Making Use of Tons of Citrus Waste

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More than 2 million tons of pulp, peel, and rag remain each year after citrus fruits are processed into juice, frozen concentrate, and sections. What to do with those mountains of waste?

When the industry was young, the only wastes were the culls and surplus fruit, which were dumped on wasteland or used as soil conditioners on cultivated land. Solid wastes from early canneries were handled in the same way. The liquid wastes were ponded or flushed into streams, lakes, or sewers. All such makeshifts were unsatisfactory and dangerous. A pile of rotting orange peels soon begins to stink; underground water supplies are contaminated; and the increased biochemical oxygen demand kills aquatic life or exceeds the capacities of sewage-treating plants.

Industrial, State, and Federal research organizations investigated the increasingly serious problem. From their efforts came several economically valuable products. Now 80 to 90 percent of citrus wastes are converted into usable products, such as dried pulp, molasses, pectin, essential oils, brined peel, citric acid, limonene, feed yeast, and biologically active materials.

From the waste peel, marc, and seeds that came from the processing lines, research men developed dried pulp, which is used extensively for feeding dairy and beef cattle and is suitable for feeding other animals. It contains about 8 percent moisture, 6 percent ash, 6 percent crude protein based on total nitrogen, 6 percent crude fat, 14 percent crude fiber, and 66 percent nitrogen-free extract. Although it must be supplemented with some other feed, it contains significant amounts of protein, fats, and minerals.

To make dried pulp, fresh peel is first ground in a hammer mill. One-half to 1 percent of lime is added to the peel immediately after grinding; the amount is carefully measured in order to get the best pressing characteristics. The lime neutralizes the acids and catalyzes the de-esterification of the pectin in the peel to form calcium pectate, which facilitates pressing and drying. Formerly the peel was allowed to stand in bins for about 45 minutes before pressing or drying to allow time for the lime to react. Now the time of reaction is shortened to 15 minutes or so by stirring the peel constantly as it moves slowly through a pug mill. Continuous presses remove as much liquid as possible. In some processing plants the pulp is heated by direct steam injection to about 120° F. during this step to facilitate the pressing. The weight of liquor removed is about equal to the weight of the pressed pulp. Direct-fired or steam-heated rotary kiln driers are used to remove the moisture from the pulp. In some mills the pulp is given a preliminary drying in direct-fired units and finished in steam-heated units. Careful control of the drying rates and temperatures is necessary to produce the fluffy, light-colored feeds that are considered desirable. About 1 ton of feed is obtained from 10 tons of cannery waste. In the past 10 years, production of dried peel has increased to approximately 200,000 tons a year.

Press or drain liquor from citrus peel contains 5 to 7 percent sugar and a total of 10 to 12 percent soluble solids. It cannot be flushed into sewers or ponded unless care is taken to reduce the biochemical oxygen demand or to prevent bad smells. Most of the press liquor is concentrated to produce molasses. Multiple-effect evaporation is commonly used. One plant in Texas uses direct heating with a submerged gas flame, followed by two stages of evaporation.

The first stage of a multiple-effect evaporator is operated under positive pressure (up to 26 pounds) and the last stage under negative pressure (down to 26 inches of mercury). Intermediate stages may be used to increase the number of pounds of water evaporated per pound of fuel consumed. Evaporators may be constructed of mild steel. Corrosion is something of a problem if not all of the acid is neutralized by the lime. A more serious problem is scaling of the heat-exchanger tubes in the evaporators, because the scale builds up rapidly, interferes with heat transfer and circulation, and must be removed about twice a week by boiling with lye. The exact nature of the scale has not been determined, but it probably is composed largely of calcium citrate, calcium pectate, and fibrous material. Trouble is encountered primarily in the first effect of the evaporator. Some operators give the press juice a preliminary heating to 212° F. or higher in an auxiliary heat exchanger, which can be cleaned easily. The heating precipitates some material, which is removed in a continuous clarifier, and lengthens the time the evaporators can be operated between cleanings.

