

CHAPTER II

LITERATURE REVIEW

2.1 Structure of Citrus Fruits in Relation to Processing

Citrus fruits are botanically classified as berries. They are superior fruits with all of their tissues derived from the ovary. This is in contrast to the apple in which some of the tissues are derived from enlargement of the calyx and receptacle.

Citrus fruit has a complex structure with many implications for citrus processing. The general factors to be focused are follows:
(6)

2.1.1 Special shape:

Citrus fruits commonly converted to processed products include grapefruit, oranges, lemons, limes and mandarins. Structurally these fruits are very similar except for their shape. Lemons and limes are usually oblong (prolate) with their major axis from stem to stylar (blossom) end.

2.1.2 Size:

Common measurements for the equatorial diameter of the several fruits are : 3.8 to 5 cm (limes); 4.4 to 6.4 cm (lemons); 5 to 7.5 cm (mandarins, tangerines); 5.7 to 9.5 cm (oranges); and

9.5 to 14.5 cm (grapefruit). These differences in fruit size between species, and sometimes between cultivars within the same species, require different sizing of equipment for juicing and some other preliminary processing procedures. Extraction is done by placing sized fruit or halved fruit into extractor cups designed for fruit within a certain diameter range. Quality and yield losses occur as small fruit goes to extractors for larger diameter fruit. The fruit does not position properly in the cup.

2.1.3 Seediness:

Another overall factor in citrus processing is seediness of the fruit. Both seedless (few seeds) and seedy varieties are commonly used for citrus processing. Seed constituents are undesirable in citrus juices, extraction and finishing processes are designed to avoid splitting and extraction of the seeds. Fortunately, lime (Citrus aurantifolia) is classified as seedless variety.

2.1.4 Parts of citrus fruits:

From outside to inside, the major parts of the citrus fruit are: the peel or rind (epidermis, flavedo, oil glands, albedo and vascular bundles); segments or sections (segment wall, juice vesicles and seeds); and the core (vascular bundles and parenchymous tissue).

The epidermis of a citrus fruit consists of an epicuticular wax layer in platelets (7), the cutin matrix (a mixture of cutin,

wax and cell-wall material), the primary cell wall and the epidermal cell. The wax layer is deposited slowly during the development of the fruit as relatively soft and amorphous material. The wax layer hardens while exposed to the air at the surface as the fruit grows and time passes. The amount of wax in this layer depends on the species or cultivar (8); (9), climate and growth conditions (9).

The soluble solids in orange, tangerines and grapefruit, consist mostly of sugars; Lemon and lime juice are different because upon maturation citric acid is the major soluble solids constituent. Table 1 gives the sugar content of several kinds of citrus juices. Citrus juices contain a small but a very important amount of insoluble material known as cloud with high content of pectin (11).

Citrus pulp after extraction is valued as a cattle feed. Since it contains all of the soluble sugars and other soluble constituents of the peel, including minerals and vitamins. Its composition of major constituents is shown in Table 2. It is low in crude protein, fiber and fat, but high in carbohydrates.

Table 1 Approximate sugar content of some citrus juices (10)

| Variety | Locality | Sugars (%) | | |
|------------|------------|------------|-------------|----------|
| | | Reducing | Nonreducing | Total |
| Grapefruit | | | | |
| Duncan | Florida | 3.0-5.1 | 2.4-4.0 | 5.0-8.3 |
| Marsh | Florida | 2.3-4.8 | 2.6-3.1 | 5.1-7.8 |
| Lemon | | | | |
| Eureka | California | 0.78-2.6 | 0.3-0.63 | 0.81-3.2 |
| Meyer | Florida | 3.22 | 0.48 | 3.70 |
| Lime | | | | |
| Key | Florida | 0.64 | 0.12 | 0.76 |
| Tahiti | Florida | 1.29 | 0.10 | 1.39 |
| Orange | | | | |
| Valencia | Florida | 3.2-5.0 | 2.3-5.2 | 5.4-10.3 |
| Washington | | | | |
| navel | California | 4.3-5.8 | - | 7.3-10.5 |

Table 2 Typical analysis of dried citrus pulp (10)

| Constituent | % |
|---------------------------------------|------|
| Moisture | 8.0 |
| Total solids | 92.0 |
| Nitrogen-free extract (carbohydrates) | 63.0 |
| Crude fiber | 13.0 |
| Protein (N x 6.25) | 6.2 |
| Crude fat (ether extract) | 3.5 |
| Ash | 4.3 |
| Accounted-for material | 98.0 |

2.2 Sugars in Citrus Juices

2.2.1 Juices

The sweet taste of citrus fruits and juices is due to the sugar glucose, fructose and sucrose. The sweetness of some sugars relative to sucrose at 100 is D-galactose 32, D-xylose 40, D-glucose 74 and D-fructose 173.

