

Designing Distillation Equipment For Volatile Fruit Aromas

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SUMMARY

In the essence recovery process developed at the Eastern Regional Research Laboratory for the production of full-flavor fruit juice concentrates, the processing equipment consists of a rapid atmospheric evaporator which strips the volatile aromas from the heat-sensitive fruit juices without damage, and a continuous-distillation column which rectifies the volatile flavoring compounds to 100 or 150 times their original concentration in the single-strength juice. The aroma-bearing distillate is later returned to the vacuum-concentrated juice to restore its natural flavor and aroma. Many commercial producers have been aware of serious losses of some of the significant flavor constituents, particularly in the processing of Concord grape juice. By the application of distillation theory, these losses can be attributed to an inefficient stripping section in the column. McCabe-Thiele diagrams are presented to show that an adequate column design requires not only a longer stripping section than has generally been employed but also, preferably, liquid feed to the column as well as a high vaporization rate at the reboiler.

INTRODUCTION

The essence recovery process for the production of full-flavor fruit and berry juice concentrates, developed from the original work by Milleville and Eskew (1944) and later modified by Claffey *et al.* (1958), has been used in commercial production for more than 10 years. New units are put onstream at the rate of one or two a year.

Fig. 1 is a flow sheet and a schematic drawing of the process. The feed juice, previously expressed from the fruit, in some cases depectinized and filtered, is first preheated and flash-vaporized. Usually, 8 to as much as 45% by weight of the juice is in the form of vapor at this point, and is separated from the stripped juice in a cyclone. The juice is further concentrated in a vacuum pan, while the aroma-laden vapors are rectified in the distillation column.

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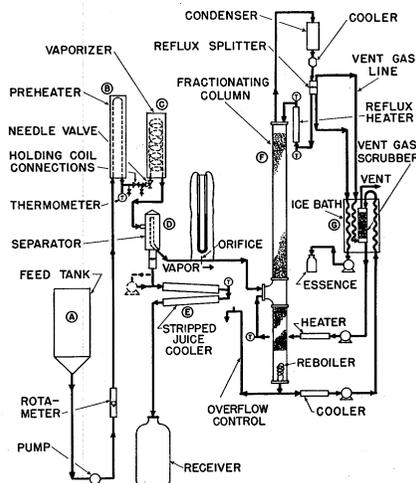


Fig. 1. Flow sheet and schematic drawing of the essence recovery process. Juice from Tank A is brought to boiling in Preheater B, then flash-boiled in Vaporizer C. Aroma-laden vapor passes to fractionating column E and is distilled to 150-fold essence. Noncondensable gases from column pass through chilled scrubber G before venting.

The column is characterized by a vapor feed, a rather long enriching section, and a very short stripping section. The first design (Milleville and Eskew, 1944) shows the vapors entering the reboiler with no stripping section, and the tower is simply an enriching column. Later designs show a progressively longer stripping section (Eskew *et al.*, 1950; Redfield and Eskew, 1953; Claffey *et al.*, 1958) on the column, but all show vapor feed to the tower.

These designs were developed purely empirically because of the complexity of the natural fruit aromas and because of the lack of fundamental vapor-liquid equilibrium data for the various aroma constituents.

DISCUSSION

Nature of volatile fruit constituents. Volatile fruit aromas and flavors, so far as is known, are virtually all organic compounds. Table 1 lists the

Table 1. Some volatile constituents of Concord grape juice.

Compound	Boiling point (°C, 1 atm.)	Solubility in water (g/100 ml)
Methyl anthranilate	266.5	0.70 @ 81°C
Ethyl acetate	77.1	8.6 @ 20°C
Methyl acetate	57.8	31.9 @ 20°C
Acetic acid	118.1	∞
Butyric acid	163.5	5.62 @ 1.1°C
Caproic acid	202	0.4
Glyoxylic acid	decomposes	very sl. soluble
Acetylmethyl carbinol	148	sl. soluble
Acetaldehyde	20.2	∞
Acetone	56.5	∞
Methanol	64.7	∞
Ethanol	78.4	∞

volatile flavoring compounds of Concord grape juice as reported by Holley *et al.* (1955), with the normal boiling point and solubility in water of each compound.

