# WATER ACTIVITY CONCEPT AND ITS ROLE IN FOOD PRESERVATION

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## INTRODUCTION

Food preservation involves the action taken to maintain the desired properties or nature of foods, within a time frame, so that it remains safe and pleasant to consume. A stable food product can be developed by applying different processing techniques and by keeping it in appropriate conditions. Food stability determination from a scientific basis rather than empiricism is a challenge to food scientists and engineers. A relatively complete coverage of food preservation is available in the Handbook of Food Preservation and other references [9, 11].

Water is an important basic element in foods. For a long time, the industry has known how important it is to check free water. The water activity ($a_w$) measurement forms the basis of this and provides important information about the quality of a product. Finally it provides information regarding the possibility of microbiological growth on the surface. Only with this conclusions can be made about the stability and durability of a sample [17].

The relative equilibrium humidity of a product, which is ascertained through its partial pressure of water vapor on the surface, depends on the following factors: Chemical compound; Temperature; Water content; Storage environment (T/RH); Absolute pressure; Packing.

Free water in products is jointly responsible for the growth of undesirable organism such as bacteria or fungi, which produce "toxins" or other harmful substances. Bat also chemical/biochemical reactions (e.g. the Maillard reaction) increasingly take place and possibly change the following factors of a product: Microbiological stability, Chemical stability, Content of proteins and vitamins, Color, taste and nutritional value, Stability of the compound and durability, Storage and packing, Solubility and texture [5, 15, 26].

The thermodynamic description of these osmotic solutions has been the object of intense reach all along the last century, particularly those involving sugars and/or salts.

Most thermodynamic models used to describe vapor-liquid equilibrium of osmotic solutions are based on relations involving Gibbs free energy of the system [24].

In 1994, within the Science and Technology for Development (CYTED) Program, Project' Development of intermediate moisture foods (IMF) a survey was conducted in eleven countries, collecting information on 260 traditional IM and HM food [7].

The binary combination of $a_w$ and pH acts as a relevant hurdle in many of these products preventing proliferation of pathogenic microorganism, while the rest (antimicrobials, thermal treatment, etc.) play a secondary role, mainly against spoilage flora [7].

This paper present recent research nationally and internationally [1-29] regarding the concept of water activity and its role in food preservation. This article presents information related to the processing of fruit and vegetables by combined methods.

## I. APPROACHES AND SUGGESTIONS

### 1.1. Water activity

Water activity is a fundamental property of aqueous solutions, and by definition is the ratio of the vapor pressure of the water in the substrate (p) to that of pure water at the same temperature ($p_o$):

$$a_w = \frac{p}{p_o} \qquad (1)$$

Water activity is a measure of how efficiently the water present can take part in a chemical (physical) reaction. If half the water is so tightly bound to a protein molecule that it could not take part in a hydrolysis reaction the overall water activity would be reduced. Water activity ($a_w$) is defined as where p and $P_o$ are the partial pressures of water above the food and a pure solution under identical conditions respectively. The tightly bound water has no tendency to escape from a food as a vapor and therefore exerts no partial pressure and has an effective water activity of zero. Water

activity is clearly a function of composition but is also a function of temperature. The $a_w$ is related to the boiling and freezing points, equilibrium relative humidity (ERH; see above equation), and osmotic pressure. Water activity ranges from zero (water absent) to 1.0 (pure water). For an ideal solution $a_w$ is independent of temperature, and in actual practice, $a_w$ of a given solution varies only slightly with temperature within the range of temperature permitting microbial growth. The relationship between water potential and water activity is given by the next equation, where the value of k depends on temperature and is, for example, 1.37 at 25°C and 1.35 at 20°C.