In a recent installation, submerged gas burners are used to give the press juice a preliminary heating and concentration to about 22 percent solids. Carbonation by the products of combustion forms a precipitate, which is removed in continuous thickeners. Either method reduces the amount of suspended matter in the final product and improves the quality. Analyses of 13 samples of Florida citrus molasses showed an average of 71.4 percent total solids, 42 percent sugars, 3.8 percent crude protein, 1.1 percent pectin, and 4.8 percent ash. The pH value was 4.7.

Citrus molasses is dark brown and bitter. It is used mainly in cattle feeds, in which it is usually mixed with other materials, although it can be fed full-strength. Some is mixed with wet citrus pulp and then dried to make a feed. The amount of total digestible nutrients in the molasses is about 57 percent. Some is used as a fermentation substrate in the production of alcohol.

Production of citrus molasses increased from none in 1940–41 to nearly 42,000 tons in the 1949–50 season.

ANOTHER USE for press juice is in the production of yeast, particularly *Torulopsis utilis,* which grows rapidly and is therefore less susceptible to contamination than other yeasts. It is rich in vitamins of the B complex and is a good supplement in feeds. About half the dried yeast is crude protein. It is deficient in methionine, one of the essential amino acids, which, however, is present in cereal proteins. A ration containing this yeast with some cereal would provide all the essential amino acids.

Research workers in the Southern Regional Research Laboratory, the United States Citrus Products Laboratory in Winter Haven, Fla., and a commercial cannery worked together to develop a process for the production of feed yeast. Their experiments included the operation of a 200-gallon-per-hour pilot plant. They developed a continuous method, which gives a good yield. The juice from the feed mill is first passed through an 80-mesh screen to remove particles of pulp. Then it is diluted with water to a sugar concentration of about 2 percent, heated to 200° F. to destroy micro-organisms, cooled, and pumped continuously into the yeast propagator. A concentrated nutrient solution is metered into the propagator in proportion to the feed rate. The propagator is kept thoroughly aerated by air introduced through porous stone candles in the bottom of the tank. The product from the propagator flows continuously into a collecting tank and thence to special centrifuges which separate the yeast as a thick cream. The yeast cream is dried on a drum drier, pulverized, and packaged.

As nutrients, phosphates and nitrogen compounds must be added. Some benefit can be obtained from the phosphorus in the juice, but it must be supplemented. About 0.19 pound of ammonium sulfate, 0.045 pound of anhydrous ammonia, and 0.045 pound of 75 percent phosphoric acid are required per pound of yeast. The acidity in the propagator is easily controlled within the range of pH 4 to 4.5 by varying the ratio of ammonia to ammonium sulfate. With the method of aeration used, from 500 to 700 cubic feet of air was required per pound of yeast produced. Cooling coils were installed in the propagator to dissipate the heat of fermentation and maintain a constant temperature of 95° F.

A pure culture of *Torulopsis utilis* is grown in the propagator. Continuous feeding of the pasteurized press juice and nutrients is started and maintained as soon as the actively growing culture fills the propagator. No new culture is needed so long as the yeast grows rapidly. The problem of foaming is controlled by closing the top of the propagator and providing a large overflow tube to a collecting tank where the foam is broken.

Fermentation proceeds rapidly and the rate of feed an hour can equal one-third the propagator volume. This means an average retention time of only 3 hours, which is considered short for fermentations. Yields of yeast are progressively smaller with increasing sugar content of the feed. At a 2 percent concentration, the yield is 44 percent of the sugars consumed. Utilizations better than 95 percent of the sugars and two-thirds of the total organic matter were obtained. The drum-dried yeast analyzed 47 percent crude protein and 3.3 percent phosphate (as the pentoxide). The product is light in color, fluffy, and, though not washed, only slightly bitter.

THE ISOLATION OF OIL from the rind of the lemon is one of the earliest chemurgic applications of citrus fruit. Hand pressing of the peel against sponges has been practiced in Sicily since the 18th century; at one time the United States imported nearly a half million pounds of lemon oil annually. Machinery has made possible the production each year of more than 1,500,000 pounds of oils from citrus peels.