These compounds and all other known volatile flavoring compounds of apple, strawberry, raspberry, cherry, peach, pineapple, pear, and banana juices as given by McGlumphy (1951), Bedoukian (1950), Katz (1955), and White (1950) can be classified according to their boiling points and their solubility in water.

Concord grape essence as listed in Table 1 is quite typical of all fruit essences in this respect, and because we have some knowledge of its consti-

Table 2. Classification of volatile fruit flavor constituents.

Group	Boiling point	Solubility	Compounds
I	Lower than water	Complete miscibility	Ethanol, methanol, acetaldehyde, acetone, methyl ethyl ketone, etc.
II	Lower than water	Limited solubility	Ethyl acetate, methyl acetate, ethyl formate, ethyl propionate, diacetyl, <i>n</i> -butylaldehyde, formic ester, iso-butylaldehyde, hexene
III	Higher than water	Complete miscibility	Acetic acid
IV	Higher than water	Limited solubility	methyl anthranilate, butyric acid, caproic acid, acetylmethyl carbinol, <i>n</i> -butanol, isobutanol, 1-butanol 2 methyl, <i>n</i> -hexanol, caproic aldehyde, 2-hexenal, furfural, ethyl butyrate, ethyl caproate, <i>n</i> -caproic acid, cinnamic acid, amyl aldehyde, benzoic esters, hydro-cinnamic acid, benzaldehyde, menthone, benzyl alcohol, menthol, geraniol, geranyl butyrate, linalyl formate, linalyl acetate, linalyl valerate, linalyl caprylate, ethyl iso-valerate

tents and very little of most of the other fruits, this discussion will be limited to Concord grape essence. However, each class of compounds present in grape essence is also present in all of the other fruit essences listed.

Table 2 is a partial list of compounds found in the essences of various fruits.

Group I, exemplified by lower aliphatic alcohols, ketones, and aldehydes, represents compounds completely miscible with water in all proportions and with a boiling point below 100°C. Group II, as represented by the aliphatic esters ethyl and methyl acetate, contains compounds whose boiling points are also less than that of water but which have a limited solubility in water. Group III, compounds with a boiling point above that of water and also completely miscible in water, is represented by acetic acid. Group IV compounds, including a large number of very-high-boiling esters such as methyl anthranilate, have limited solubility in water. Glyoxylic acid, which decomposes before reaching the boiling point, could represent a fifth group.

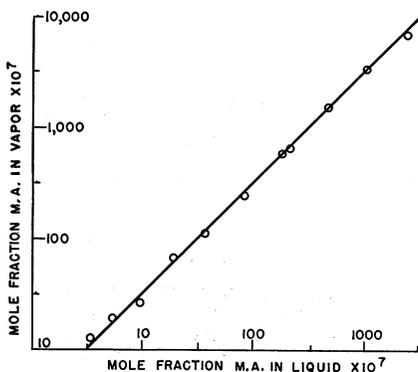


Fig. 2. Vapor-liquid equilibrium curve for low concentrations of methyl anthranilate in water.

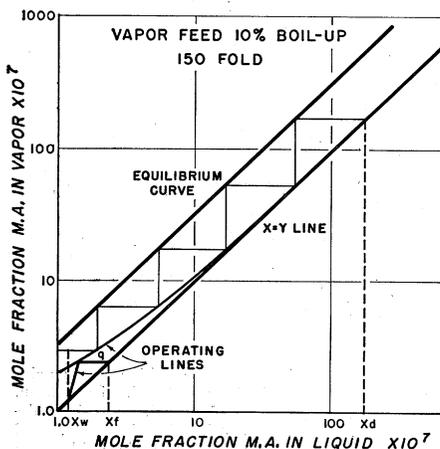


Fig. 3. McCabe-Thiele diagram of a typical run of Concord grape juice in pilot-plant essence-recovery unit. Coordinates show methyl anthranilate concentrations.