The principle sugars in Florida Valencia orange juice, grapefruit, lemon and orange juices were found to be sucrose, glucose and fructose in a ratio of 2:1:1 (12). Sugars other than glucose, fructose and sucrose occur in traces but do not contribute to flavor or nutrition and seem to be of minor importance. Quantitative analyses of Shamouti and Valencia oranges, grapefruit and lemon juices (13) showed a fructose to glucose ratio of about 1:1. Lemon contained 0.8% fructose, 0.8% glucose and 0.2% sucrose. Lime had 0.9% fructose, 0.9% glucose and 0.3% sucrose. The analysis showed the presence of the sugar alcohol sorbitol in some fruits, but none in citrus.

Sucrose is the only disaccharide in citrus fruit juices other than the tentative identification of the disaccharide trehalose, $O-\alpha-D-Gp-(1\rightarrow1)-\alpha-D-Gp$. It is believed that sucrose is the main sugars of translocation and its concentration in citrus is about equal to and up to double that of glucose and fructose. Sucrose occurs in very low concentrations in lemon and lime juices (about 0.2%) but has been positively identified in them by several

techniques.

Tree-ripened fruits of the early and midseason varieties accumulate sugars but mainly sucrose increases. In Valencia oranges the fruits mature in a season where the daily mean temperatures are rising and respiration is increased, consequently only a small increase of sucrose results. Glucose and fructose remained relatively constant in these orange and tangerine juice while sucrose increased.

Advantages of citrus fruits and juices in the diet are well accepted and appreciated. Sugars provide calories, vitamin C occurs in exceptionally high levels, and other vitamins and minerals provide valuable nutritional benefits. The amount of these valuable nutrients and some other physical and chemical properties of lime juice are shown in Table 3 and 4.

2.3 Pectin

The word pectin must be regarded as a generic term which is applied broadly for the pectic substances. Various pectic compounds are found in vegetables and fruits, being most abundant in limes, lemons, grapefruit and oranges. Pectin is often referred to as the ingredient that makes jelly gel and is the naturally occurring cloud stabilizer in fruit juices, especially citrus. Fruit juice consistency, referred to as "body" by the juice industry, is the result of pectin being present.

Table 3 Some physical & chemical properties of fresh lime and lime juice (2)

| | |
|--|------|
| Weight/one fruit (g) | 52.9 |
| Juice content (cm ³)/one fruit | 23 |
| Total soluble solid (Brix) | 7-8 |
| pH | 2.1 |
| Total Sugar (%) | ●.28 |
| Citric acid (%) | 5.5 |
| Ascorbic acid (mg)/100 (g) | 34.0 |

Table 4 Lime composition in East Asia (14)

| Composition of Foods, 100 g, Edible Portion and As Purchased | | | | | | | | | | | | | | | | | | |
|--|-----------------------------------|---------------------|---------------|--------------|-----|-------------------------|------------|-----|------|------|-----------------|------|------|---|---------------|----------------------|-------------|----------------------|
| | Refuse in as pur- chased | Food Ener- gy | Mois- ture | Pro- tein | Fat | Car- bohy- drates | Fi- ber | Ash | Ca | P | Fe | Na | K | β -caro- tene equi- valent | Thia- mine | Riba- fla- vin | Nia- cin | Asco- bic Acid |
| Lime (<u>Citrus Auranti- folia</u>) Fruit, Raw; | (%) | (Calo- ries) | (%) | (g) | (g) | (g) | (g) | (g) | (mg) | (mg) | (mg) | (mg) | (mg) | (mg) | (mg) | (mg) | (mg) | (mg) |
| Edible Portion | 0 | 36 | 91.0 | 0.5 | 2.4 | 5.9 | 0.3 | 0.2 | 13 | 11 | tr ^b | 2 | 82 | 10 | 0.03 | 0.02 | 0.1 | 46 |
| As Purchased; refuse, rinds and seeds..... | 23 | 28 | 70.1 | 0.4 | 1.8 | 4.5 | 0.2 | 0.2 | 10 | 8 | tr ^b | 2 | 63 | 5 | 0.02 | 0.02 | 0.1 | 35 |
| Juice | 0 | 24 | 90.0 | 0.5 | tr | 8.3 | tr | 0.3 | 9 | 8 | 0.1 | | | | 0.02 | 0.03 | 0.2 | 25 |
| Rind | 0 | 71 | 71.4 | 2.7 | 0.2 | 24.3 | 3.2 | 1.4 | 228 | 42 | 1.0 | 8 | 348 | 110 | 0.08 | 0.07 | 0.8 | 68 |

a lime (Citrus Aurantifolia)

b trace

Pectin is a lyophilic colloid with a negative charge and does not have an isoelectric point. Like most lyophilic colloids the important factor in its stabilization is its hydration rather than its charge. The charge may be neutralized without coagulation, but a dehydrating agent such as alcohol will coagulate it. An impure pectin of high ash content can carry a positive charge. Dry pectin is difficult to disperse; when introduced into water the particles hydrate on the surface forming a gummy coating which slows down the imbibition of water. Mechanical mixtures of powdered pectin with sugar, salt or wetting with alcohol are used to aid the dispersion (6). Potassium, sodium and ammonium salts of both pectin and pectic acid are easily dispersed in water.

