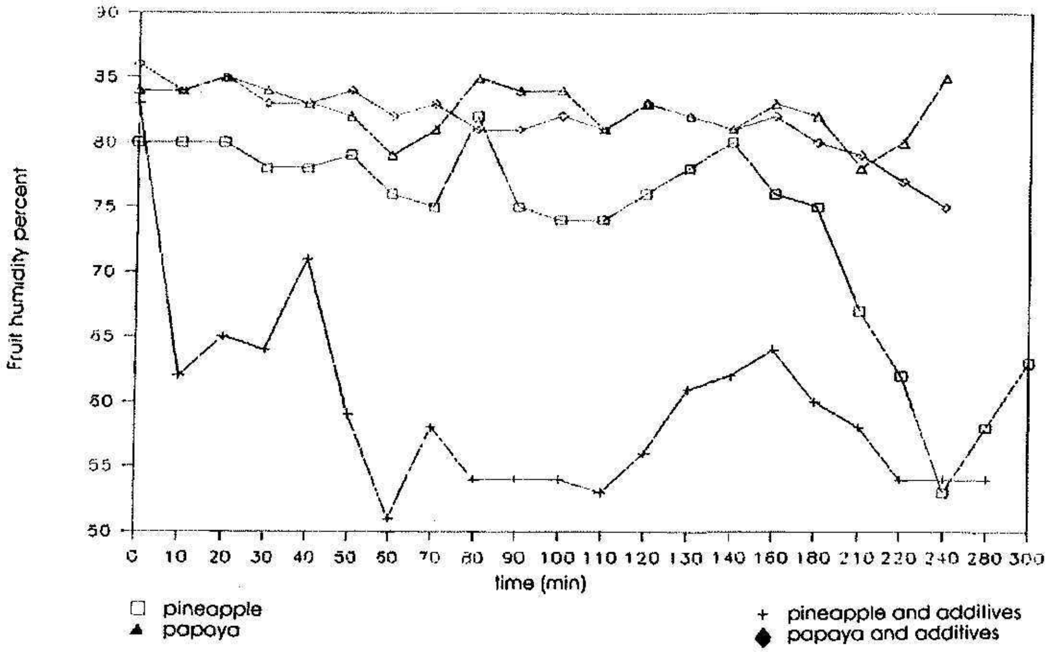

FIG. 1.—Fruit humidity percent variation as a function of dehydration time.

layers; second, while some of the water molecules absorbed from the fruit will migrate to the solution's outer layers (far away from the fruit) those that are still near the fruit will migrate back to the fruit. If the speed of the first event is greater than that of the second, then we would have a constant drop in the humidity until equilibrium is reached. However, the results obtained indicate otherwise. Therefore, this finding suggests that the speed of the second event is either equal to or faster than that of the first (time = 60 to 120 min in diagram 1). This may cause a temporary rise in the humidity of the fruit.

The limiting factor in the speed of the osmotic drying process is the speed at which the water molecules travel through the osmotic solution rather than the speed at which the water molecules travel through the fruit. Mechanical agitation applied to the systems in this experiment proved to be inefficient since poor homogeneity was observed in the solution after the fruits were removed from it. If an efficient mechanical agitation were applied to the solution during the process, its effects would appear in the latter parts of the process. In other words, agitation during the first hour of the process is unnecessary in order to accelerate the dehydration rate. It is in the latter stages of the process that agitation would be efficient, since it would be helping the water molecules to travel faster through the osmotic solution, far from the fruit's surface. These correlated observations give an insight to those reported earlier by Hope and Vitale (6) and Ponting et al. (10).