However, it has a limited solubility in water and therefore probably steam-distills. Thus it can be considered in group IV.

Of all the organic compounds reported in various fruit essences, every one (except acetic acid, in Group III) can be recovered in the overhead product of a distillation column. This fortunate circumstance, together with the fact that these compounds are all quite heat-stable, certainly accounts for the success achieved from the outset in essence recovery.

Compounds of the first group, the lower aliphatic alcohols, aldehydes, and ketones, are easily distilled and enriched because of their low boiling points. The compounds of Group II, such as the aliphatic acetates, are also probably easily recovered because of their low boiling points and because they have limited solubilities in water. The high boilers with limited solubilities in water, Group IV, compose by far the most numerous compounds of the fruit aromas and are found in many essential oils. These compounds are recovered in the overhead product of a distillation column because they form heterogeneous minimum boiling azeotropes which boil below 100°C at normal conditions. Their ease of separation by distillation can be determined only from vapor-liquid equilibrium data (Roger, 1961).

Column design. The rational design of distillation equipment requires vapor-liquid equilibrium data for virtually each constituent in a given essence. Except for methyl anthranilate (Fig. 2) (Roger, 1961) and acetic acid (Perry, 1950), these data, unfortunately, are not available. We will, however, study the design of a distillation column based on the recovery of methyl anthranilate in the distillate, remembering that it represents the group of compounds, found in most fruit aromas, which is probably the most difficult to rectify, and that it has been historically considered the characteristic constituent of Concord grape juice, although present knowledge proves this to be a great oversimplification of flavormatics.

Fig. 3 is a McCabe-Thiele diagram of a typical run of Concord grape juice in a pilot essence-recovery unit as shown schematically in Fig. 1. In this run, a 73° Brix concentrate was produced in a single pass by vaporizing 83% of the juice. The column was fed the vapors at the feed plate. An electrical heating coil supplied heat at the reboiler to provide a reboil rate of about 12% of the feed. Product was removed from the reflux splitter

at 155-fold, which means that one volume of essence was recovered for every 155 volumes of single-strength juice processed.

Note that the diagram in Fig. 3 is constructed on log-log paper rather than on the usual arithmetic paper. Because such low concentrations are involved, the log-log plot is more convenient (Brown *et al.*, 1950), considering that concentrations encountered are one ten-millionth mole and vary over a 200-fold range. The log-log plot is constructed in the same manner as an arithmetic plot. The equilibrium curve is shown here as a straight line (Roger, 1961). At these low concentrations the vapor-liquid equilibrium curve for methyl anthranilate and water follows Henry's law, which is a straight line with a 45° slope on log-log paper.

The $X = L$ line, normally a 45° line passing through the origin, is also a straight line here with a 45° slope, passing through points 1, 1; 10, 10; 100, 100; etc.

The q line is a horizontal line passing through the intersection of the feed composition line X_f and the $X = Y$ line. A horizontal q line represents a saturated vapor feed to the distillation tower.

The operating lines are curved lines on the log-log plot, and must be drawn from the over-all material-balance equation of the upper part of the tower above the feed plate and the lower part below the feed.

Table 3 gives the flow rates of each

Table 3. Column streams composition.

Stream	Total moles per hr	Mole fract. M.A.
Feed	2.60	2.37×10^{-7}
Overhead	0.016	1.74×10^{-7}
Bottoms	2.58	1.18×10^{-7}

stream in pound moles per hour and mole fraction of methyl anthranilate in each stream.

A material balance over the upper part or enriching section of the tower is written as:

$$V_n = L_{n+1} + D \quad [1]$$

A material balance over methyl anthranilate is then:

$$V_n Y_n = L_{n+1} X_{n+1} + D X_D \quad [2]$$

which is the equation for the enriching operating line.

