

Fractional Distillation

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Fractional distillation of liquid mixtures has become an important chemical engineering unit operation, especially in the petroleum industry. It was thought wise, therefore, to develop an adequate description or explanation of this operation that could be easily understood, not only by students, but by technical men who were unfamiliar with the subject. A group of graduate students and the author discussed this question at considerable length and the following explanation is the result of these conferences.

It is a well known fact that if we have two liquids, *a* and *b* mixed together, *a* being more volatile than *b*, and if these liquids are boiled in a simple still, as indicated in Figure 1, the vapors coming from the boiling liquid will contain a greater proportion of *a* than did the liquid. It is natural to suppose that if there is a series of redistillations, there would eventually be obtained practically pure *a*, but a considerable proportion of *a* would be left behind in the various liquid residues. Fractional distillation is a method invented many years ago in which these separate distillations and condensations are combined in one unit so that the final result is a more or less complete separation of *a* and *b*.

A common type of fractionating column used for continuous fractional distillation of binary mixtures is indicated in Figure 2. This column is loosely filled with a solid material and affords a surface on which the liquid which passes down the column can come in contact with the vapors passing up the column. In an ideal apparatus, all heat extracted from the column is removed at the top, and all heat added enters at the bottom. No heat transfer is permitted through the sides of the column. The feed, at its boiling temperature, enters somewhere in the middle of the column at a point where the composition of the boiling liquid inside of the column is approximately the same as the composition of the feed.

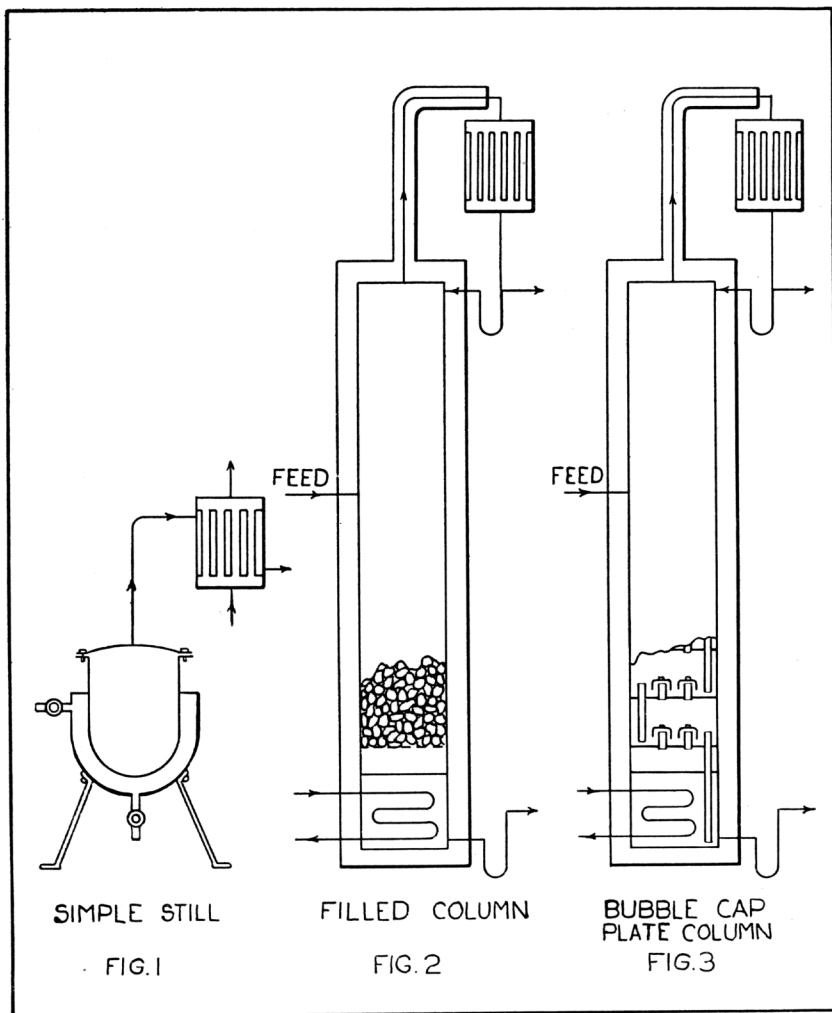
It can be stated that this apparatus is nothing more nor less than a counter-current scrubber or extractor in which there is a liquid, passing down the column, constantly growing richer in the less volatile component *b*, at the expense of the more volatile component *a*; while at the same time a vapor, passing up from the bottom of the column, is constantly increasing in its concentration of the more volatile component *a* at the expense of the less volatile component *b*.