Apparently, additives tend to stop the initial humidity drop in pineapples. Yet, after 3 h a sharp drop is observed. After 4 h, the humidity

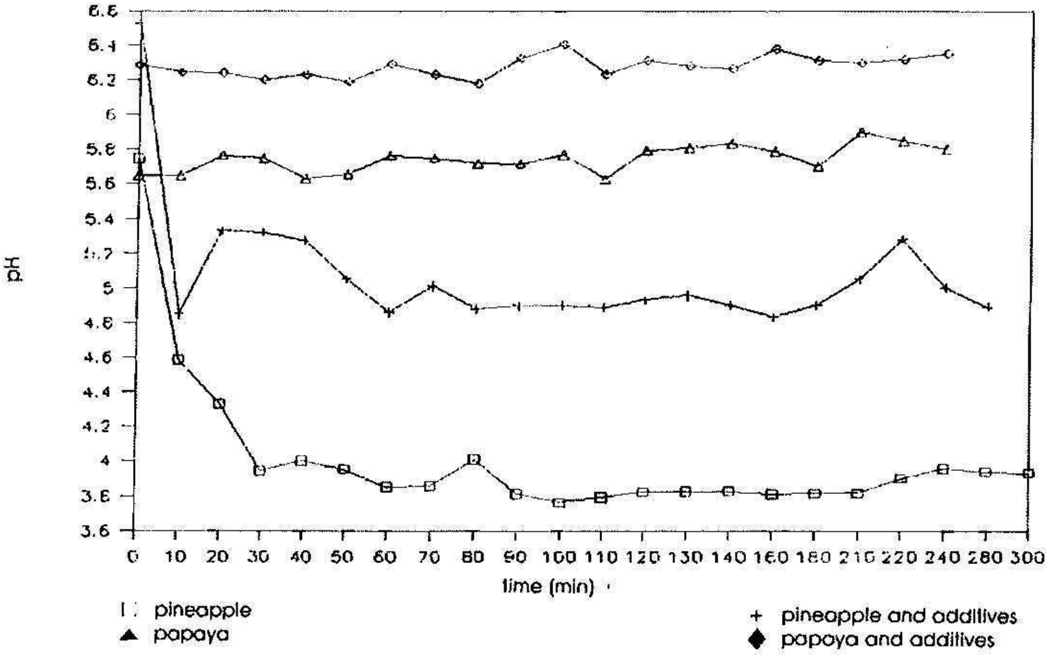

FIG. 2.—Solution pH variation as a function of dehydration time.

percentage is the same for pineapples immersed in the sucrose solution both with added preservatives and without.

There may be a relationship between the pH of the osmotic solution and the capability of the solution to induce osmotic drying in the fruits. This subject needs further investigation.

An osmotic solution composed of only sucrose and water is susceptible to pH variations. The addition of preservatives at the p/m level induces considerable changes in the pH of the solutions (5.7 to 6.4) (fig. 2). Because of the high acidity of pineapples, there is a sharp drop in the pH of the solution for the first hour of the process. Afterwards, the solution maintains its acidity fairly constant for the rest of the studied time (fig. 2). The amount of acid lost by the pineapple is the same in sucrose solutions both with and without additives (solution pH drop is 1.8 and 1.9 units, respectively). This means that the preservatives affect the final pH of the solutions but not the final pH of the fruits.

With papaya, both solutions' final pH stayed fairly constant throughout the process. It appears that the papaya's lower acidity is not sufficient to produce sharp changes in the solution's pH. Once again, preservatives reflected a rise in the solution's pH as when pineapple was immersed in it.

As expected, while both fruits' Brix increased at a constant sharp rate, the Brix of the solution remained fairly constant (fig. 3). The fruit/syrup weight ratio is greater than 4:1. The syrup has more than three times the amount of sugar than the fruits. Since all the sugar present in