Solutions of pectins vary greatly over a wide range of viscosity, which is the resistance offered by a liquid to flow. Viscosity of a dispersed pectin in water is dependent on concentration, pH, salts and size of the polygalacturonic acid chain. Temperature produces a marked effect on the viscosity of a pectin solution with viscosity decreasing as the temperature increases. The increase in viscosity resulting from increased pectin concentration is not a straight line but rather a parabola. Aqueous solutions of 2% citrus pectin are definitely pseudoplastic. With the addition of suspended solids and sugar they became strongly non-newtonian.

The effect of salts on the viscosity of pectin solutions below pH 2.75 is negligible. Above this pH the normal viscosity of the pectin solution is lowered by small quantities of these

salts whose hydroxides are not precipitated in the pH range of 3 to 7. When certain soluble salts, such as copper, nickel, lead, iron, aluminum, manganese, sodium, calcium, and magnesium are added to a pectin solution, an abnormally high viscosity results. The increase in viscosity varies with the nature and amount of metal added and is also dependent upon the hydrogen ion concentration. When added in excess, certain metallic salts will coagulate pectin from solution, assuming that there are sufficient free carboxyl groups available for reaction with the cations.

2.4 Concentration of Citrus Juice

2.4.1 Vacuum evaporation

Vacuum concentration has several advantages. It makes possible the low-temperature concentration of heat-sensitive foods such as orange juice; it can increase the rate of evaporation by increasing the difference between the boiling temperature of the product and the temperature of the heating medium. (15)

A common sequence of flow in the vacuum concentration follows: A valve is opened to permit high-pressure steam to flow through a large steam ejector to develop the initial vacuum in the evaporator. When the desired vacuum is reached, preheated juice is pumped into the heat exchanger, steam is admitted into the steam chest and boiling begins almost immediately. The vapors are separated and removed. Vapors may be condensed by mixing with cold water in parallel or counter flow barometric condensers provided

there is adequate differential between the temperature of the vapors and that of the condenser water. Heikal et al (16) concluded that concentrating lime juice under vacuum up to 42% total soluble solid was the most suitable concentration method. Pruthi et al (17) did the research on cashew apple concentrated juice and found that the important physico-chemical characteristics like ascorbic acid, pH, color and flavor of vacuum concentrated cashew apple juice were better than open-pan concentrated cashew apple juice. However, volatile substances other than water are "boiled off" in concentrating by evaporation. These include volatile flavors of fruits. (15)

2.4.2 Freeze concentration

Freeze concentration plants include three fundamental elements: (18)

- a) A crystallizer (also called "freezer", "Chiller" etc) which produces a slurry of lime crystals. In some cases, an appendage to the freezer called a crystal growing tank is employed.
- b) A separation device wherein the ice crystals separated from the mother liquor. Centrifuges are most commonly employed, although some manufacturers prefer a wash column or filter press.
- c) A refrigeration unit to cool the liquid, remove the heat of crystallization and the frictional heat resulting from hydraulic flow, wall scraping and agitation of the slurry.

The maximum concentration obtainable in freeze concentration equipment depends upon the liquid being concentrated, its

viscosity, and other properties. Generally, concentration can be carried to the point where the slurry at the prevailing low temperature becomes too thick to be pumped. With equipment of ordinary design, it is possible to concentrate most comestible liquids to the point that about 50% of the total weight is solids. In freeze concentration, ice is removed for the primary purpose of putting the liquid into a more concentrated form. The ice is a waste product having little or no value other than as a refrigerated material and is ultimately discarded.

In indirect contact ice crystallizers, the evaporating refrigerant or coolant is separated from the processed liquid by a rigid metal wall. The typical indirect contact crystallizer is a tubular heat exchanger. The tubes are submerged below the level of the evaporating refrigerant or coolant in the shell. Indirect contact crystallizers are employed where the desired product either the concentrated liquor or the melted ice-would suffer from contact with the refrigerant. All known commercial installations for the freeze concentration of comestible liquids employ crystallizers of the indirect-contact type. In indirect contact crystallizers, ammonia or freon is ordinarily selected as the refrigerant.