Solving for Y_n we get:

$$Y_n = \frac{L_{n+1}}{V_n} X_{n+1} + \frac{D}{V_n} X_D \quad [3]$$

Below the feed we have for the stripping operating line:

$$\bar{V}_m Y_m = \bar{L}_{m+1} X_{m+1} - W X_w \quad [4]$$

$$Y_m = \frac{\bar{L}_{m+1}}{\bar{V}_m} X_{m+1} - \frac{W}{\bar{V}_m} X_w \quad [5]$$

With a boil-up of 12.3% of the feed we have the following vapor velocity, \bar{V} , rising up the column from the reboiler:

$$2.60 \times \frac{12.3}{100} = 0.32 \text{ moles/hr} = \bar{V}$$

With a vapor feed then, the vapor flowing *above* the feed plate, assuming an adiabatic tower, will be:

$$V = 0.32 + 2.60 = 2.92 \text{ moles/hr}$$

Similarly, since 0.016 mole is removed as product, the liquid reflux is given by:

$$L = V - D$$

$$L = 2.92 - 0.016 = 2.90 \text{ moles/hr}$$

Substituting in the above equation we have for the enriching line:

$$Y_n = \frac{2.90}{2.92} X_{n+1} + \frac{0.0161 \times 174 \times 10^{-7}}{2.92} \quad [6]$$

$$Y_n = 0.993 X_{n+1} + 0.959 \times 10^{-7} \quad [7]$$

This, then, is plotted by assigning values to X_{n+1} and solving the equation for Y_n , and connecting the points by a smooth curve. Similarly, the stripping line is given by the equation:

$$Y_m = \frac{2.90}{0.32} X_{m+1} - \frac{2.58}{0.32} (1.18 \times 10^{-7}) \quad [8]$$

and

$$Y_m = 9.06 X_{m+1} - 9.51 \times 10^{-7} \quad [9]$$

This is also plotted in Fig. 3, as the stripping operating line below the feed plate.

Stepping the plates off in the usual manner starting at the intersection of the X_D line and the $X = Y$ line, as is done in Fig. 3, gives the number of ideal plates required for the separation.

The slope of the enriching operating line, as seen in Eq. 7, is 0.993, practically unity. In other words, the upper part of the tower is operating very close to total reflux. In making a 150-fold essence, almost all of the vapor reaching the top of the tower is condensed and returned as reflux.

Eq. 9, the stripping operating line, has a slope of 9.06. As seen in Fig. 3, this is a very steep slope and allows no room for stepping off plates. This is because the reboiler is returning vapor equal to only 12% of the feed. To obtain effective stripping the slope of the operating line must be changed to approach unity as an ideal. Remembering that the slope is the ratio of the liquid flowing down the tower below the feed plate divided by the vapor rising in counterflow to it, and that the liquid rate is fixed by the desired essence-fold, a lower slope when using saturated vapor feed can be obtained only by increasing the reboil rate.

This typical run gave a methyl an-

thranilate recovery in the essence of 46%, while 49% was in the bottoms or waste stream. The remaining 5% was an unaccounted-for loss.

In designing distillation equipment, one must pick desired terminal conditions. In the following designs it was felt that a 90% methyl anthranilate recovery was not unreasonable. Also, realizing that more reboil vapors are necessary to improve stripping, designs shown below have various reboil rates to illustrate the effect of this variable on the stripping efficiency.

Fig. 4 shows such a design using vapor feed and a 25% reboil rate from the reboiler.

Here we see that the upper and lower operating lines intersect at a point above the vapor-liquid equilibrium line. This represents a theoretically impossible tower. It is analogous to operating a distillation column below the minimum reflux ratio, except that the column here is operating below the minimum reboil rate. It is impossible to obtain a 90% methyl anthranilate recovery under these conditions, no matter how long a stripping section is installed. This is why it is dangerous to assume that simply adding stripping length to the tower will improve its efficiency. Although a slight increase in efficiency could thus be achieved, it would still be impossible to attain the design condition of 90% recovery in the overheads.