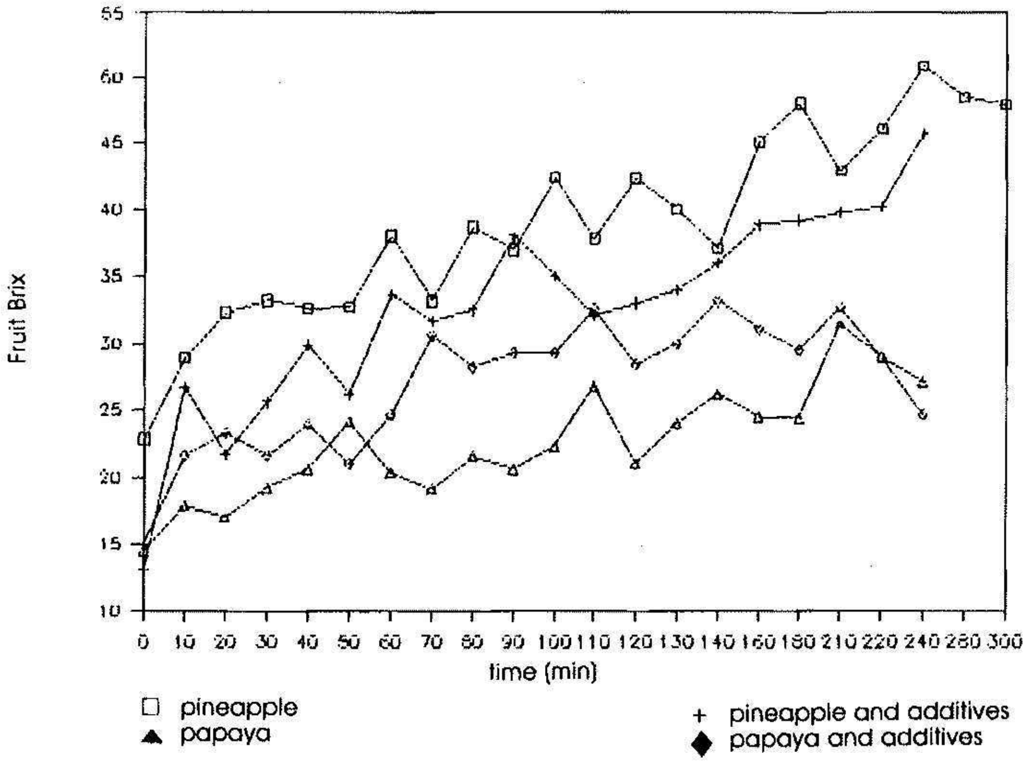

FIG. 3.—Fruit Brix variation as a function of dehydration time.

the system is either in the syrup or in the fruit, the migration of sugar molecules from the syrup to the fruit would have a greater impact on the fruit's Brix than in the syrup. In addition, the loss of water multiplies the effect of Brix increase in the fruits. Yet, the main reason for the difference in Brix change between the fruit and the syrup lies in the fact that there is much more syrup than fruit in the system. Therefore, a small change in syrup Brix would lead to big changes in the fruits' Brix.

It seems that pineapple absorbs sugar faster than papaya (fig. 4). In order to see how much more permeable to sugar the pineapple's cell structure is compared to that of papaya, a quantity known as the permeability coefficient must be used.

The diffusion coefficient:

$D = (dn/dt)\,[LA/(c_1-c_2)]$ where dn/dt is the rate of flow through the fruits' cell structure; L is the thickness of the fruit; A is the area of the fruit; and c_1-c_2 is the sugar concentration difference between the fruit and the solution.

If the area of the fruit pieces is taken to be constant for all the samples then,

$$D \propto (dn/dt)\quad [L/(c_1-c_2)]$$

The permeability coefficient is defined as:

