Dow
Liquid Separations

DOWEX
Ion Exchange Resins

Juice Enhancement by Ion Exchange and Adsorbent Technologies

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Applications

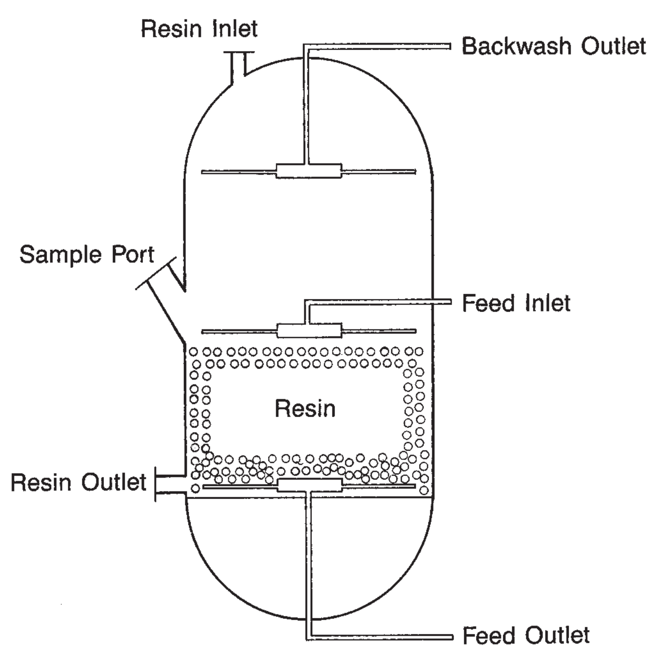
The basic purification processes used in treating juices involve either adsorbing impurities or exchanging less desirable ions for more desirable ions. Both processes use a solid matrix to accomplish their respective task. In the case of ion exchange resins, these materials can not only exchange ions but they can also function as adsorbents. Typically, these purifications occur in a batch-wise manner. The method of contact between the adsorbent and the juice is either in a stirred tank or in a fixed bed column. Usually a stirred tank process is reserved for powdered activated carbon. Fixed bed column processes are normally used for ion exchange and polymeric resins.

A stirred tank adsorption is carried out by mixing the juice with the appropriate amount of powdered carbon for approximately one hour. the juice/carbon slurry is then pumped through a filtration device, typically a plate and frame pressure filter, to separate the spent carbon from the juice. The spent carbon along with the filter aid, typically diatomaceous earth, are subsequently discarded.

A fixed bed column (figure 1) is predominantly used with the granular or spherical polymeric adsorbents and ion exchange resins. This design usually passes the juice and the chemical regenerants down through the packed bed of material. In this way, the maximum capacity of the material is utilized prior to regeneration. An advantage of this system over the stirred tank process is that the fixed bed system lends itself to complete automation, whereas the stirred tank process is labor intensive. Another advantage of the polymeric materials is that the adsorbed species can potentially be recovered for future use.

The main purpose of purifying most fruit juices is to take advantage of their naturally high sugar content. Most fruit juices contain approximately 10 to 15% sugars in varying proportions of sucrose, glucose and fructose depending upon the type of fruit. The juice processing plant, in purifying a portion of their juice, can take advantage of this sugar source by using it as a substitute for purchased sugar in their canning and bottling lines. Purified fruit juices are also used in various juice-added soft drinks. The common purification processes include decolorization, deflavorization and demineralization. Deacidification and discrete organic removal are also practiced in selected industries. The predominant juices use for blending purposes are derived from bland fruits such as: white grapes, pears and apples. Pineapple mill juice has been purified and used as a canning syrup since 1947[2]. Reduced acid frozen concentrated orange juice has been commercially available in the U.S. for over five years. Debittered orange juice is an example of the latest commercial improvement in fruit juices.

Figure 1



Grape Juice is a bland, slightly colored, fruit juice. Grape juice, like other fruit juices, typically contains approximately 10% carbohydrates. Due to these physical characteristics of low taste and color, a purified grape juice is often used as a substitute for other sugars (cane and beet). White grape juice is typically processed using adsorbents and ion exchange resins. The adsorbent materials are used to remove any residual color and flavor from the juice, whereas ion exchange resins are used to remove the ionic constituents and nitrogenous species.

