Feb. 14, 1956 A. L. JONES ET AL 2,734,633

THERMAL DIFFUSION METHOD

Filed June 24, 1952 2 Sheets-Sheet 1

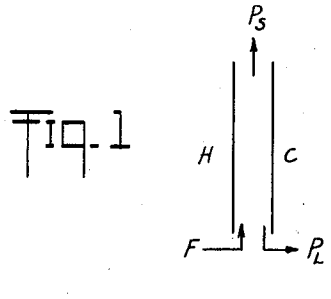


Fig. 1

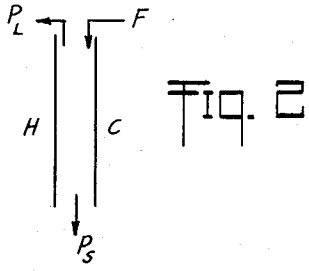


Fig. 2

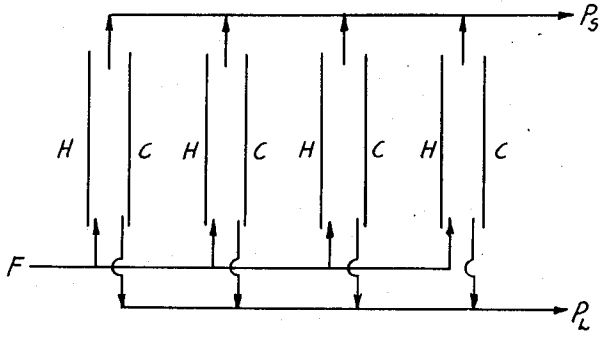


Fig. 3

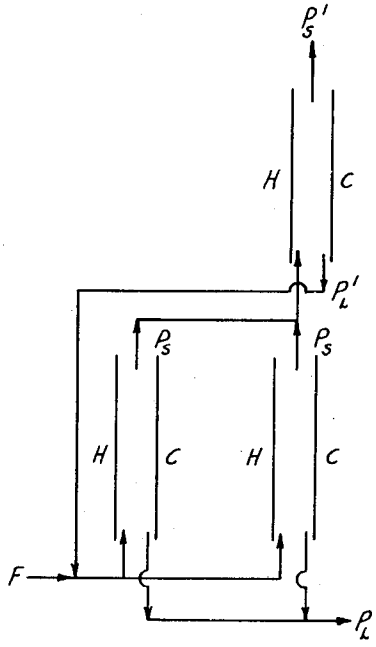


Fig. 4

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THERMAL DIFFUSION METHOD

Filed June 24, 1952 2 Sheets-Sheet 2

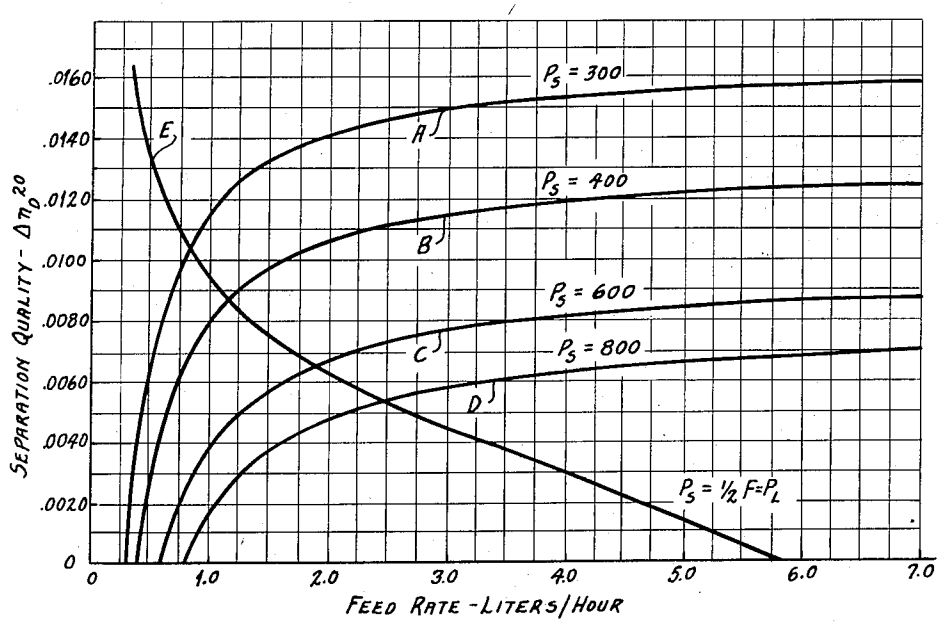
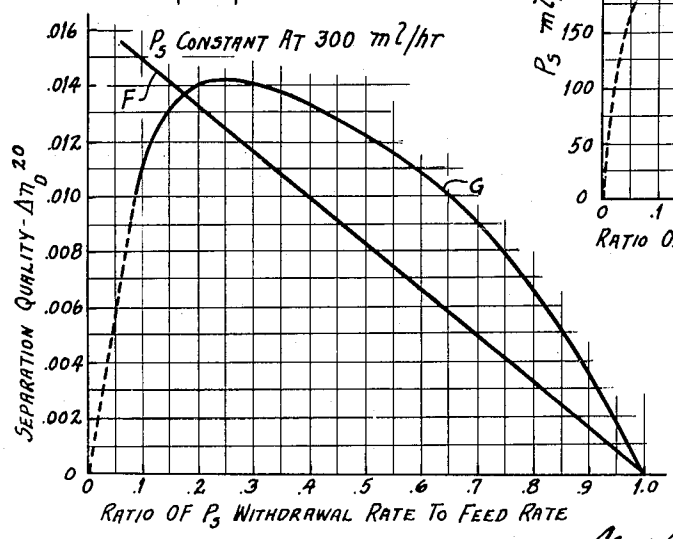


Fig. 9

Fig. 6



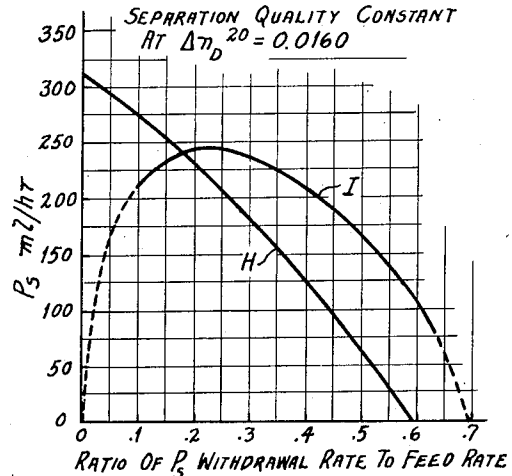


Fig. 7

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United States Patent Office 2,734,633 Patented Feb. 14, 1956

2,734,633

THERMAL DIFFUSION METHOD

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Application June 24, 1952, Serial No. 295,316

2 Claims. (Cl. 210—52.5)

This invention relates to a continuous method for separating materials by liquid thermal diffusion.

It has been known for some time that it is possible to separate by liquid thermal diffusion materials that are incapable of separation by any other known method or that are separated by other methods with great difficulty. It was at first believed that thermal diffusion of liquid could be carried out only in a discontinuous, i. e., batchwise, manner. More recently it has been discovered that it is possible to carry out liquid thermal diffusion in a continuous manner.

In essence the process of liquid thermal diffusion consists in subjecting a thin film of the liquid mixture, a term intended herein to include mixtures of liquids, liquid solutions and liquids containing highly dispersed materials, all liquid under the temperature conditions in a thermal diffusion column, to a temperature gradient across the film. This is usually accomplished by confining the liquid mixture in a vessel or column having two closely spaced parallel or concentric walls, one of which is maintained at a higher temperature than the other. In a more recently proposed method of continuous liquid thermal diffusion, the liquid mixture is continuously introduced into such a vessel or a column and dissimilar fractions enriched and impoverished, respectively, with one of the components in the liquid mixture are continuously withdrawn from remote ends thereof, the slit width, i. e., distance between opposed wall faces of the apparatus being extremely small, i. e., of the order of about 0.01 to about 0.15 inch and most preferably within the range of 0.02 to 0.06 inch, as suggested for example in U. S. Patents Nos. 2,541,069–71.