$$P \propto D/L$$

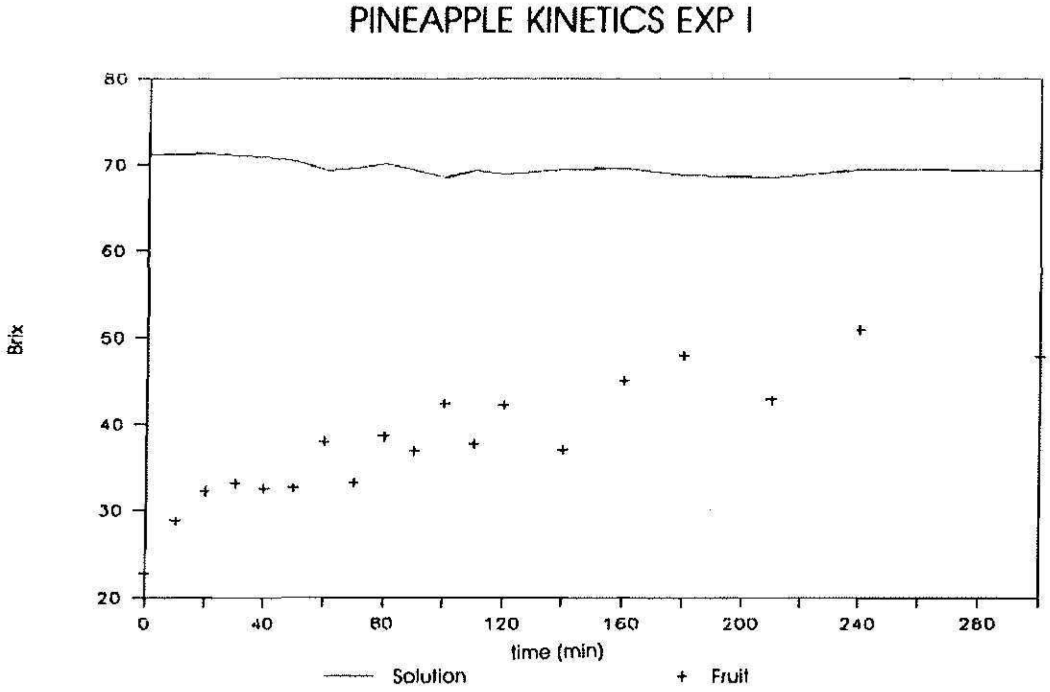

FIG. 4.—Solution Brix vs Fruit Brix variation as a function of dehydration time.

Therefore,

$$P \alpha \ (dn/dt) \quad [(1/(c_1 - c_2)] \qquad (8)$$

assuming that the Brix content is an indirect measure of the mass of sugar per volume of solution. If the Brix inside the fruit is d_1, the solution's Brix is d_2, and the mass of sugar (m) which diffuses through the fruit in time T is the fruits' Brix difference at 210 min., then we can roughly estimate the permeability of the fruits' cell structure towards sugar (table 1). Pineapple as a final product would have a higher Brix than papaya, making it a sweeter product. The use of additives does not alter the Brix change rate.

Even though the osmotic solutions with additives had initially a higher a_w than the ones without, they had a stronger driving force (fig. 5 and 6). The driving force leading to diffusion is the Gibbs energy difference between regions of different concentration (8). If we take the change in the Gibbs energy (dG) as being caused by the change in a_w (used as an indirect measure of water content), then the driving force of the solution (F_t) would follow the proportion:

$$F_t \quad \alpha \ dG \ \alpha \ (RT) \quad dc/c \qquad (8)$$

where, $R = 8.314 \ JK^{-1}mol^{-1}$; $T = 294$ K; dc = solution's a_w, change at 210 min.; c = solution's initial a_w. Table 1 provides an idea of how much preservatives increase the driving force of the osmotic solution. The fruits that were immersed in solutions with additives lowered their a_w faster than the ones in solutions without additives. If a comparison is

TABLE 1.—*Osmotic solutions' driving force and fruits' permeability toward sugar*

Sample	F_t (Jmol^{-1})	P (x10^{-3})
Pineapple without additives	53.6	4.7
Pineapple with additives	221.0	3.7
Papaya without additives	40.7	2.1
Papaya with additives	127.1	2.5

made of the humidity percentage (fig 1) and the a_w profiles (fig 6) of the system composed of pineapple in a solution with additives, both patterns are similar. This is a corroboration of the conclusions arrived at in the explanation of the dehydration pattern of the mentioned system.