$$\Psi(M_{pa}) = K \ln a_w \qquad (2)$$

Not only is the availability of water in the surrounding liquid phase of importance to fungi, but the water content of the adjacent gas phase. The water content of the atmosphere is expressed in terms of relative humidity, the ratio of the water vapor pressure of the gas phase being considered to that of a saturated atmosphere at the same temperature. It is hence the same ratio as water activity but expressed as a percentage.
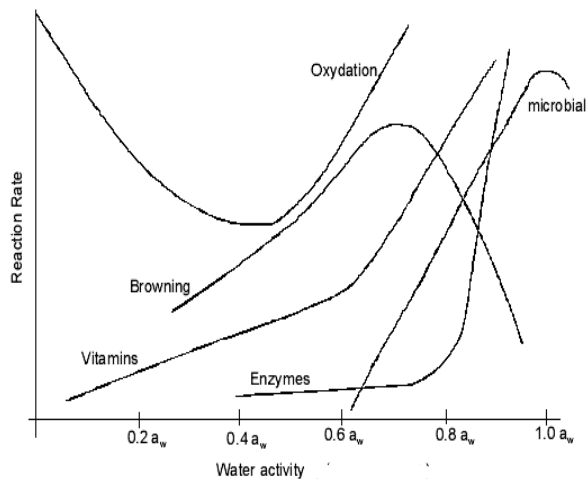


**Figure 1.** The variation of oxidation, browning, enzyme activity, vitamin inactivation and microbial activity [12, 20].

Water activity ($a_w$) indicates the availability of water's medium for chemical reactions, biochemical transfer or exchange through a semi permeable membrane.

Result's Law is very accurate within the range of 0.95 to 1.0 water activity, whereas the Norrish equation is reasonably accurate down to about 0.55. Result's Law applies to solutions of

small molecular weight compounds for which the calculated $a_w > 0.95$.

$$a_W = A n_{H2O} / (n_{H2O} + n_{solute}), \qquad (3)$$

where: A- activity coefficient; $n_{H2O}$- moles of water in solution (assumed to be 1 for solutions with $a_w > 0.95$); $n_{solute}$ - moles of solute

The Norrish equation [15] is used for solutions, and is valid when the molecular weight and the Norrish k value are known. For a single solute, the Norrish equation reduces to:

$$a_w = X_W \times \exp(-k_i \times X_i^2) \qquad (4)$$

where: aw = water activity;
$X_W$ = mole fraction of water;
$X_i$ = mole fraction of solids in ingredient i;
$k_i$ = Norrish constant for ingredient i.

Present work evaluated the ability of Norrish's equation to model the water activity of solutions of sugars.

## 1.2. Water activity ($a_w$) concept

The concept of $a_w$ has been very useful in food preservation and on that basis many processes could be successfully adapted and new products designed. Water has been called the universal solvent as it is a requirement for growth, metabolism, and support of many chemical reactions occurring in food products. Free water in fruit or vegetables is the water available for chemical reactions, to support microbial growth and to act as a transporting medium for compounds. In the bound state water is not a available to participate in these reactions as it is bound by water soluble compounds such as sugar, salt gums, etc. (osmotic binding), and by the surface effect of the substrate matrix binding) [7].

These water-blinding effects reduce the vapor pressure of the food substrate according to Raoult's Law. Comparing this vapor pressure with that of pure water (at the same temperature) results in ratio called water activity ($a_w$). Pure water has an $a_w$ of 1, one molar solution of sugar – 0.98, and one molar solution of sodium chloride -0.9669. A saturated solution of sodium chloride has a water activity of 0.755. This same NaCl solution in a closed container will develop an equilibrium relative humidity (ERH) in a head space of 75.5%.

A relationship therefore exists between ERH and $a_w$ since both are based on vapor pressure [7]:

$$a_w = \frac{ERH}{100} \qquad (3)$$

The ERH of a food product is defined as the relative humidity of the air surrounding the food at which the product neither gains nor loses its natural moisture and is in equilibrium with the environment. The definition of moisture conditions in which pathogenic or spoilage microorganisms cannot grow is of paramount importance to food preservation. It is well known that each microorganism has a crystal $a_w$ below which growth cannot occur. For instance, pathogenic microorganisms cannot grow at $a_w < 0.62$. The so-called intermediate moisture foods (IMF) have $a_w$ values in the range of 0.65 - 0.90 (Figure 2).
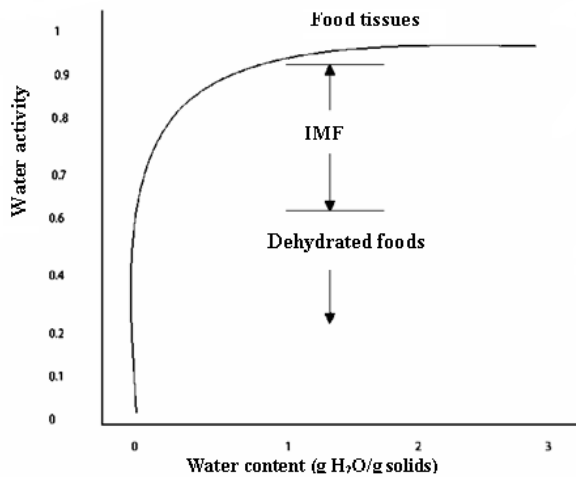