In separating ice crystals from the liquor, centrifugation is appropriate. With a centrifuge, it is possible to subject the ice slurry to a force 1,000 or more times that of gravity. Under these circumstances, most of the liquid withheld by capillary attraction between two adjacent continuous crystals.

Experience with centrifugation of hundreds of crystalline materials indicates that for efficient separation the following should prevail:

1. Crystals should be as large as possible, the larger the crystal, the fewer the points of contact per unit volume.
2. Crystals should be uniform in size.
3. Crystal habit should approach the sphere as closely as the laws of nature will permit. Continuous spheres always touch at a point. No contact lines are involved, as is the case with crystals having a cylindrical shape. No contact areas are involved, as is the case with crystals having a flat surface.

2.5 Dehydration

Drying is probably the oldest form of food preservation. Sun and wind currents were utilized exclusively at first, and later artificial heat was used. Hot-air drying was improved by exposure of solids to streams of hot-air, by atomization of liquid food products into heated air (spray-drying), by drying liquid and semisolid foods by contact with heated rollers (drum-drying), and finally by combination of heat and low pressure (vacuum-drying). Freez-drying in which the food is frozen and drying occurs by sublimation of water from the solid phase also has been introduced commercially. (19)

2.5.1 Fundamental aspects of dehydration

2.5.1.1 Selection of raw materials for drying

This is run on the basis of characteristics best suited to this method of preservation. In early development, drying and dehydration was applied as a salvage operation to economically conserve foods produced in surplus quantities. This period was followed by empirical testing to determine the suitability of different varieties of fruit and vegetable, the determination of optimum maturity for drying and the selection of those varieties which are most acceptable in the dried form as determined by color, flavor, texture, nutritive value and storage stability. At present it is still not possible to define the characteristics desired in fruits and vegetables objectively, our knowledge of the factors limiting suitability is insufficient to serve as guide to existing practice.

2.5.1.2 Control of undesirable changes in quality during preparation for drying

As a result of investigation of the factors involved in changes in color, flavor and texture during washing, peeling, cutting and drying, the nature of both the changes due to uncontrolled growth and activity of contaminating microorganisms and of tissue enzymes involved was evaluated.

2.5.1.3 Reduction of moisture content

Moisture content of the material to be dehydrated must be

rapidly reduced to the level required for optimum storage stability under conditions of minimum damage to quality. As a result of improvement of knowledge of the factors influencing the migration or movement of water from the interior of the product to the outer surface and of evaporation of moisture as water vapor at the surface, hot-air drying has reached the stage where it can yield acceptable fruit and vegetable products. The moisture level required for improved storage stability has been determined for most food products and this level has been attained by combination of multistage drying and in-package desiccation under conditions in which heat damage is minimized. Mass transfer operations have been improved by recognition of naturally occurring barriers to moisture transfer and their elimination or reduction.

2.5.1.4 Production of porous structure during drying

In conventionally spray-dried products the desired porosity can be obtained by agglomeration of the powdered product and subsequent redrying while under agitation on conveyor drier.

2.5.1.5 Retention and restoration of volatile flavors.

Various methods have been developed to improve retention of flavors in dried foods. These include drying under conditions such that flavor loss during dehydration is reduced by reducing temperature or pressure of the product being dried, by recovery of

volatile essences and their return to the product during the drying process, by recovery of volatile flavors and their combination with flavor fixing or holding substances resulting in solid flavor-sealed products which can be granulated and added back to the finished product, or by development of flavor from flavor precursors by the activity of naturally occurring or added enzymes.

2.5.1.6 Improvements in packaging

Protective flexible packages of foil, film, fiber and combinations, plus the use of bactericides, make it possible to "tenderize" dried fruit. Sealing under vacuum or inert gas in tight packages also contributes to improved products.

2.5.2 Dehydrated citrus juices

Citrus juices are 85 to 90% water, and many attempts have been made to remove all the water and prepare a completely dehydrated product. Throughout the years, almost every conceivable method of dehydration has been applied to citrus juices in attempts to prepare instant citrus juice powders, particularly orange. Production of instant orange juice and other citrus juice powders is technologically feasible by freeze-drying, some types of spray drying, vacuum puff drying and foam-mat drying, but there are general considerations which should be studied with regard to any type of dehydration process.

From a logical approach to the economics of dehydrated juice products, two general conclusion must be reached:

1) The removal of the remaining water from a concentrated juice product would not improve the quality of the reconstituted products. At the ultimate, it might be accomplished without much deterioration in quality, but it would not seem reasonable to expect the quality to be improved;

2) removal of additional water from a concentrate would require additional energy and would increase processing costs thus, a product with equal or lesser flavor quality will be produced and it will cost more. What advantages would that extra cost provide? The most obvious advantage would be increased convenience, presuming the product would be stable at room temperature, and easy to store and reconstitute. Minimized weight should be an advantage so that eventually, at some point in the market, the additional cost for dehydration might be recovered in transport, storage and marketing advantages.