We stated earlier that pineapple had a higher tendency to absorb sugar than papaya. This statement is supported by the weight change profile for pineapple vs papaya. Since the molecular weight of sucrose and water is 342 and 18, respectively, in order to see a decrease in the fruits' weight during the immersion process, the water/sugar exchange ratio would have to be greater than 19:1. The profile (fig. 7) indicates that the weight of pineapple actually increases during the initial 2 h of the process. It is not until the pineapple has absorbed sugar, that it starts losing weight due to water loss. This means that although the mobility of water is much higher than that of sugar, the semipermeability of the pineapple's cell structure is not as effective in preventing the absorption of sugar while losing water. This agrees with the conclusions

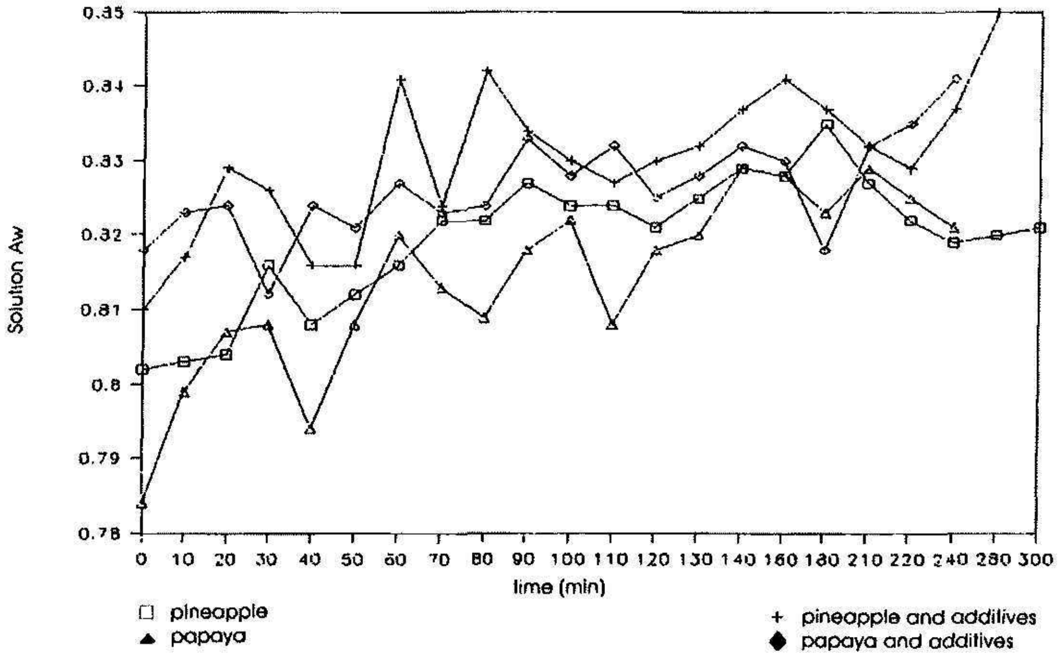

FIG. 5.—Solution water activity variation as a function of dehydration time.