In Italy, when the sugar content of the grape must is not sufficient to yield a high quality wine, purified grape juice is added to the must prior to fermentation. This gives the must the additional carbohydrates necessary to yield a high quality wine without disturbing the delicate flavor and color balance of the wine. In the United States, purified grape juice is used as a blending stock for various fruit drinks, carbonated beverages, and wine supplements.

Figure 2

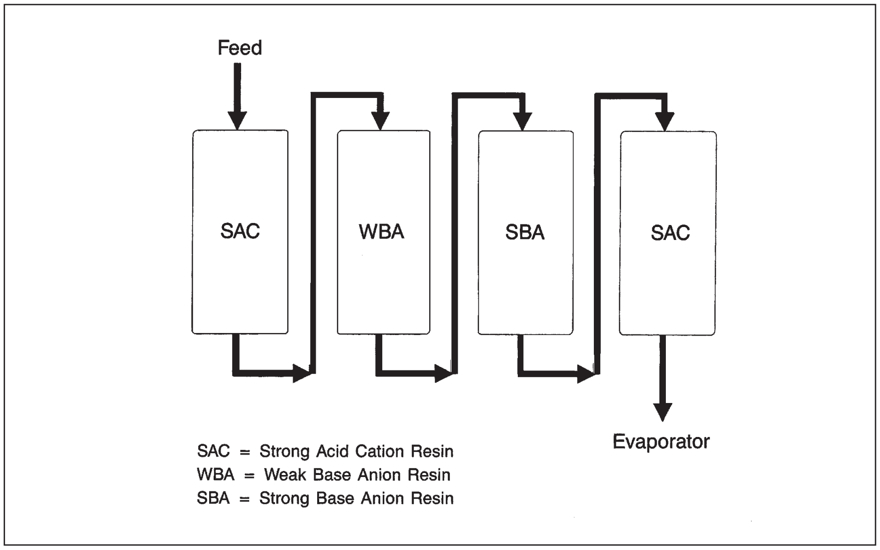
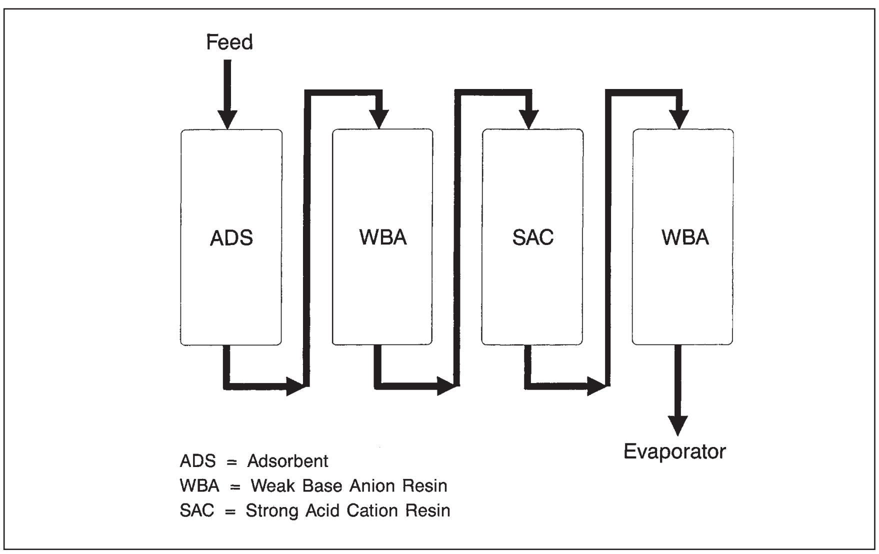


Figure 3



The processing scheme in Italy is outlined in figure 2. The strong acid cation resins are in the H^+ form during juice treatment. The weak base anion resin is in the free base form for treatment. The secondary anion resin is a macroporous strong base resin used in the chloride (Cl^-) form. The lead strong acid cation resin exchanges H^+ ions for the K^+, Ca^{++} and Mg^{++} ions found in the juice. The weak base anion resin removes the free acidity and some color bodies from the juice. The grape juice is now relatively mineral free. The strong acid cation resin picks up any nitrogenous materials which have leaked through the other resins. The decolorized and demineralized grape juice is then sent to an evaporator for concentration. The resultant juice is now suitable for blending into a low sugar grape must for fermentation. Similar practices are carried out in the United States, where the final product is not only used for wine but also for blending stock in fruit juice drinks and carbonated juice beverages.