2.5.3 Method of Dehydration

2.5.3.1 Spray drying

Milk, fruit juice, corn syrup, soluble coffee and many other liquid foods are dried by spraying into a chamber where heated air is circulated to remove water rapidly from the suspended droplets

(A schematic diagram of spray dryer is shown in Fig. 1) Spray drying of juices is complicated by tendency of these products to turn into a heavy viscous syrups and candies instead of powders. In order to secure powders, it is necessary to lower the moisture content rapidly and cool before particles come in contact with one another on walls of the equipment. Drying aids are extensively added before drying fruit and vegetable juices. These included corn syrup solids, milk solids; gums, pectic substances, methyl cellulose, lactose, sucrose and dextrin. The design of equipment is an important factor in spray drying fruit and vegetable juices. Particle size is obviously important since the smaller the droplets, the more rapidly the moisture may be removed. If particles are not of uniform size, large particles may come out wet, making it difficult to properly locate the boundary between drying and cooling zones. The size and uniformity of droplets formed are determined by the design and operation of spray-liquor system and this also affects the thermal efficiency and continuity of operation. The spray liquid may be dispersed into the drying chamber by a pressure nozzle, or the centrifugal or spinning disc atomizer. Because of its high capacity and better control is used commercially for spray-drying milk, milk products and certain fruit and vegetable juices. The characteristic particles formed commercially are round and hollow or porous in the interior. These characteristics are affected by the nature of material to be dried, the manner of spraying and the subsequent treatment during the drying operation. The size, shape, and operation of the drying chamber are important to secure dry powders.