The whole fruit, waste cannery peel, or flavedo, the colored part of the peel, can be used. The material is ground and pressed in screw extractors or pressed between fluted rolls to yield an oil emulsion. A recently developed juice extractor, which presses the whole fruit, delivers separately the edible juice and an oil emulsion. The emulsion is screened and the oil separated by centrifuging. The centrifuged oil is placed in cold storage, where waxes separate, the wax-free product being known as cold-pressed oil. These methods are used particularly with lemons, oranges, and grapefruit. Less than half the peel oil in the fruit is recovered from the fruit used. These oils are sometimes concentrated under vacuum to produce concentrated oils in which a major part of the limonene has been removed.

Distilled oils also are prepared from limes, oranges, and lemons. The whole fruit, peel, or liquid effluent from cold-pressed oil preparation is subjected to steam distillation. The oil separates readily from the distillate. Distilled oils are generally inferior to cold-pressed oils. A distilled oil of excellent quality is obtained in some juice canneries by flashing the juice under vacuum. Additional distilled oil is obtained during the manufacture of molasses from the first effect or during flashing of the press juice, but it has little value for flavoring purposes.

Cold-pressed oils are used for flavoring, especially in bottled and fountain beverages, cakes, candies, and pies. Some oils, particularly the distilled, are used to perfume soaps. The amount that can be used for these purposes is limited and much less than the potential supply. Scientists are trying to find other uses in plastics and as solvents; particularly are they seeking further use for the distilled oil that is recovered during other operations. Other outlets are needed; the potential supply from waste cannery peel is about 20 million pounds annually.

The principal constituent in all the citrus-peel oils is *d*-limonene, which constitutes 90 percent or more of the oil. It contributes little to the flavor of the oil, and its presence results in somewhat less stability. Aldehydes (citral), higher alcohols, higher acids, esters, and hydrocarbon compounds give flavor and aroma to the oil.

Citrus seeds are a source of food oils. Some seed oil was produced in Florida in the late 1930's, but operations were suspended until 1946. During the 1948–49 season the estimated oil recovery was between 300 and 400 tons in Florida. The potential supply from wastes from Florida citrus canneries is estimated at more than 5,000 tons. Some varieties of citrus fruit, such as the navel orange and the Marsh seedless grapefruit, have few seeds, but others, the Seedling orange and Duncan grapefruit, for example, contain many.

In the extraction of juice from fresh fruit, the seeds accompany the juice and are removed by screening, along with some pulp. The adhering pulp is removed by further screening, after which the seeds are dried in rotary driers and sent to oil-extraction plants, where the oil is removed by screw presses or hydraulic presses. The yield of oil is about 600 pounds a ton of dried seeds. The fresh oil is pale amber and extremely bitter, but the bitterness can easily be removed and the oil refined by the methods commonly used with other seed oils. Seeds of grapefruit and oranges are processed together. The oil is used in cooking oils, including a hydrogenated modification, and in detergents. The principal constituents of the seed oils are glyceryl esters of oleic, palmitic, and linoleic acids, and smaller amounts of the esters of stearic, arachidic, and linolenic acids.

Juice from processed lemons is used primarily to make citric acid. A ton of lemons yields 15 to 50 pounds of citric acid. The whole fruit first is passed through presses and washed to remove the juice. Then it is placed in fermentation tanks to liquefy some constituents, coagulate others, and ferment the sugars. It is then heated and filtered, and the citric acid is precipitated with lime and calcium carbonate. Citric acid is released from the lime salt by adding sulfuric acid. Water is removed by evaporation, and crystallization proceeds in lead tanks. The purification procedure is somewhat complicated. It involves decolorization and treatment with charcoal, sulfide, and ferrocyanide to prepare citric acid of acceptable pharmaceutical quality. Eighty-five percent of the acid in the lemons is recovered. In this country, citric acid is used primarily as a food-flavoring acid and in plasticizers.

Citrus peel, left after the juicing or peel-oil operation, is a good source of pectin, which has been used in making jelly since the eighteenth century. It was isolated and named in 1825. Work on it progressed sporadically until 1912, when patents on its production were obtained. The patents stimulated further activity, particularly after 1930. New uses are being discovered constantly; if some of the promising ideas are developed commercially, production should exceed the present 6 million pounds a year.