**Figure 2** Typical equilibrium of water content vs. water activity in foods [8]
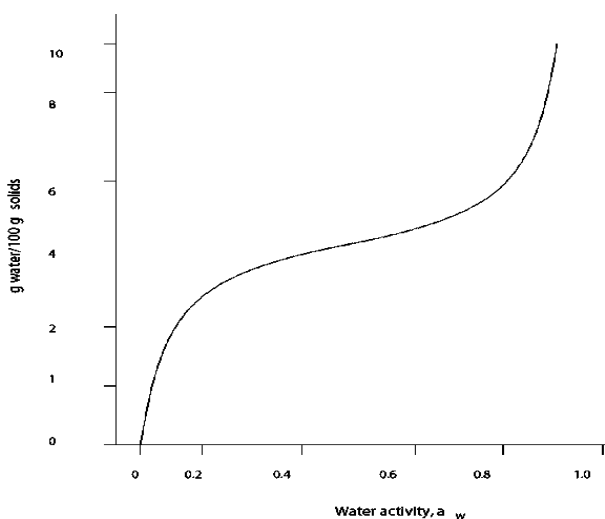


**Figure 3.** Equilibrium of water activity vs. moisture content, typical in foods *Lower region of isotherm* [7].

With $a_w$ at 0.3, the product is most stable with respect to lipid oxidation, non-enzymatic browning, enzyme activity, and of course, the various microbial parameters. As $a_w$ increases toward the right, the probability of the food product deteriorating increases [7].
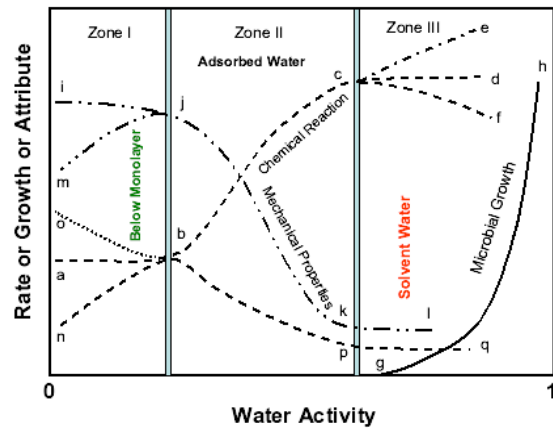


**Figure 4.** Stability diagram based on the water activity concepts [18, 19].
*where: gh = Microbial growth trend; oa, ab, nb = chemical reaction trends below BET-monolayer; bc, bp = chemical reaction trends in the adsorbed water; ce, cd, cf, pq = chemical reaction trends in the solvent water region; ij, mj = mechanical properties trends below BET-monolayer; jk = mechanical properties trend in the adsorbed water region; ki = mechanical properties trend in the solvent water region [19].*
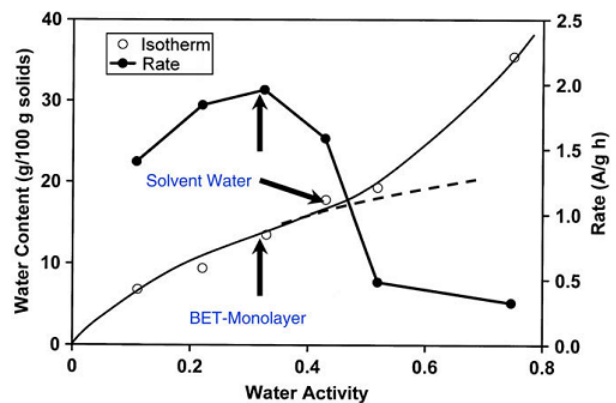


**Figure 5.** Enzymatic browning rate at 70$^o$C in gelatinized starch medium. Indicate water activity at BET-monolayer [1].