It has now been found that improved results can be obtained in the continuous separation of dissimilar materials in liquid mixtures by thermal diffusion by introducing the liquid mixture into one end of a thermal diffusion column, withdrawing a relatively small fraction at the opposite end of the column and withdrawing the balance at the feed end of the column.

The method of this invention is particularly efficient when the two dissimilar fractions withdrawn from the column are unequal and when the smaller fraction is withdrawn at the end remote from the feed end of the column. The method is, therefore, particularly applicable to processes for concentrating materials present in small amounts within relatively large quantities of parent material, e. g., the concentration of stigmasterol from soy bean oil, or the separation of a small amount of an odorous material from a fish oil.

In the accompanying drawing,

Figures 1 and 2 represent schematic illustrations of typical flow patterns;

Figure 3 represents the flow pattern of a typical installation wherein a number of thermal diffusion columns are used in parallel;

Figure 4 represents a flow pattern and installation designed to achieve maximum concentration of an extremely difficultly and inseparable material; and

Figures 5 to 7 are graphs illustrative of the results obtainable with the method of this invention as compared with those obtainable under comparable conditions in center feed methods.

In the drawing the symbols "H" and "C" represent hot and cold walls, respectively, the walls themselves being indicated schematically by a vertical line adjacent the symbols. The symbol "F" represents feed and the symbols "Ps" and "P_L" represent the small and large product withdrawals or fractions, respectively. The arrows indicate the direction of flow.

Referring now particularly to Figure 1, one preferred embodiment of the method of this invention is that of introducing the feed at the bottom of a thermal diffusion column and adjacent the hot wall thereof. A small fraction Ps is withdrawn at the top of the column and a large fraction P_L is withdrawn at the bottom but adjacent the cold wall.

It has been found in practice that the efficience, i. e., the product of the degree (as measured by the separation between F and Ps) and product (Ps) rate of separation, of a given column, such as is illustrated schematically in Figure 1, increases as the rate of feed increases while the rate of withdrawal of product Ps remains constant. While it is to be understood that the invention is not to be limited by any theoretical explanation offered herein, it is believed that this increase is due to the effect of thermal circulation within the column induced by the fact that one wall is relatively hot and the other is relatively cold. When the feed is introduced at the bottom and adjacent the hot wall at a rate below the rate of thermal circulation, i. e., the rate at which the liquid would circulate due solely to differences in density of the liquid adjacent the hot and cold walls induced by relative heating and cooling, some of the liquid descending adjacent the cold wall recirculates along with the feed, and consequently remixes with the feed, in order to maintain the thermal circulation within the column. As the feed rate is increased the amount of liquid that recirculates after descending along the cold wall decreases until a point is reached at which substantially all of the liquid descending adjacent the cold walls is removed as fraction P_L and substantially all of the feed introduced ascends toward the top of the column. Although it would appear reasonable to assume that further increases in rate of feed would result in no greater degree of separation at the top of the column, due to flow of excess feed directly to the withdrawal port for the fraction P_L, the surprising discovery has been made that feed rates above the rate of thermal circulation result in improved separation at the top of the column.

As the feed ascends adjacent the hot wall, it is subjected to thermal diffusion due to the temperature gradient to which it is subjected. The further it ascends the more one material in the liquid becomes concentrated in the ascending stream and the less concentrated it becomes in the descending stream adjacent the cold wall. When the ascending stream reaches the top of the column a portion thereof is withdrawn as fraction Ps.

While the method of this invention is feasible when fractions Ps and P_L are equal, its advantages over methods in which the feed is introduced intermediate the ends of the column become more and more apparent as the ratio of rate of withdrawal of fraction Ps to rate of feed is reduced. Ratios of withdrawal below about 1.5:10 are within the range in which the method of this invention has real advantages over methods hitherto proposed in which the feed is introduced intermediate the ends of the thermal diffusion column. Ratios below 1:10, particularly as low as about 1:100 are preferred.

It is to be understood, of course, that the fraction Ps may be enriched in either the material sought to be elim-

inated from the feed or the material that is to be concentrated therefrom.