It should not be implied that this "scrubbing" action depends on solubility. The column is, strictly speaking, a condensing and distilling apparatus. The extraction by the liquid of the less volatile component *b* from the vapor depends on condensation, and the removal by the vapor of the more volatile component *a* from the liquid depends on distillation.

The result of this counter-current distillation and condensation is a product at the top of the column consisting of a vapor which is largely *a*, the more volatile component, while at the bottom of the column the liquid withdrawn is largely *b*, the less volatile component.

The efficiency of this process of separation depends, first of all, upon the intimacy of contact between the vapor and the liquid, and this, in turn, depends to a certain extent upon the ratio of liquid coming down to vapor going up.

Of course there is a limit to this ratio, as it would be impractical to condense all of the vapors at the top of the column and return them as a condensate or reflux. The capacity of the column under these conditions



would be zero. In other words, there would be no product from the top of the column, and therefore no separation.

The amount of condensate formed at the top of the column, or the proportion of the vapor which is condensed at that point, is determined by the degree of fractionation desired. This, in turn, affects the capacity of the column.

The height of the column determines, to a certain extent, the time of contact between the vapors and liquid, and this affects the efficiency of fractionation. Therefore, the greater the height, the more efficient the fractionation. Maintaining the same degree of fractionation and increasing the height of the column will increase capacity, because less reflux is required at the top of the column.

The capacity of the column is also affected by its cross section or diameter, as this factor affects the time of contact between the vapor and the liquid. If a greater amount of product is desired, or a greater amount of feed required to be handled, naturally there should be greater cross-section within the column for this counter-current extraction.

The modern fractionating column has a much more complicated interior construction than the one described in Figure 2. The filled column previously described is not particularly efficient from the standpoint of furnishing adequate contact between liquid and vapors because there is a tendency for the liquid coming down the column to segregate near or on the walls, whereas the vapors going up the column have a tendency to pass up through the center, and therefore the two never meet. From a practical standpoint it is necessary to redistribute the liquid and vapor at various points in the column in order to obtain adequate contact. The modern fractionating column makes use of specially designed distributing plates, one above the other, whose function is to redistribute both the liquid and the vapor so that there is far more intimate contact between them. Such a column is indicated in Figure 3.

It follows that a column of this type can produce a greater contact between vapor and liquid within a given space or height. Such a column will effect the same degree of separation, and at the same time will not have the height of the less efficient column previously described.

The capacity of a column of given height can be increased by utilizing this modern design. The use of this more efficient design permits the return of less reflux condensate to the top of the column, while maintaining the same degree of separation. In other words, any modification of the column or its operation, giving a longer time of contact or a more intimate contact between the liquid going down and the vapor coming up, increases the efficiency of the column, but it is possible to increase the capacity and maintain the same efficiency under these new conditions by decreasing the amount of liquid condensed and returned to the top.

The above discussion has been based on a binary mixture. The same reasoning can be applied to a mixture containing more than two components. The fractional distillation of a complex mixture presents some interesting factors not involved in binary mixtures.

It is customary to take off at the top of the fractionating column, operating on a complex mixture, a "cut" composed of the more volatile constituents. If a simple distillation is made of the "cut," the last few drops will come over at a certain definite temperature. This temperature is commonly called the "end point" of the "cut." This specification does not indicate the degree of fractionation obtained in the specific column under the particular operating conditions. The "end point" shows that there is no higher boiling material present in this particular fraction, but it does not indicate how much of the more volatile material has been separated from the original mixture. Furthermore, if the material remaining after the "cut" has been taken off, were separately distilled, the initial boiling point might be considerably below the "end point" of the "cut."

Any skilled operator can adjust a very inefficient fractionating column so that the "overhead cut" has a specified and definite "end point."

In order to determine the degree of fractionation that has been realized in a column handling a complex mixture, it is necessary to determine the boiling point of the remaining liquid after various definite fractions—for example, 10%, 20%, etc.—have been taken off in a simple distillation of the "cut," or to determine the percentage that comes over in a simple distillation of the "cut" between various definite temperatures.