In general the rule of water activity concept is: Food products are most stable at their ''BET-monolayer moisture'' content or ''BET-monolayer water activity'' and unstable above or below BET-monolayer. However, experimental evidence showed that optimal moisture for stability was in the multilayer adsorption region. In many other instances it has been shown that optimal water content for stability is not exactly the BET-

monolayer. The reason for this variation is due to the fact that the BET theory of adsorption was developed based on many simplified assumptions, which are not realistic when food is considered [21].

## 1.3. Water Activity and Shelf Stability

Water activity, unlike water content, can determine a food's shelf stability. It can predict which microorganisms will be potential sources of spoilage and infection (the difference between bacterial pathogens and fungal physiology, or, $a_w$ of 0.91 versus that of 0.70). The water activity of a food is instrumental in maintaining its chemical stability.

Consider that water activity is partially responsible for minimizing non-enzymatic browning reactions and spontaneous autocatalytic lipid oxidization reactions; prolonging the activity of enzymes and vitamins; and optimizing the physical properties of products such as moisture migration, texture, flavor, odor and shelf life. Not bad for a little relative humidity measurement. Every retail food establishment needs to know what will happen to their products as they sit on the shelf, even under ideal conditions of temperature and humidity. Shelf stability means the product 'won't get moldy, but it also affects the foods texture, moisture migration and caking and clumping [18].

Stability and food security depends on water activity and pH in the food environment. The water activity is higher with the products are perishable. Bat, even at low pH values and low $a_w$, certain yeast and mould species that can tolerate high solute concentrations might pose a risk to the stability of Intermediate Moisture Foods (IMF). Currently, consumers prefer foods (vegetables and fruits) processed at least. Therefore, safety considerations are addressed seriously by food microbiology [5, 13, 15].

There are different approaches to conservation and stability of fresh fruit products. Commercial, minimally processed fruits are fresh (with high moisture), and are prepared for convenient consumption and distribution to the consumer in a fresh-like state. Minimum processing includes preparation procedures such as washing, peeling, cutting, packing, etc., after which the fruit product is usually placed in refrigerated storage where its stability varies depending on the type of product, processing, and storage conditions. However, product stability without refrigeration is an important issue not only in developing countries

but in industrialized countries as well. The principle used by Leistner [13] for shelf-stable high moisture meats ($a_w > 0.90$), where only mild heat treatment is used and the product still exhibits a long shelf life without refrigeration, can be applied to other foodstuffs. Fruits would be a good choice. Leistner states that for industrialized countries, production of shelf-stable products (SSP) is more attractive than IMF because the required $a_w$ for SSP is not as low and less humectants and/or less drying of the product is necessary [6].

This Manuel presents information related to the processing of fruit and vegetables by combined methods. Information concerning the trade and production of fruits and vegetables in different countries is provided, as well as information on the processing of fruit and vegetable products. The combination of factors such as water activity ($a_w$), pH, redox potentials, temperature, and incorporation of additives in preserving fruits and vegetables is important, and all play a crucial role in improving the shelf life of fresh and processed commodities. During the last decade, minimally processed high moisture fruits (HMFP) which are ambient stable (with $a_w > 0.93$) have been developed in Latin American countries, under the leader of Argentina, Mexico and Venezuela [2-4].

The methodology employed was based on combinations of mild heat treatments, such as blanching for 1-3 minutes with saturated steam, slightly reducing the $a_w$ (0.98-0.93) by addition of glucose or sucrose lowering the pH (4.1 -3.0) by addition of citric or phosphoric acid, and adding antimicrobials (1000ppm of potassium sorbate or sodium benzonate, as well as 150ppm of sodium sulphite or sodium bisulphite) to the product syrup. During storage of HMFP, the sorbate and sulphite levers decreased, as well as $a_w$ levels, due to hydrolysis of glucose [2].