Referring now to Figure 2, it will be noted that the flow pattern there illustrated is similar in principle to that of Figure 1 but more or less reversed. In this embodiment the feed is introduced at the top, the fraction Ps is removed at the bottom and the fraction P_L is withdrawn at the top.

The choice of flow pattern, as between those illustrated in Figures 1 and 2, depends upon whether the thermal diffusive force has the effect of concentrating the small amount of material sought to be extracted or removed adjacent the hot or cold wall. If it becomes concentrated adjacent the hot wall, the flow pattern of Figure 1 is utilized. If it becomes concentrated adjacent the cold wall, the flow pattern of Figure 2 is utilized.

In Figure 3, four columns, each having by way of example the flow pattern illustrated in Figure 1, are used in parallel. This is an efficient means of increasing the capacity of a continuous liquid thermal diffusion system such as that contemplated by the present invention. It is to be understood, of course, that any number of columns may be used in parallel and that the flow pattern in the columns may be similar to that shown in Figure 2 instead of Figure 1, or a combination of the flow patterns shown in Figures 1 and 2 may be used.

Figure 4 is a schematic illustration of the manner in which three columns utilizing the flow pattern of Figure 1 can be utilized in both parallel and series to obtain a high concentration of a material present in only small quantities in the initial feed liquid. In the embodiment illustrated, the feed is passed in parallel through two columns and the fractions Ps of the two columns are combined and then introduced into the third column to produce a fraction Ps and a fraction P_L, the latter being recycled, if desired, to the feed for further processing.

To illustrate quantitatively how the embodiment shown in Figure 4 would work, let it be assumed that 1000 units by volume of feed liquid are introduced as F. 500 units are introduced into each of the two lower columns and a fraction of 50 units is removed from the top of each of these columns as Ps. The 100 unit quantity of Ps is then introduced into the third column whereupon 10 units of fraction Ps' are obtained from the top of the column. 900 units of fraction P_L from the bottom of the first two columns are rejected or further processed and 90 units of the fraction P_L' from the third column are recycled to a feed for further processing in the system.

The utility and advantages of the method of this invention will become further apparent from the following discussion made with reference particularly to the graphs illustrated in Figures 5, 6 and 7 of the drawing.

Curves A, B, C and D in Figure 5 show the degree of separation obtainable, at various feed rates and withdrawal rates of the small fraction Ps by subjecting a lubricating petroleum oil stock having a viscosity of 300 SSU at 100° F. and an n_D^{20} of 1.5050, referred to by the trade name of #300 red oil, in a thermal diffusion column having a height of 20 feet, a slit width of 4.25×10^{-3} feet, a slit breadth of 0.288 foot, a hot wall temperature of 600° F. and a cold wall temperature of 150° F. The flow pattern utilized was similar to that illustrated schematically in Figure 1, the red oil being fed into the column at the bottom, the small fraction Ps being withdrawn from the top and the large fraction P_L being withdrawn from the bottom. The degree of separation obtained is expressed in terms of the difference between the indices of refraction of the top product Ps and the red oil fed into the column.

Curve A shows that the separation quality of Ps, the rate of withdrawal of Ps being maintained constant at 300 cc. per hour, increases rapidly with increase in the feed rate up to about 2 liters per hour and thereafter begins to increase less rapidly. At a feed rate of 3.0 liters per hour, i. e., when the ratio of withdrawal rate of Ps to feed rate is 1:10, the separation quality has increased to 0.0149.

Curves B, C and D illustrate similarly the manner in which the quality of separation increases when the rate of withdrawal of the small fraction Ps is maintained constant at 400, 600 and 800 cc. per hour, respectively, while the feed rate is increased to 7 liters per hour.

Curve E is included in Figure 5 to provide a comparison of the method of the invention illustrated by curves A, B, C and D with a method wherein the same red oil is fed into a thermal diffusion column having identical dimensions and temperature conditions except that the rate of withdrawal of the top and bottom fractions is maintained equal ($Ps=\frac{1}{2}F=P_L$) and the feed is introduced mid-way between the ends of the column.

It appears from Figure 5, that although the center-feed, equal withdrawal rate method gives better quality of separation at very low feed rates, the quality separation diminishes rapidly as the feed rate is increased, whereas with the method of the invention the quality of separation increases with increase in feed rate. It is evident, therefore, that the method of the invention is superior from the standpoint of producing relatively high quality of separation at increased rates.