Apple and pear juice are also used as blending juice stocks for many of today's carbonated juice drinks. Upon extraction, apple and pear juice contain approximately 12% sugars (sucrose, glucose and fructose). Apple and pear juices also contain a class of color bodies, polyphenolics, which must be removed prior to their use. These color bodies are formed enzymatically upon extraction and with exposure to air. It is this same brown color that occurs when one cuts an apple and leaves it on the counter; within minutes the apple surface takes on a rather unpleasant brown hue.

These two juices are purified either by activated powdered carbon for color and flavor reduction or by polymeric adsorbents and ion exchange resins. As alluded to earlier, an activated powdered carbon system is composed of several stirred tanks and a pressure filter device. The juice is first depectinized using an enzyme. This removes most of the insoluble solids. The clarified juice is then blended with the appropriate amount of activated powdered carbon. After approximately one hour of contact time with the carbon, the juice/carbon mixture is passed through a pre-coat or pressure filter which with the aid of diatomaceous earth, removes the carbon from the juice. This process yields a bland, nitrogen reduced, decolorized juice suitable for blending with many of today's fruit-juice carbonated soft drinks.

Another means of accomplishing much the same thing as above is to use polymeric adsorbents and ion exchange resins. With the use of these materials, one can achieve a much purer source of carbohydrates than the carbon system mentioned above. The processor will also use less labor and have less solid waste with a polymer based system. A typical flow schematic is illustrated in figure 3. The lead macroporous adsorbent removes color bodies and color precursors. The first weak base anion resin removes the free acidity found in the juice along with other color bodies which leak through the adsorbent. The strong acid cation resin is used in the H^+ form to exchange with the K^+, Ca^{++} and Mg^{++} ions found in the juice. The cation resin also removes the nitrogenous compounds, which can be major contributors to off flavors and browning products. The final weak base resin removes any mineral acidity associated with the cation effluent. This resin also acts as a final color polisher. The final product is now suitable to be used either as a canning syrup or for blending.

Pineapple mill juice is the juice extracted from the waste trimmings during the canning operation. This juice contains roughly 10% sugars. The juice also contains relatively high amounts of citric acid and nitrogenous materials. As mentioned previously, the purification of pineapple wastes was developed in the mid-1940's. This process was also one of the first commercially successful food purifications using on exchange resin technology[4]. The basic process was developed by Dole and is illustrated in figure 4[2]. The primary objective in the process is to improve the quality of the sugar source so that it can be used as a canning syrup. The two strong acid cation beds remove the cationic species from the juice, namely the ash (K^+, Ca^{++}, Mg^{++}) and the nitrogenous materials. The weak base resins remove the subsequent acids from the cation effluent and, to some extent, decolorize the stream. The resultant mill juice is essentially devoid of mineral content and color. After evaporation, the syrup is suitable for canning purposes.

Reduced acid frozen concentrated orange juice is an example of specialized adsorption to meet customer needs. It has been recognized in the citrus industry that approximately 20% of the U.S. population does not drink citrus products due to the high acidity associated with them. Early efforts to remove the citric acid from citrus juices date back to the 1960's, where electrodialysis was tried on an experimental basis[3]. Other attempts were also attemped with little success. In the late 1970's, The Coco-Cola Company, Foods Division in Plymouth, Florida developed and later commercialized an acid reduction process utilizing a weak base anion resin. This process was approved by the F.D.A. and a standard of identity was given to this particular orange juice product. This product has been commercially available in the U.S. since 1991.