A variety of alternative method to preserve fruits and vegetables can be used in rural areas such as fermentation sun drying, osmotic dehydration, and refrigeration. Fruit and vegetables can be pre-processed via blanching to eliminate enzymes and microorganisms. Over the last decade, have been developed innovative technologies for obtaining shelf-stable "high moisture fruit products" (HMFP) storable for 3-8 months without refrigeration.

These new technologies are based on a combination of inhibiting factors to combat the deleterious effects of microorganisms in fruits, including additional factors to diminish major quality loss in reactions rates. Slight reduction of water activity ($a_w$ 0.94-0.98), control of pH (pH 3.0-4.1), mild heat treatment, addition of

preservatives (concentrations £ 1.500ppm), and anti browning additives were the factors selected to formulate the preservation procedure. These techniques were preceded by the pioneer work of Leistner (1994) on the combined effects of several factors applied to meat products - named "hurdle" technology [2].

## 1.4. Prediction of water activity in practical applications

Water activity $a_w$ can be influenced in at least three ways during SX the preparation of dried, intermediate and high moisture foods [9]:

*1.* Water can be removed by a dehydration, evaporation or concentration process.

*2.* Additional solute can be added. Theirs penetration of solute can be performed by moist infusion or by dry infusion. Moist infusion consists in soiling the food pieces in a water/solute solution of lower $a_w$ while dry infusion involves direct mixing of food pieces and solute in required proportions. When water/rich solid products, such as fruit and vegetables, are subjected to moist or dry infusion, three flows arise:

- a water outflow, from product to the environment;
- a solute flow, from the environment to product;
- an outflow of the product' sown solutes.

This process is called' osmotic dehydration' and allow the infusion of not only the solute used to control $a_w$ bat also the desired quantities of antimicrobial and ant browning agents or any solute for improving sensory and nutritional quality. By controlling these above complex exchanges it is possible to conceive different combinations of water loss and solid gain, from a simple dewatering process (with substantial water removal and only marginal sugar pickup) to a candying or salting process (in which solute penetration in favored and water removal limited) [27].

For porous foods, moist infusion can be also performed under vacuum. The internal liquid occluded in the open pores is exchanged for an external liquid phase (of controlled composition) due to pressure changes.

*3.* Combining 1 and 2. When the food pieces are infused with the solutes and additives and then partially dried. The advantages obtained with this combination as compared to only drying are an increase in the stability of the pigments responsible for the color, an enhancement of the natural flavor, a better texture and a greater loading of the dryer.

Whatever the procedure used to reduce $a_w$, it is necessary to know the water activity-moisture content relationship in the food. Important contributions have been made in the field of $a_w$ prediction over the past 50 years and comprehensive analysis of the procedures traditionally employed to calculate $a_w$ have been performed by [6]. In each case, the applicability of various theoretical and empirical equations was analyzed, presenting some descriptive examples.

There is no model with a simple mathematical structure capable of representing the sorption or $a_w$ lowering characteristics of foods or their components in the whole range of water activities, since the depression of $a_w$ in foods is due to a combination of mechanisms each of which may be predominant in a given range of water activity. In high and intermediate moisture foods, $a_w$ is mainly determined by the nature and concentration of soluble substances (i.e., sugars, NaCl, polios, amino acids, organic molecules, other salts) in the aqueous phase of food [7].