It is also believed to be evident, upon analysis of the curves in Figure 5, that the separation quality expressed in terms of the difference between indices of refraction of Ps and the feed, at predetermined withdrawal rates of Ps obtainable in a column of given dimensions is considerably higher, particularly when the ratio of rate of withdrawal of Ps to feed rate is low. Thus, for example, it is apparent from curve A that when Ps is withdrawn at a rate of 300 cc. per hour and the feed rate is 3.0 liters per hour (a Ps to F ratio of 1:10 or 0.1) the separation quality is 0.0149 whereas the center-feed method, at a feed rate of 0.60 liter per hour, yields 300 cc. per hour of Ps with a separation quality of about 0.0122. When the Ps rate is 400 cc. per hour, it becomes apparent from curve B that with the method of the invention a 20-foot column will deliver Ps with a separation quality of 0.0124 at a feed rate of 7 liters per hour (a Ps to F ratio of 0.57:10 or 0.057) whereas the center-feed method, operated at a feed rate of 0.80 liter per hour, will deliver Ps with separation quality of about 0.0106.

Referring now to the graph illustrated in Figure 6, the ordinate is plotted in terms of Δn_D^{20} and the abscissa is plotted in terms of ratio of Ps withdrawal rate to feed rate. Curve F shows the separation quality of Ps obtainable with #300 red oil by the method of the invention utilizing the 20-ft. column described with reference to Figure 5, the dimensions and temperature conditions being identical and the Ps withdrawal rate being maintained constant at 300 cc. per hour. Curve G shows the separation quality obtainable with the center-feed method in a 20-foot column, the dimensions and temperature conditions likewise being identical to those described with reference to curve E of Figure 5 and the rate of withdrawal from the top of the column being likewise maintained at a constant of 300 cc. per hour. The curves of Figure 6 show that with ratios of Ps withdrawal rate to feed rate below about 0.15 the method of the invention yields superior separation qualities.

Curves H and I in the graph of Figure 7 provide a further comparison of the thermal diffusion method of the invention with the center-feed method, curve H representing the rates of withdrawal of the Ps fraction at various ratios of Ps withdrawal rate to feed rate, the separation quality being constant at 0.0160. Curve I shows the various Ps withdrawal rates likewise obtainable at a constant separation quality of 0.0160 with the center-feed method at various ratios of Ps withdrawal rate to feed rate. Comparison of the curves reveals that at ratios below about 0.17 the volume of Ps of a given quality is considerably higher with the method of the invention than with the center-feed method.

It is to be understood of course that, while results will vary considerably with different liquid mixtures and with different separating conditions, i. e., the dimensions of the thermal diffusion column and the temperatures of the hot and cold walls, the basic principles of the process illustrated by the foregoing disclosure made with reference particularly to the separation of #300 red oil, are applicable to the separation of other materials. It is to be specifically understood, therefore, that it is within the scope of the invention to subject to thermal diffusion materials other than #300 red oil and to vary considerably the temperature conditions, flow rates and apparatus dimensions.

We claim:

1. In a process for continuously separating, by thermal diffusion in a column defined by two walls spaced apart substantially uniformly between about 0.01 and about 0.15 inch, one of said walls being maintained at a temperature appreciably higher than the other, a liquid mixture into two fractions containing dissimilar materials that are normally liquid under the conditions of separation and which are included in a material normally liquid under the conditions of separation, the improvement which comprises subjecting said liquid to continuous thermal diffusion by continuously introducing said liquid at a rate above the rate of thermal circulation in the column into one end of the column, continuously removing from the other end of the column, a first liquid fraction containing a high concentration of one of the dissimilar materials that was contained in the initial liquid, and continuously removing from the feed end of the column a second liquid fraction containing a lesser concentration of said dissimilar material than was contained in the initial liquid, the ratio of the rate of removal of the first fraction to the rate of feed being less than about 1.5:10.

2. The improved method defined in claim 1 wherein the ratio of rate of withdrawal of the first fraction to the rate of feed is between about 1:10 and 1:100.

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