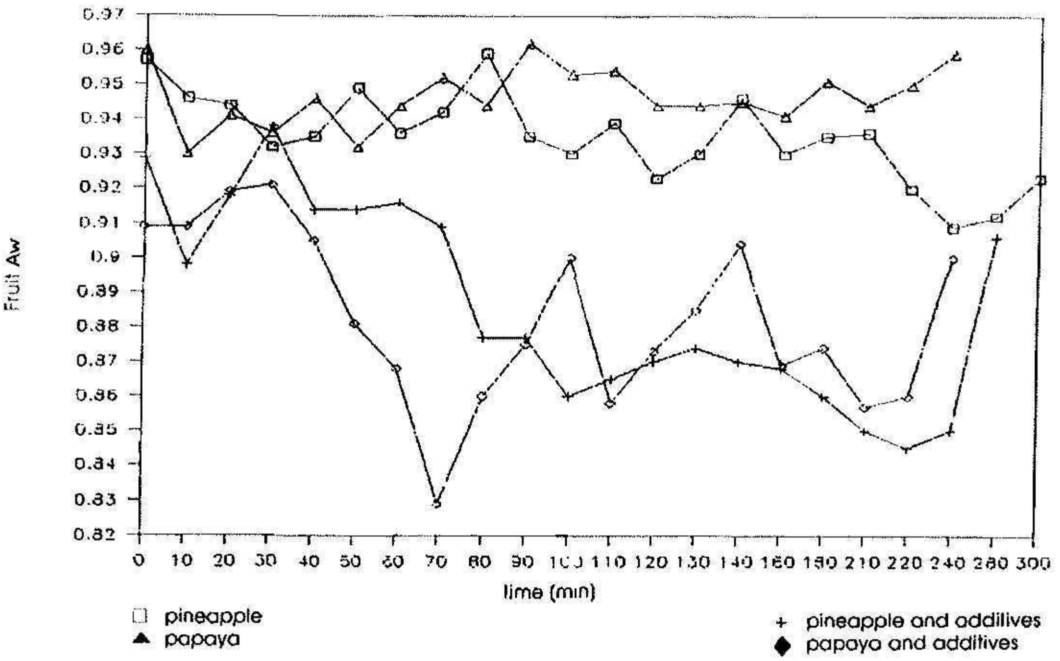

FIG. 6.—Fruit water activity variation as a function of dehydration time.

arrived at while discussing the Brix variation in the fruits during the process.

Papaya's weight percentage change demonstrates that it loses water while gaining little sugar in contrast to pineapple (fig. 7). The fact that

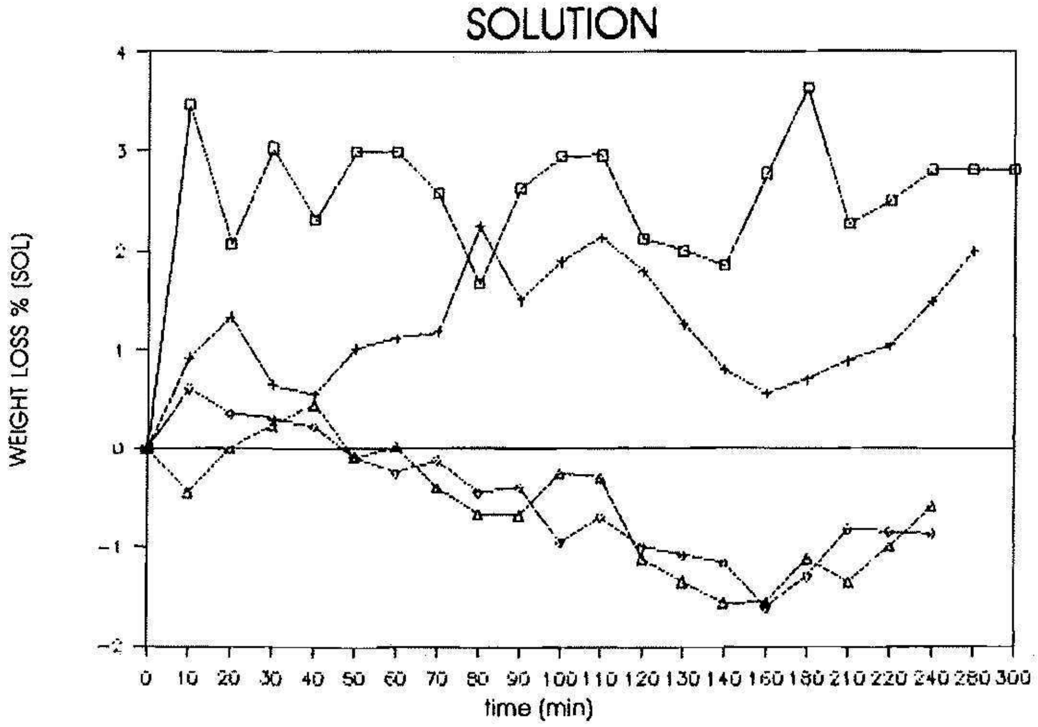

FIG. 7.—Fruit weight variation as a function of dehydration time.