A number of equations, based on the thermodynamic properties of binary and multicomponents electrolyte and non-electrolyte solutions, have been studied theoretically and experimentally for calculating or predicting the $a_w$ of these foods. Figure 6 summarizes several of theoretical and empirical models suggested for the calculation of $a_w$ in semi-moist and moist food [28].
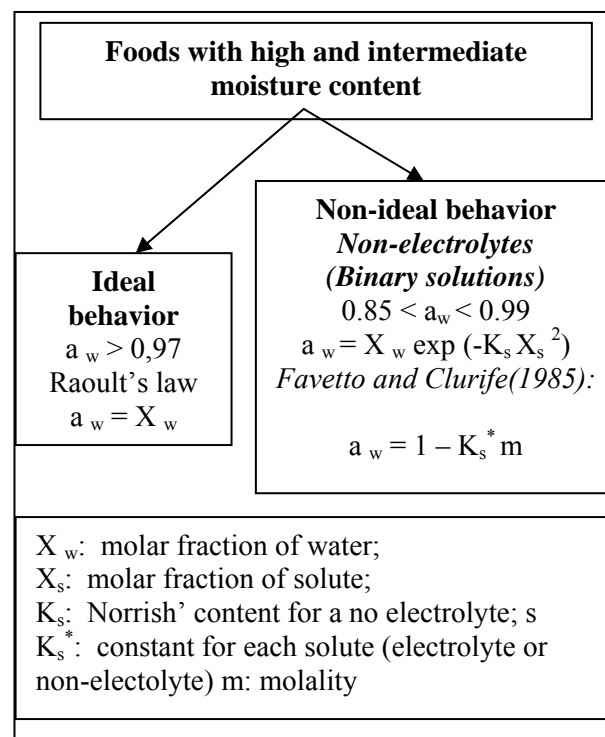
**Figure 6.** The applicability of various theoretical and empirical equations [28].

In low/moisture foods, adsorption of water rim surfaces is responsible for $a_w$ reduction [9]. Although the physical chemistry of surfaces has provided the food scientists with a large number of the critical equations, the relationship of water sorption -$a_w$ cannot be predicted but must be experimentally determined due to many reasons. As food sorbs water, it can undergo changes of constitution, dimensions and other properties and sugars contained in the food may experience phase transformations.

The moisture sorption isotherm integrates the hygroscopic properties of numerous constituents whose sorption properties may change duet physical/chemical interactions induced by heating and other pre/treatments. Critical compilations of empirical and theoretical adsorption models for fitting experimental water sorption isotherms of food and food products have been made by [7, 10].

The Brunauer, Emmett and Teller (BET) formula (application range $0.05 < a_w < 0.45$) is one of the most widely used models to characterize the monolayer water. The theory supposes, among other things, that the binding energy of the monolayer is the same for all the water molecules and on the other layers is equal to that of pure water.

Although the theoretical assumptions are incorrect for heterogeneous food surface interactions, for practical purposes this equation has been found very useful in determining the optimum moisture content (i.e., that corresponding to the monolayer water) for storage chemical stability of dehydrated foods [20].

The Guggenheim, Anderson and Boer (GAB) equation (applicability range $0 < a_w < 0.9$), now recognized as the most versatile sorption model and recommended as such by the European COST 90 Project, modifies the BET model to take into account the energies of interaction between the first and distant sorbet molecules at the individual sorption sites. Id also allows calculation of the monolayer water [14].

## 1.5. Recommended equipment for measuring $a_w$

Many methods and instruments are available for laboratory measurement of water activity in foods. Methods are based on the properties of solutions. Water activity can be estimated by measuring the following: Vapor pressure, Osmotic pressure, Freezing point depression of a liquid or solid, Boiling point elevation, Dew point and wet bulb depression, Suction potential, or by using the isopiestic method, electric hygrometers etc [7].

Fruits are a good example of foods stuffs that accept pH reduction without affecting the flavor significantly. Important development on IMF based on fruits and vegetables are reported elsewhere. The extensive research conducted in India by Dr. Jayaraman and co-workers has generated important information on this product category [9]. The water reduction capacity of sugar and salts in their amorphous and anhydrous state at different $a_w$ in present in Table 1.

**Table 1.** Water activity reduction capacities of sugars.

| Moisture content, gH$_2$O/100 g Solids | Sugars | | | | |
|---|---|---|---|---|---|
| | Sucrose | Glucose | Fructose | Lactose | Sorbitol (adsorption) |
| **A W** | **Anhydrous** | | | | |
| 0.60 | 3.0 | 1.0 | 14.0 | 0.01 | 17.0 |
| 0.70 | 5.0 | 3.5 | 22.0 | 0.01 | 22.0 |
| 0.80 | 10.0 | 7.5 | 34.0 | 0.05 | 37.0 |
| 0.90 | - | 12.5 | 47.0 | 0.10 | 76.0 |
| **A W** | **Amorphous** | | | | |
| 0.60 | 14.0 | 1.0 | 18.0 | 4.5 | 25.0 |
| 0.70 | 20.0 | 3.5 | 30.0 | 4.7 | 35.0 |
| 0.80 | 35.0 | 8.0 | 44.0 | 4.7 | 55.0 |
| 0.90 | 65.0 | 22.0 | 70.0 | - | 110.0 |
| | | | | | |