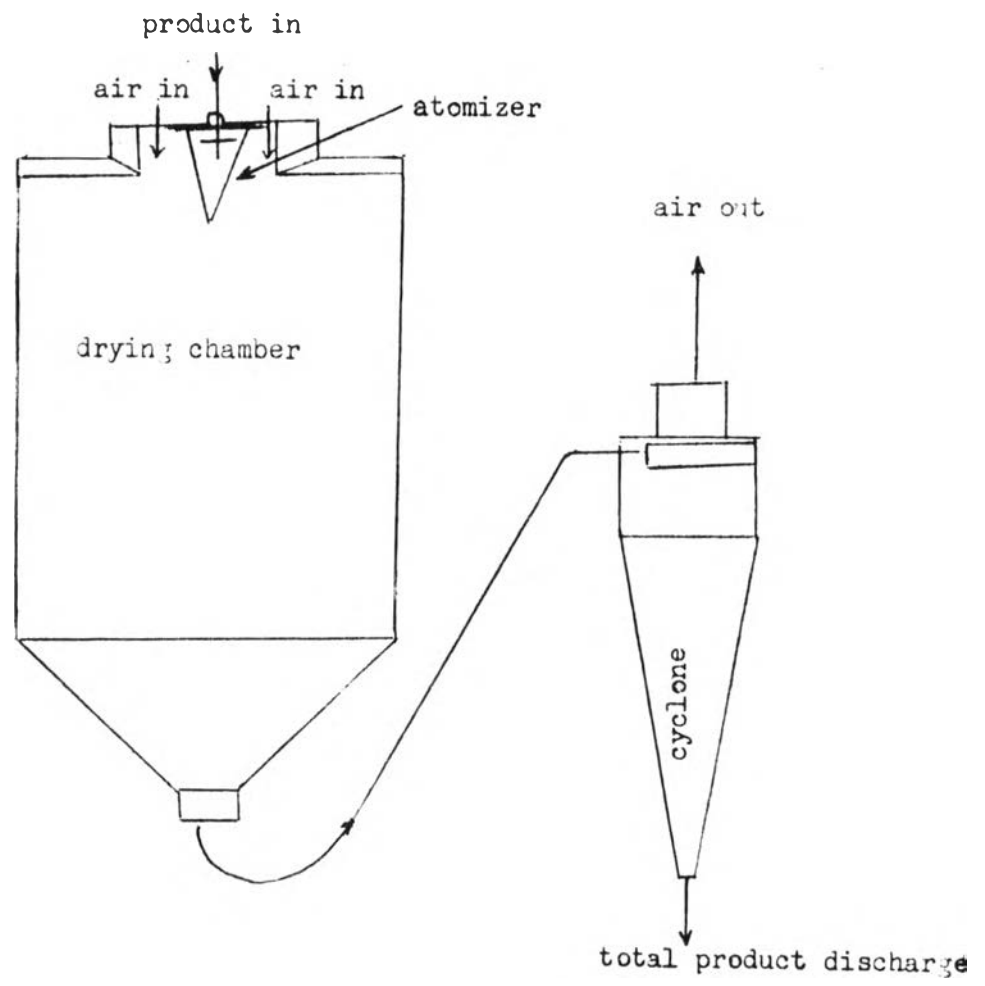


Fig. 2 Schematic diagram of spray dryer

Recent advances have improved speed of dissolving and dispersing spray-dried products. Spray drying tends to produce low-density, fine powders which do not wet readily, floating and clumping so water cannot penetrate uniformly throughout the mass. "Agglomeration" was developed for spray-dried detergents because fluffy powders tended to cause sneezing. Coarser granules were desired to avoid this irritation, and also to avoid clumping which delayed dispersion.

2.5.3.2 Vacuum "puff" drying

Five-fold orange juice concentrate was dried in a Florida plant to a powder containing about 1% moisture that was reported to retain 97% of the original ascorbic acid content (6). A mixture of orange juice concentrate and corn syrup containing about 60% orange solids and 40% corn syrup solids could be made to "puff up" during drying in a vacuum oven, to give an open, porous structure, which lost water readily. The product, however, had about 3% moisture content and was very hygroscopic. Moisture content could not be reduced further without the product burning or developing a heated flavor. The use of in-package desiccants such as calcium oxide further reduced the moisture content to about 1.5% or less during 75 days conditioning at 21°C. The product then was reported to have excellent stability at room temperature (6). Ascorbic acid retention of this product was reported to be 90 to 100%, and even after 6 months at 38°C was still 90%. Notter et al. (20) reported that ascorbic acid was somewhat less stable in the product from orange

juice concentrated without added corn syrup than in those containing corn syrup solids. The product from this process still had two principal disadvantages, however. The flavor did not approximate that of single strength canned juice or of frozen concentrated orange juice. The need for in-package desiccants or secondary drying techniques introduced additional costs that had exceeded possible savings in transportation and storage. Thus the product was not competitive in the market.

2.5.3.3 Freeze-Drying

Many attempts have been made to prepare citrus juice powders by freeze-drying, but few reports have been published. In freeze-drying, water vapor is removed from the frozen juice by sublimation under vacuum, to prepare high quality dehydrated citrus juice products. Because the citrus juice remains frozen throughout drying and is, therefore, not subject to heat damage, that powder probably represents the optimum quality obtainable in a dehydrated juice product. Those investigators reported, however, that because of the difficulty in maintaining high Brix concentrates solidly frozen for vacuum sublimation, freeze-drying of orange juice was much easier to control and maintain if beginning concentrations were about 30^o Brix or less. Above 30^o Brix, unless conditions were precisely controlled, the material soon reached its eutectic point, began to melt under vacuum and puffed up so that the process became puff-drying instead of freeze-drying. Because of the difficulty of

controlling this process, which was inherently expensive and required both high vacuum and refrigeration, freeze-drying appeared to be technologically feasible for preparing a high quality dehydrated orange juice, but not commercially practical. Also, because the lowest moisture content achieved in this process was about 3%, the product still required an in-package desiccant or secondary drying. Freeze-drying has proved practical for certain foods such as coffee and meat. One reason for this has been the relatively high value of the solids in these products. Orange juice and other citrus juices enjoy wide markets and popularity, but they are consumed at relatively high (10-13%) solids contents. Coffee and tea may be consumed at 0.5-2.5% solids, so they have a much higher value on a solids basis. Products of this type are prime candidates for freeze-drying, or other relatively costly dehydration processes. (6)

2.5.3.4 Foam-Mat Drying

Citrus juices, like other liquid foods with high sugar contents, can cause considerable problems with many high-temperature dehydration systems. Such materials, when held at much above room temperature, tend to "syrup" as the water is removed. Combinations of sucrose and invert sugar (about half glucose and half fructose) are especially difficult to crystallize without syringing. Such products usually require two stages of drying: (1) an early stage to remove most of the moisture (about 75 to 85%), by use of the highest temperatures possible for optimum efficiency, and (2) a later stage

to remove residual moisture (the last 10 to 15%) during cooling to solidify the sugar components, and make them brittle so they can be easily removed from the drying medium. In the late 1950s a new process, called "foam-mat" drying, was developed at the U.S. Department of Agriculture Western Regional Laboratory in Albany, California. That process enabled drying at two or more temperature stages and appeared to be ideally suited for liquid form, high-sugar foods. The starting material for this process is a 5 or 6 fold citrus juice concentrate, prepared by one of the commercial evaporation processes described above. A stabilizer, methyl cellulose, is added to about 0.5% (solids basis), which would amount to less than 0.05% in the reconstituted juice. In that process the liquid concentrate is mixed with a foaming agent such as methyl cellulose, soya albumin, certain algins, etc. The foam is spread in a thin layer on a drying tray or belt and dried in a blast of hot air at atmospheric pressure. The foam creates a porous structure that aids in rapid drying. Flavor damage is slight during the drying process. In 1964, when relative costs of different dehydration processes for orange juice were compared, operating cost per kilogram of dry product, for a plant manufacturing 1.8 million kg per year, would be 66¢ for freeze-drying, 33¢ for puff-drying and 22¢ for foam-mat drying (6).