The basic flow schematic is illustrated in figure 5. The process can handle either freshly extracted, stabilized juice or concentrated juice which has been reconstituted back to 15° Brix[7]. The juice is then pumped downflow through the weak base anion resin where the resin

Figure 4

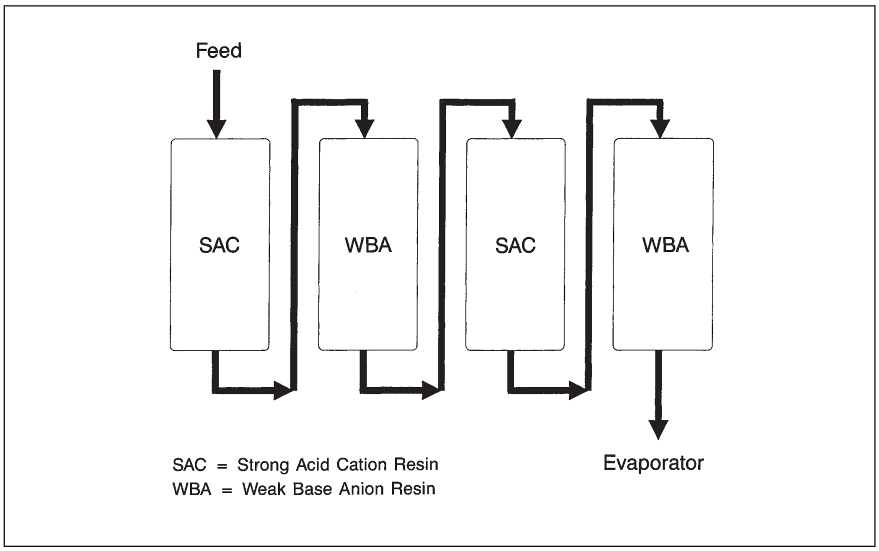


Figure 5

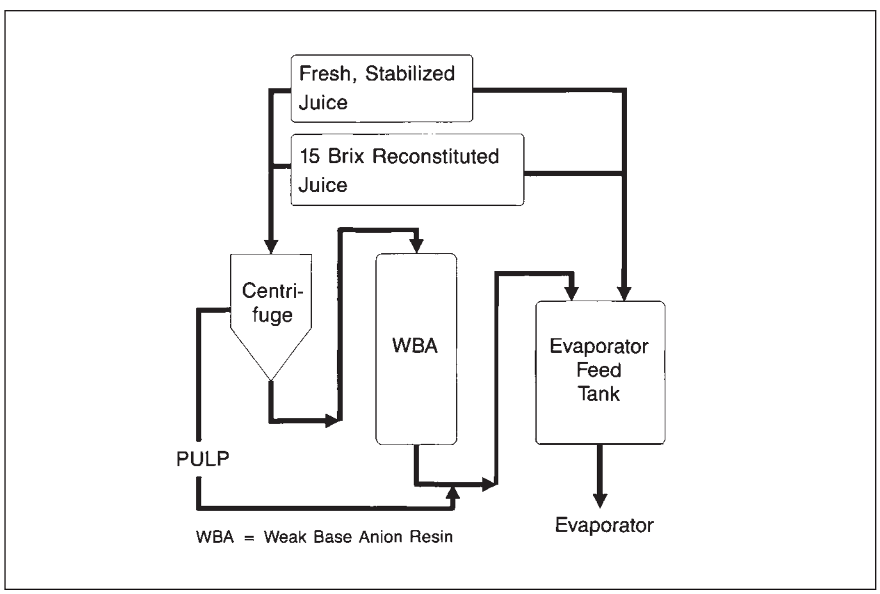
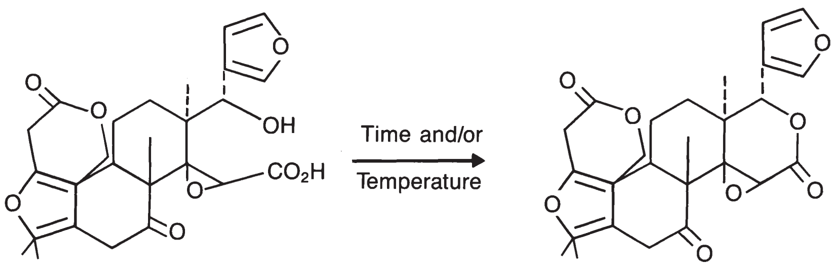