To determine the desired $a_w$ in syrup ($a_w$ equilibrium), the Ross equation is used:

$$a_{W\ equilibrium} = (a_w)fruit \times (a_w) sugar \qquad (4)$$

where $a_w$ fruit is the water activity of the fruit and $a_w$ sugar is the water activity of sugar, both calculated at the total molarities of the system. The product of the morality of sucrose in the fruit water and solution must equal the desired water activity in equilibrium. $A_w$ values of the sugar are obtained using the Norrish equation:

$$a_{w\ sucrose} = X_1 \exp(-kX_2^2) \qquad (5)$$

Where: $k$ is a constant for sugars, $X_1$ and $X_2$ are the molar fractions of water and sugar, respectively. Some K values for common sugars and polyols are listed in Table 2.

Phosphoric or citric acids are generally used to reduce the syrup's pH so that the final pH of the fruit-syrup system is in equilibrium in the desired range (3.0 to 4.1). Monitoring of $a_w$ and pH in the fruit and syrup until constant values for these parameters are reached can determine the time

**Table2**. Norrish constant values for common sugars and polyols.

| Sugars | k | Polyols | k |
|---|---|---|---|
| Sucrose | 6.47 ±0.06 | Glycerol | 1.16 ±0.01 |
| Maltose | 4.54 ±0.02 | Mannitol | 0.91 ±0.27 |
| Glucose | 2.25 ± 0.04 | Arabitol | 1.41 |
| Lactose | 10.2 | Propylene Glycol | 4.04 |
| Sorbitol | 1.65 ±0.14 | | |

to equilibrate the system. This may be from three to five days at constant room temperature depending on the size of fruit pieces.

## 1.6. Application of Norrish equation: example

The water activity of a sucrose-water solution (2.44:1 w/w) can be estimated by means of the Norrish equation. The mole fractions are: $X_1$ = 0.887 and $X_2$ = 0.1125. The Norrish constant ($k$) for sucrose is 6.47 (Table 2). Substituting $X_1$ and $X_2$ into the Norris equation results in the estimated water activity of the sucrose-water solution.

To prepare the syrup or brine, a sufficient amount of sugar or salt is dissolved in water in order to reach the desired $a_w$. Concentrations of sculpture dioxide and potassium sorbate are prepared, reaching a final concentration of 100-150ppm and 1000-1500ppm, respectively. In the case of fruit products, citric or phosphoric acid are used to lower the pH of the syrup so that the final pH at equilibrium is in the range 3.0-4.1. High moisture food products (HMFP) are very different from IMF products and need to be dehydrated. HMFP have a lower sugar concentration, 24-28% w/w compared to 20-40% w/w, and higher moisture content, 55-75% w/w compared to 20-40% w/w, which makes them similar to canned food products. HMFP can be consumed directly after processing or bulk stored for processing out of season [2].

Sample calculation for preparation of stable mango product [4], the process conditions and ingredients required to prepare 20kg of a stable mango product are: fruit pulp 16°Brix (16% soluble solids), acidity 0.5% (% citric acid). The fruit pulp is conditioned from 16°Brix (16% SS) to 40°Brix (40% SS) by adding sucrose. Sucrose is added to the pulp in order to act as a water activity depressor. The water activity of the pulp ranges from 0.97 to 0.98 [4]. Calculation to obtain the amount of fruit pulp in the feed, sugar, citric acid, and free water in the final product:
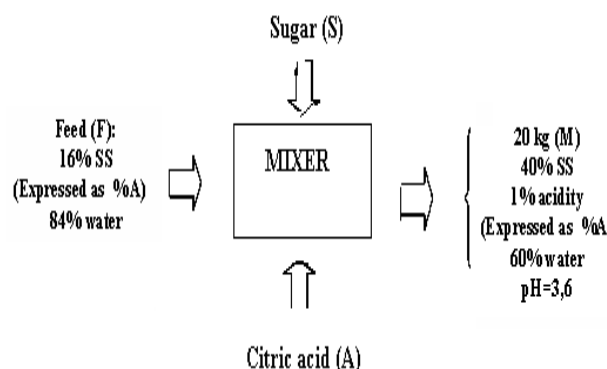