2.6 Drying Aid

While encapsulation or "locking-in" of citrus essential oils on a dry carrier is well known (21, 22), only scant information is

available regarding similar process for water soluble essences. Approximately 75% of the initial aroma volatiles was retained in the optimal maltodextrin sucrose carrier, as against 50% by the best method (23). Extensive work by Thijssen and Rulken (24), Flink and Karel (25) indicated that retention of volatile compounds during freeze drying is highly dependent on composition: in various model system retention increased with decreasing molecular weight of the carbohydrates and increasing total soluble solids up to about 20%. Monzini and Maltini (26) had already ascertained that the addition of sucrose to lemon juice permitted it freeze-drying under less drastic conditions, by raising the structural softening temperature several degrees. Maltini (27) reported that the addition of sucrose in the proportion of $\frac{1}{3}$ to $\frac{1}{2}$ of the total solid residue permitted raising the temperatures. The sublimation temperature and melting temperature by about 4-5°C, with considerable operational and economic advantages in freeze-drying. In contrast, addition of citrus fruit pectin and carboxy methyl cellulose to lemon juice did not alter the thermodynamic behavior of the system to any great extent. Kopelman et al (28) studied the effect of various combinations of carbohydrates (mono- and disaccharides and maltodextrins) on retention of orange volatiles under constant drying conditions. Throughout the test, the aroma retention improved with increase of the dextrose equivalent of the corn syrup solids. These findings are in agreement with those reported for freeze drying of model systems (25).

2.7 Quality of Citrus Juice Powder During Storage

Among the deteriorative reactions limiting the storage life of dehydrated fruit juices, the most important are non-enzymatic browning and loss of ascorbic acid (29). The shelf life of citrus powders is reduced by water absorption, caking and non-enzymatic browning. The first two effects are favored by the amorphous structure of the sugars, resulting from the dehydration process, and are mainly controlled by composition, storage temperature and water activity (30). The third effect is associated with the Milard reaction between reducing sugars and amino compounds, acid caramelization of the sugars, and degradation of ascorbic acid (31). The browning of citrus products is accompanied by development of off flavor and evolution of carbon dioxide and similarly to caking, it is strongly affected by storage temperature (32) and water activity.

2.7.1 Ascorbic acid retention

Karel and Nickerson (33) determined the effects of water and of oxygen on browning and loss of ascorbic acid in dehydrated orange crystals. The results showed that oxygen had little effect on the rates of destruction of ascorbic acid in the stored orange crystals (at 37°C). The observed differences in rates of ascorbic acid destruction between air and vacuum stored samples were considered insignificant. Water content and water activity, on the other hand, have a very drastic influence on the rates of ascorbic acid destruction. It was found that the rates of destruction of ascorbic acid in orange crystals increase with increasing moisture content. This

is in agreement with data of Lea, (34). The result also indicated that food materials similar to the orange crystals used in this study did not require packaging under vacuum, The major destruction of ascorbic acid due to increased in moisture contents are not affected by atmospheric oxygen. Foda et al. (35) found high retention of ascorbic acid in the case of freeze dried orange juice powder. Annu et al. (36) reported that ascorbic acid retention of mango was better in the case of 15° Brix than 20° Brix. This might be either due to the dilution of the reducing sugar and amino acids with which ascorbic acid could react under aerobic and anaerobic condition to produce brown pigments (37) or due to better retention of the ascorbic acid, added to raise the level. Sucrose was also known to help in the better retention of colour, flavor and ascorbic acid (36).

2.7.2 Caking

It is well known that the hygroscopic character and caking ability of dried food products with a high sugar content are ascribed to be amorphous state of sugars (30). Prevention of caking and stickiness depends upon the knowledge of the environmental conditions that govern the transformation from the amorphous to the crystalline state. For this reason, during storage of dried sugar containing products, adequate moisture and temperature conditions must be maintained to avoid sugar crystallization with the resultant loss of certain desirable product properties. Flink and Karel (38), Omatete and King (39) showed that sugar crystallization during storage

promotes the loss of volatile compounds entrapped in freeze-dried carbohydrate solutions. Amorphous sucrose is theoretically unstable but the very high viscosity of the medium prevents a molecular rearrangement and stabilize the amorphous state for a relatively long time (40). The sorption of water imparts mobility to the sucrose molecules and this results in the transformation of sucrose from the metastable amorphous state to the more stable crystalline state (41). Makower and Dye (30) showed that the rate of crystallization of amorphous sucrose, evaluated from changes in moisture content, followed an exponential law with respect to time after an initial induction period.