Most commercial pectin in the United States is obtained from citrus peel, which is one of the richest sources; about 2 million tons of the raw material is available annually. Fresh peel contains 3 percent or more of pectin;

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washed, dried peel contains at least 30 percent. Dried apple pomace, the only other source of pectin that has been used on a commercial scale in this country, contains less than half that much pectin.

When peel is used as a source of pectin it must receive more gentle treatment than that used in processing for feed or soil conditioning. The procedure developed at the Western Regional Research Laboratory includes blanching and washing in a continuous jacketed washer that has a screw conveyor. Blanching destroys an enzyme in the peel which changes the properties of pectin; washing removes sugar and colored and bitter constituents. Leached peel can be used directly for pectin extraction or stored dry to provide for year-around operations. It can be dried by artificial heat or in the sun.

Common commercial practice employs a hot-acid extraction of pectin from citrus peel in a batch process. Vigorous stirring during the 1-hour extraction period causes disintegration of the peel. The liquor then requires screening or pressing and a filtration for clarification. The high viscosity of the dispersion must be reduced by maintenance of a fairly high temperature, which causes some degradation of the pectin. Methods for extraction designed to simplify the process and maintain high quality of pectin are being investigated at the Western Laboratory.

The liquor can be concentrated and sold as such, provided food-grade acids are used in the extraction, or it can be treated with alcohol or with calcium or aluminum salts to isolate the pectin. When precipitation is by a salt, the salt must be removed by washing with acidified alcohol. The pectin as finally obtained is dried and ground and sold by its ability to form a jelly with 65 percent soluble solids. In 1950 no standard for that grade had been established, but definite moves were under way to do so.

Pectin is purified by several precipitations in dilute alcohol or by formation of a precipitate with certain metal ions, which are later removed by means of acidified alcohol. Citrus pectin contains about 85 percent anhydrogalacturonic acid, about 5 percent methylene groups present as methyl ester, and smaller amounts of sugars such as arabinose, galactose, and rhamnose.

Citrus pectin has a relatively high molecular weight, ranging from 60,000 to 120,000, which partly accounts for its ability to form jellies, films, and fibers.

The use of pectin in jellies, marmalades, candies, and jams is generally well known, as is its use in pharmaceutical preparations for digestive disturbances. The more recent development of low-methoxyl pectin, which increases the usefulness of pectic substances, is of special interest.

Pectin, when treated with alkali, acid, or an enzyme called pectinesterase, contains free acid groups that will react with small amounts of calcium salts. No sugar or other solids are required in order to make a gel with low-methoxyl pectin.

A procedure for making low-methoxyl pectin, worked out at the Western Laboratory, comprises treatment of the cooled extraction liquor with ammonia to cause removal of part of the methoxyl groups from the pectin, and then precipitation of the altered pectin by addition of acid. The washed low-methoxyl pectin gel may then be partly neutralized, dried, and ground.

The uses of low-methoxyl pectin are many and varied. The usual type of milk pudding can be prepared by adding low-methoxyl pectin and sugar to milk, heating, and stirring until the pectin has dissolved. Flavoring can be added and the whole allowed to cool. This pudding is smooth and not pasty. The gelling agent in this case is the low-methoxyl pectin, which combines with the calcium ion in the milk.

A quick dessert for housewives, campers, and sportsmen can be prepared with low-methoxyl pectin. Milk powder, flavoring, and a combination of sugar and pectin are mixed, then vigorously stirred into cold water. In 5 minutes a fluffy pudding is ready for eating or for a pie filling.

Those who like a gelatin dessert, but do not care to eat gelatin or much sugar, can make low-solids gels from low-methoxyl pectin and a calcium salt, like calcium monohydrogen phosphate. The flavor may come from fruit juices or from synthetic flavors. Color and sugar or saccharin are added as desired.

Low-methoxyl pectin lightens dinner problems in another way. A fruit mix, like canned fruit cocktail, can be processed with this pectin and sugar to form a canned gelled salad or dessert. The Army used nearly 30 million cans of this dessert during the Second World War. Canned tomato aspic also is made possible by low-methoxyl pectin.