Fig. 5 is a similar design, again with vapor feed and a recovery of 90% of the methyl anthranilate in the 150-fold essence; however, the reboil rate has been increased to 50% of the feed rate. This gives a very practical tower requiring 9 theoretical steps to achieve the design conditions. (Only part of the enriching section is shown.)

Although this is a good design with respect to terminal conditions, it would require 35-40% more steam than the column represented by Fig. 4. A further increase in reboil rate can be obtained by feeding the tower with liquid at its boiling point instead of vapor, and supplying all of the heat of vaporization at the reboiler. Using the same terminal conditions as before, Fig. 6 shows such a column design. Note that the q line is now a vertical line. This represents liquid feed entering the column at its boiling point. The effect, then, of a vertical q line is to expand the stripping section and to compress the enriching section. Although the previous designs required about the same number of theoretical steps, the liquid-feed tower makes for a more balanced design, requiring 4.6

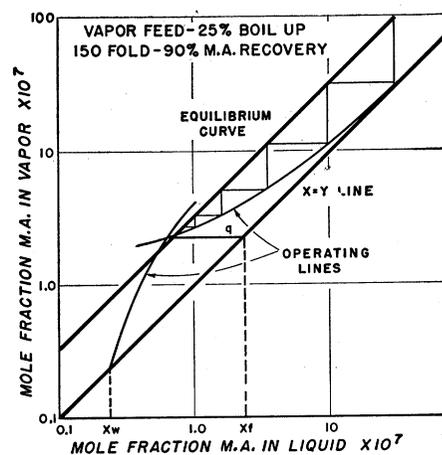


Fig. 4. McCabe-Thiele diagram for essence column design with 25% boil-up rate, vapor feed, and 90% recovery of methyl anthranilate in the overhead fraction.

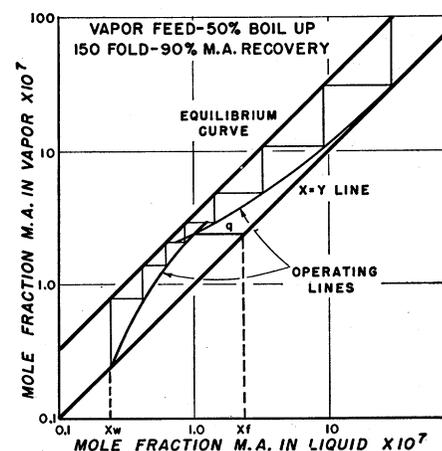


Fig. 5. McCabe-Thiele diagram for essence column design with 50% boil-up rate, vapor feed, and 90% recovery of methyl anthranilate in the overhead fraction.

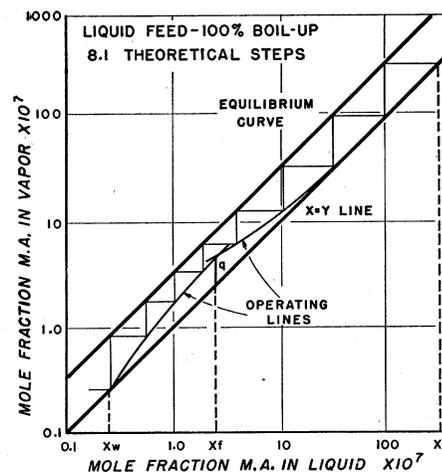


Fig. 6. McCabe-Thiele diagram for essence column design with 100% boil-up rate, liquid feed, and 90% recovery of methyl anthranilate in the overhead fraction.

theoretical steps in the enriching section and 3.5 in the stripping section.

These conclusions are in accord with generalizations given by Robinson and Gilliland (1939), particularly: "If the feed enters as a liquid and a small percentage of it is removed as distillate, the main task of the column is to strip all of the volatile constituents from the residue, which means the use of a large exhausting column."