2.7.3 Off-flavor

Off-flavor can be developed from the oxidation of the lipid fraction or a change in the essential oil, limonene, an important essential oil (42). The volatiles which show the most significant increase when a change in flavor becomes detectable are furfural and diacetyl. Furfural has been identified in orange juice powder after storage by Tatum et al. (43) and Dinsmore and Nagy (44). Shaw et al. (45) have shown that this compound is formed during the heating of a solution of fructose and ascorbic acid. Tatum, et al. (43) and Huelin et al. (46) have demonstrated that its origin is the degradation of ascorbic acid. El'0 de et al. (47), Scanlan et al. (48) demonstrated the formation of diacetyl in solutions of sugar and amino acids. Blair et al. (49) found

terpineal in high concentrated orange juice after storage or overheating. Blair et al. (49) ascribed the origin of this substance to hydration of limonene. Furfural does not seem to be very significant as far as flavor change is concerned (50). Although the increase of α -terpinol is associated with a bitter taste, this bitterness is not due to this single substance. The volatiles which exhibit the most significant increase in orange juice powder during storage or heating, before the critical time for flavor alteration is attained, have been found to be furfural and diacetyl (50). Diacetyl seems to be able to play a significant part in the early changes of flavor of the product. The increase in furfural content during storage or heating of the dry product seems to originate from ascorbic acid degradation; the origin of diacetyl may be also a non-enzymatic browning reaction and/ or oxidation of acetoin.

2.7.4 Browning

Among the deteriorative reactions limiting the storage life of dehydrated fruit juices, the most important are non-enzymatic browning and loss of ascorbic acid. Numerous investigations on this subject had established that the water content of the dehydrated material had a decisive effect on the rate of these reaction (29). Much less is known about theoretical critical moisture contents for browning and other autocatalytic reactions. Salwin (51) suggested that moisture contents corresponding to monomolecular coverage give optimum stability. Rockland (52) showed that stability may be

related to the rate of change in moisture content with change in water activity. Hodge (53) reported that non-enzymatic browning reactions resulted in the formation of water. Eskin et al. (31) reported that non-enzymatic browning reactions are accompanied by carbon dioxide evolution, either due to Strecker degradation of amino acid compounds or due to deterioration of ascorbic acid. Karel and Labuza (54) reported that in model systems containing sucrose and citric acid, at low moisture content, hydrolysis of sucrose can occur, leading to non-enzymatic browning. All of the water present in the crystals including that adsorbed in a monomolecular layer, appeared to be available for reactions resulting in browning and there was no critical moisture content below which there was no browning (33). The mechanism of this reaction requires the participation of water as well as the dissolution of sucrose in the aqueous phase (55)

Draudt and Huang (56) detected the browning intermediates in to be sugars in combination with amino acids. Some of the non-enzymic compounds originated from acid catalysed degradation of fructose (43) and few from dereaction of hexoses with amino acids. Another reason for browning and caking might be the instability of the juice solids at that temperature (20).

Browning due to sugar amino reaction (57) appeared to be very much less compared to browning due to the degradation products of ascorbic acid. The increased level of reducing sugar also confirmed that browning was mainly due to degradation products of ascorbic acid. (36)

2.8 Uses

, As an acidulant, lime juice is used for some of the same purposes as lemon juice. Lime beverages, however, are quite distinct in flavor character from the corresponding lemon product and appeal to different consuming groups. In general, lime beverages seem to be accepted more widely by adults than children. Among the uses of lime juice are: as limeade, in iced tea, on seafood, in mixed drinks and as a flavor enhancer on such fruits as avacados. A major outlet for lime juice is in syrups and concentrates for beverage use. Lime juice is very popular as a thirst quencher in the preparation of coolers and cocktails as well as in citrus flavored punches. Favorite mixed drinks which contain lime juice include gin rickey, gin and tonic gimlet, rum and soursop, and Scarlett O'Hara. Many other drinks, such as the Margarita and daiquiri, may contain either lime or lemon juice.

In mixed juice beverages, lime blends well with other citrus juice, with apple and with apricot puree to give an unusual mellow taste. Among the several applications in food products, lime juice is used in lime cream chiffon pie and the popular Key lime pie, souffles and parfaits. Many old timers in South Florida use "Old Sour" which is fermented lime juice seasoned with salt. When used on fish and shellfish dishes, meats and in salad dressing, this preparation is said to greatly improve the flavor(b).