**Figure 7.** Modeling of stable mango product [4].
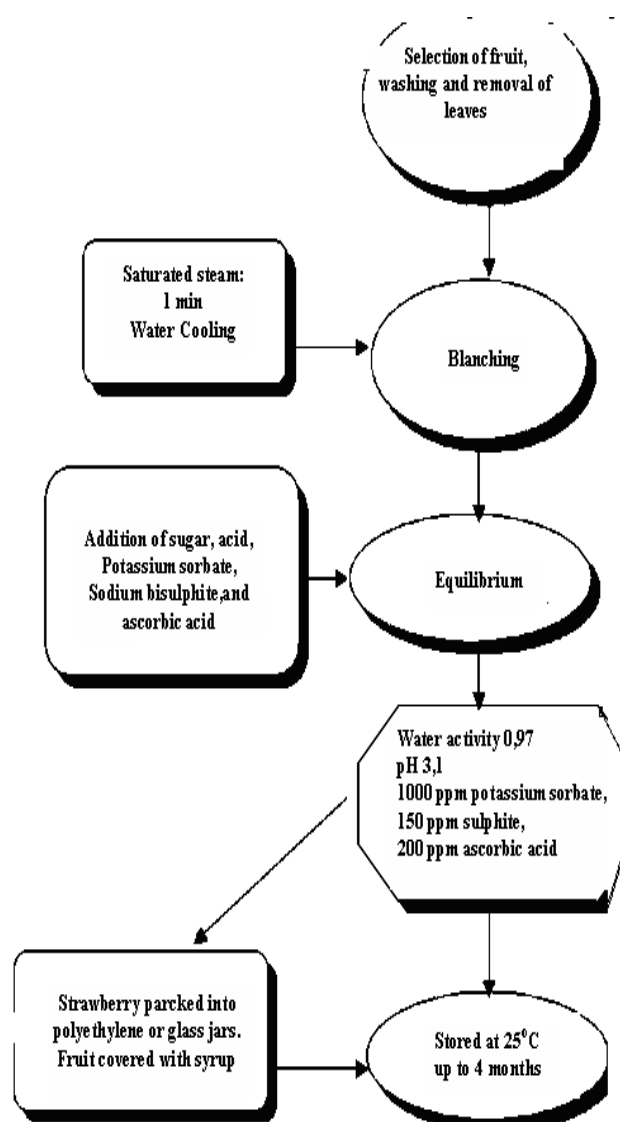


**Figure 8.** Flow process diagram for the reparation of shelf-stable high moisture whole strawberries [3, 4].

The fruit prods were stored for at least 30 days at 35°C, exhibiting door acceptability, microbial stability, and fresh-like appearance [4, 7]

## 2. QUALITY AND FOOD SECURITY

Theoretical and experimental study of water activity concept allows us to evaluate the choice of method of preserving food. Further research needs to be targeted towards the stability in each macro–micro region and to explore more generic rules for stability

Quality and food security depends on *p*H and water activity ($a_w$) in food environment. Foods with water activity are perishable. Water activity, *p*H, temperature, and other parameters, have a direct impact on the growth of microorganisms, thus $a_w$ and pH are two the most important parameters. Free water that is available to molds, yeasts, and bacteria is responsible for their growth and even toxin production. Or it may participate in chemical/biochemical reactions (e.g. Maillard reactions), which might deteriorate: texture, flavor, color, taste, nutritional value of a product, and its stability → shelf-life time [5, 13, 14, 22].

Water activity ($a_w$) has its most useful application in predicting the growth of bacteria, yeasts and moulds. For a food to have a useful shelf life without relying on refrigerated storage, it is necessary to control either its acidity level (pH) or the level of water activity ($a_w$) or a suitable combination of the two. This can effectively increase the product's stability and make it possible to predict its shelf life under known ambient storage conditions [14, 25].

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