Liquid feed to the tower under the conditions of essence recovery does pose some problems, since the flavors are removed from the juice as vapor. In the conventional designs it is of course the heat supplied to the preheater and vaporizer which in reality supplies most of the heat to the tower. For a liquid-feed tower, very little additional heat would be required in actual practice because the flavor-laden vapors could be condensed in the first effect of a multiple-effect evaporator to utilize their latent heat, while the condensate from these vapors was pumped to the feed plate of the tower. Steam normally supplied to the first-effect evaporator would instead be used in the column reboiler.

An even more economical method might be to use the flavor-laden vapors to supply heat at the reboiler and to pump the condensate into the tower as feed. The heat removed at the still condenser could be utilized in the first-effect evaporator. This would realize considerable steam saving, which is quite significant in seasonal food-processing operations. A saving in cooling water would also be effected.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental studies were conducted in the Engineering and Development Laboratory of the Eastern Utilization Research and Development Division, United States Department of Agriculture.

Fig. 7 shows the pilot-plant arrangement

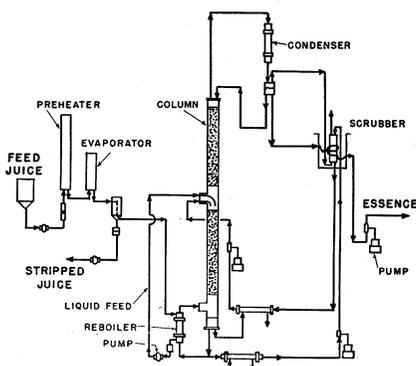


Fig. 7. Pilot-plant arrangement used to test-column design shown in Fig. 6.

ment used to test the column design shown in Fig. 6. The flavor-laden vapors are condensed in the column reboiler, and the condensate is pumped to the tower as liquid feed. The other essentials of an overhead condenser and scrubbing of noncondensable vent gas with column bottoms are as for previous designs.

Four runs were made using a 4-in.-inside-diameter glass tower packed with 1/4-in. Raschig rings as shown in Fig. 7. The stripping section was 42 in. and the enriching section 51 in. long. The tower was operated as close as possible to design conditions. However, liquid feed about doubles the flow of liquid in the stripping section of the column over vapor feed, causing flooding at a lower vapor mass velocity. This required the reduction of reboil rate, below design values.

Quick-frozen Concord grape juice of excellent quality, previously de-tartrated by settling at 28-30°F, was used for the tests. The results showed an increase in the recovery of methyl anthranilate in the overhead product and a reduction in its loss to the bottoms or waste stream. The data, although erratic, showed recoveries in the essence of 81-110% of the methyl anthranilate fed to the tower, with the average over 90%. Concentrations of methyl anthranilate in the essence ranged from 175 to 213 ppm, higher than any values previously achieved. The concentration in the column bottoms was significantly low, with values ranging from 6 to 20 parts in 100 million, averaging 11 parts. The average loss of methyl anthranilate to the waste stream was 3% of that fed to the tower. The uncertainty in the bottoms analysis, and the fact that the bottoms stream represents 98% of the total feed to the tower, cause wide variations in the over-all methyl anthranilate balance over the equipment. An average unaccounted-for loss of 6% over the system was noted.

These data certainly demonstrate that better recoveries of important flavoring constituents in fruit essences can be achieved by more careful column design. These results are well within the accuracy of engineering calculations particularly when considering that the equilibrium data used are based on the methyl anthranilate-water system rather than the actual system containing other solvents, and that less than the design reboil rate had to be used to prevent flooding the tower.

There is certainly a need for more vapor-liquid equilibrium studies of various fruit essences to provide basic

data necessary for rational design work. True, a separate column cannot be constructed to suit each individual fruit essence. However, sufficient generalities and similarities certainly exist among the various fruit essences to permit the design of a column that would be suitable for the most difficult conditions of the various fruits likely to be processed at a given plant.

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The authors express their thanks to Edward S. DellaMonica of the Eastern Regional Research Laboratory for conducting chemical analyses of volatile components in the various process streams.