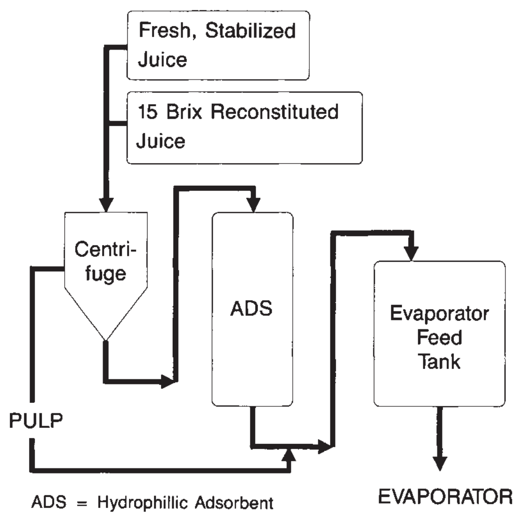
Figure 6



Limonoic Acid
α- Ring Lactone; Nonbitter

Limonin; Bitter

Figure 7



preferentially removes citric acid over the ascorbic acid and folic acid, vitamin C and vitamin E, respectively. It is important to process enough juice so that the pH of the effluent out of the weak base anion resin falls below 4.6. This insures that the ascorbic acid and the folic acid have been displaced off the resin by the stronger organic acid, citric acid[7]. After the resin column, the juice is pumped into a holding tank where the pulp from the centrifuge can be added back. At this stage, fresh, untreated juice or juice concentrate can be added to the deacidfied juice in order to maintain a uniform taste and flavor to the product. The resultant juice blend is then sent to an evaporator for concentration[7].

Debittered orange juice is another example of a highly specific adsorption utilizing a polymeric adsorbent. The navel orange is primarily grown as an eating orange. However, during the harvest approximately 20% of the fruits are culled due to skin blemishes and the like. These culled fruits are later sent to a processor to be turned into juice and juice byproducts. All oranges contain a chemical species called limonoic acid d-ring lactone in their phloem. The distribution of this lactone is related to the quantity of seeds in any particular variety as the seeds contain the largest concentration of this lactone[7]. Since navel oranges contain no seeds, there is a large preponderance of this lactone distributed throughout the various membrane structures in the navel fruit. Upon expression, this lactone esterifies to limonin (figure 6), which is highly bitter. The general population can taste limonin down to levels averaging 6 parts per million. Navel orange juice averages 20 to 30 parts per million[7]. Due to this intense bitterness, navel orange juice has historically been used as a blending juice where sufficient quantities of sugar can be added to the final product in order to mask the taste.

Various methods to debitter navel orange juice have been attempted since the early 1970’s. These methods include enzyme treatments, growth regulators, chemical masking and adsorbents. The use of a styrene/divinylbenzene polymeric adsorbent has been commercially practiced since the mid-1980’s in Australia. The first commercial plant in the U.S. was brought on line in 1988. A basic flow schematic for this process is similar to the one shown in figure 7. The one main exception is that there is no untreated juice blended in with the treated juice prior to evaporation. After the treated juice has been concentrated, it is now suitable for use in standard orange juice products.

10.5 Summary

As illustrated in the above examples, fruit juice purifications are quite diverse and serve the producer and the customer in a variety of different ways. From the purification of waste streams (pineapple mill juice), to the select adsorption of bitter compounds, the use of adsorpents and ion exchange technology make vital contributions to the juice and beverage industry. These techniques make fruit juice products and their respective beverage products quite palatable and available to the consumer at reasonable prices. Even though this technology is rather new to the food processing industry, the benefits derived from its use have given the producer and the consumer a much wider selection of fruit juice products.

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