Sparkling, clear, bright films can be prepared with low-methoxyl pectin. The ability of the calcium to hold together the pectin molecules, like rivets fastening steel beams, makes this possible. Spraying sticky stuff, such as candied fruit, with, or dipping it into, a solution of sodium pectinate and then a solution of a calcium salt covers it with a gel of sodium calcium pectinate. The gel is rapidly dried, after which it is impervious to sugar and is relatively nonsticky. Candied fruit, when coated in this way, can be packaged mechanically instead of manually.

Salted oily nuts have always been a messy food item. Coating almonds or other nuts with pectinate containing a food dye and salt gives a clean, colorful, and tasty product. Other food flavors, such as smoked salt, cloves, or chocolate, could be incorporated in the film. Vitamins for health can be included. The possibilities for use of the film seem endless.

Fibers and films of certain salts of low-methoxyl pectin are easily prepared and are water-insoluble and fire-resistant. The cost of these materials may restrict their utilization to specialty purposes, but the attractive possibilities of their use in open-weave fabrics, decorative ribbons, and meat casings have not been explored.

Low-methoxyl pectin is now available from commercial concerns. Further investigation of its properties probably will lead to other new uses.

The conclusion might be reached that extraction of pectin destroys the feed value of the peel. The possibility exists, however, that the liquor from the blanching and washing operation can be concentrated to produce molasses, the peel from the extractor can be dried, and the ammonium sulfate solution from the peeling operation can be concentrated. By suitable mixing of the three components, a feed or soil conditioner could be obtained. Thus the peel would be utilized completely.

Research has converted citrus waste into new, valuable products. Practically all of it is used; hardly any goes down the sewer. Citrus molasses and dried citrus peel go into feeds; citrus essential oils and citric acid are used in foods; citrus pectin makes a jelly failure almost impossible, and has been altered for use in puddings and films. Grower, processor, and consumer have benefited. Further work is needed on uses of some of the byproducts, such as pectin and limonene, to develop new uses for citrus molasses or the press liquor from which it is made, and to improve present processing methods.

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PREPACKAGING fruits and vegetables at the farm shipping point offers obvious advantages in the reduction of shipping costs and in the utilization of wastes on the farm, but it cannot be widely recommended until certain problems are solved.

No package will improve the quality of its contents. All highly perishable commodities decline in quality after harvest. The best handling methods only slow down the rate of decline. Studies made since 1948 by the Department of Agriculture in cooperation with the Dickman Farms, Ruskin, Fla., highlight the importance of adequate refrigeration at every step along the way from the time a product is harvested until it is sold to the consumer.

For example, packaged broccoli retained a good green color for 15 to 20 days when held at 40° F. or below, but turned yellow in 2 or 3 days at 70°. Sweet corn lost sugar at the rates of 3.5 percent at 32°, 20.8 percent at 50°, and 59.4 percent at 86° during the first 24 hours after picking. Prepackaged sweet corn delivered in New York at temperatures in the 40's was graded as good to very good in quality but that delivered at temperatures above 50° was inferior.

In tests so far, chemical treatments of various types appear to offer little benefit. Dips in ascorbic, citric, or hydrochloric acid did not prevent discoloration in corn and cauliflower. Instead, these solutions accumulated great numbers of micro-organisms.

Chlorine used in the hydrocooler water—where the vegetables were precooled immediately after harvest—did not completely sterilize the surfaces of the vegetables. It reduced the micro-organism count, however, and held it to a reasonable minimum. Approximately 100 parts per million of chlorine gave as satisfactory results as higher concentrations.

In general, the results show all packages should be perforated to allow for exchange of gas or air. Normal leaks through seams or poor seals do not provide sufficient ventilation to prevent fermentation. In turn, off-flavors and off-odors soon develop when the packaged vegetables are held at high temperatures.

Some products can be packaged more successfully near the terminal than at the distant farm market. For example, tomatoes need to be ripened to a marketable stage before they are packed. Otherwise they ripen unevenly and make an unattractive package. Also they may develop decay in the several days required to put them into retail channels.

For continuous growth of the prepackaging industry, marketing facilities must keep pace. At present, most wholesalers and retail stores lack refrigeration facility to handle adequately a line of prepackaged produce.—*Harold A. Schomer, Bureau of Plant Industry, Soils, and Agricultural Engineering.*