TABLE 2.—*Regression results from humidity (H_2O kg/100 kg dry matter) vs time, where* $K = x/t$

Sample	Rate	Reg. Coef.
Pineapple without additives	1.20	0.96
Pineapple with additives	0.92	0.96
Papaya without additives	1.05	0.87
Papaya with additives	1.60	0.99

the solution gains weight when papaya is submerged in it shows that it gains water at a higher ratio than 19:1 sugar (fig. 7). Again, these results confirm our earlier statements on the fruits' Brix.

Generally speaking, all the studied systems showed a zero order kinetics. Following a rigorous treatment, we obtained plots of humidity in terms of kg water per 100 kg of dry matter vs time for the first 2 h of the immersion processes. Results show linearity at $k = x/t$ (Reg. Coef. $= 0.94$), where x is humidity and t is time. This means that the speed at which water is removed from the fruits is independent of initial humidity. This is a confirmation of earlier studies which showed that initial fruit humidity is not a determining factor for the dehydration rate (9,4).

Taking into consideration a 5% rejection region with 2 degrees of freedom, the statistical F test showed no significant differences among

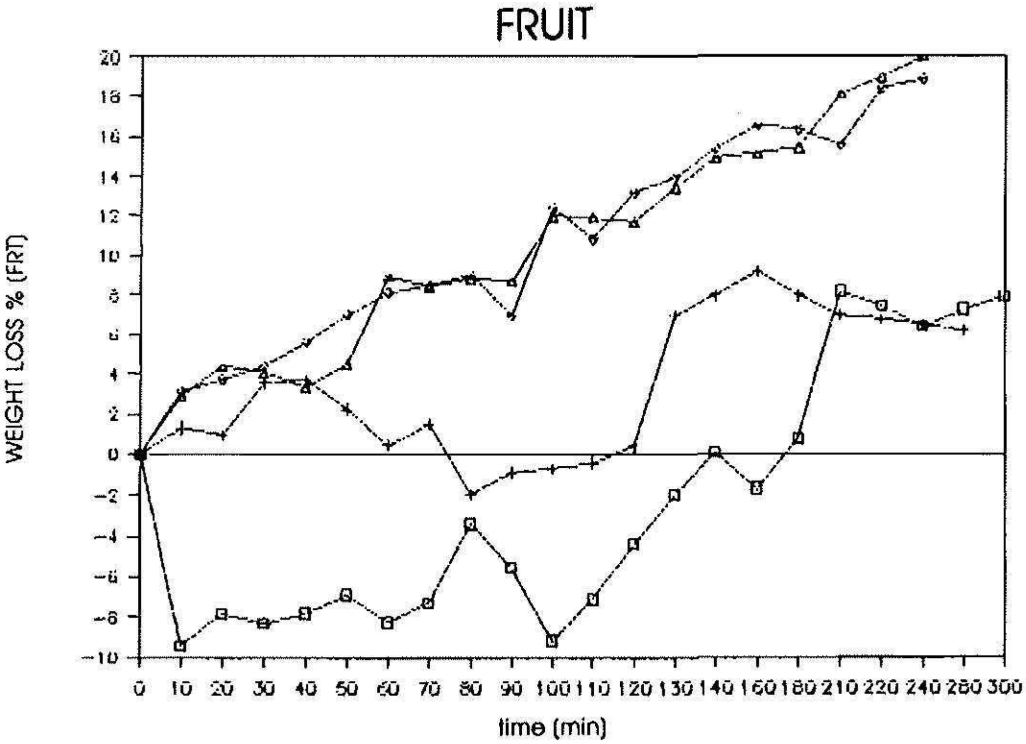

FIG. 8.—Solution weight variation as a function of dehydration time.

the standard deviations of the sample triplicates of the analysis tested. Since all the experiments, samplings, and analyses were performed in the exact same way, all the results obtained in this study were reproducible.

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