Oct. 23, 1956 E. N. MARSH 2,767,850

THERMAL DIFFUSION METHOD

Filed Dec. 18, 1953

Fig. 1

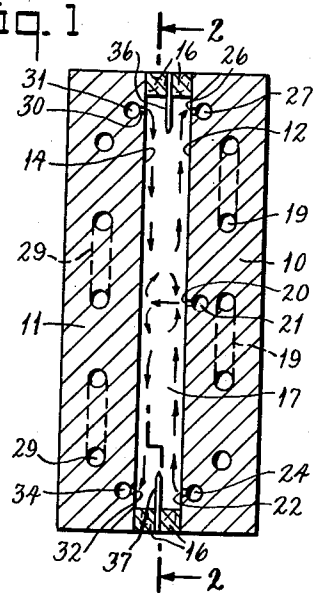


Fig. 2

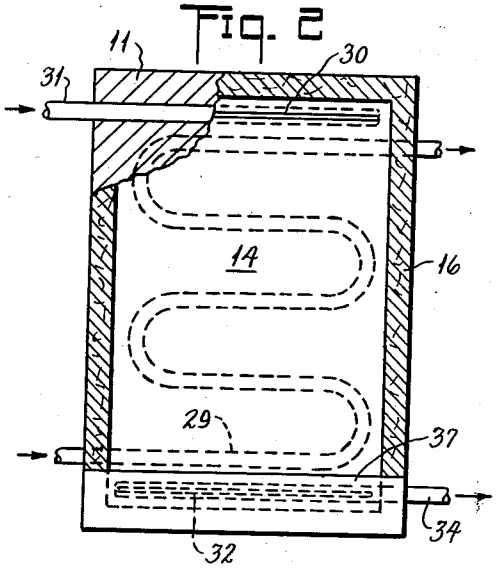


Fig. 3

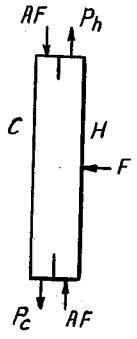


Fig. 4

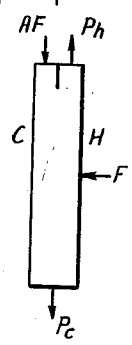


Fig. 5

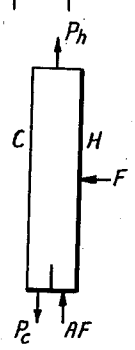
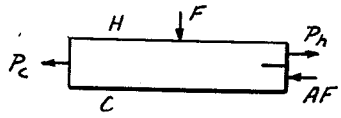


Fig. 6



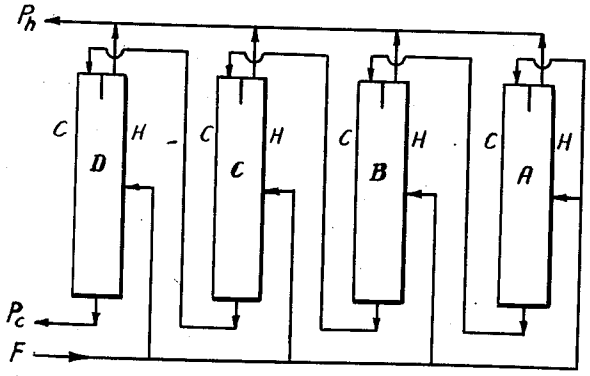


Fig. 7

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THERMAL DIFFUSION METHOD

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5 Claims. (Cl. 210—52.5)

This invention relates to an improved continuous liquid thermal diffusion method and apparatus and particularly to improvements in the flow patterns of thermal diffusion methods and apparatus of the types described in U. S. Patents 2,541,070 and 2,541,071 to Jones and Hughes and in U. S. Patent 2,521,112 to Beams.

The Jones and Hughes patents referred to above describe a continuous method for separating, by thermal diffusion, two fractions containing dissimilar materials that are normally liquid under the conditions of separation and which are included in a mixture that is normally liquid under the conditions of separation. The term "dissimilar components," as used in the Jones and Hughes patents and in the description of the present invention, is intended to refer to two or more components in or of a liquid or liquifiable mixture. These components may be dissolved in a common solvent, they may be liquid components of a mixture or one of the components may be a solvent and other the solute.

The method of the Jones and Hughes patents in essence involves continuously introducing a liquid mixture into apparatus comprising a substantially vertical and narrow separation chamber at a point intermediate the upper and lower ends thereof. The chamber is formed by smooth side walls, the opposed faces of which are closely and uniformly spaced apart. One of these walls is relatively heated and the other is relatively cooled to impose a temperature gradient across the separation chamber or slit formed by these walls and consequently also across the thin film or layer of liquid mixture in the chamber. As a result of the relative heating of the liquid immediately adjacent the "hot wall," a term used in a relative sense, and the relative cooling of the liquid immediately adjacent the "cold wall," a term likewise used in a relative sense, two phenomena take place. One of these is the well-known phenomenon of thermal circulation or convection which resolves the liquid in the chamber into two countercurrently moving fractions, one ascending adjacent the hot wall and the other descending adjacent the cold wall. The other phenomenon, not so well-known, is that of thermal diffusion whereby different amounts of energy of translation are imparted to dissimilar molecules in the mixture with the result that one type of molecule tends to accumulate adjacent the hot wall and the other tends to accumulate adjacent the cold wall. Consequently, the ascending fraction in the chamber becomes progressively more concentrated in one type of dissimilar molecule and the descending fraction becomes progressively more concentrated in the other type or impoverished in the first type of dissimilar molecules. Withdrawal of a portion of the ascending fraction from the top of the separation chamber and withdrawal of a portion of the descending fraction from the bottom of the separation chamber results in achieving significant separations of dissimilar components in the liquid mixture subjected to thermal diffusion.

In the Beams patent, it is likewise proposed to introduce the liquid mixture continuously into a thermal diffusion chamber at a point intermediate its ends. The separation chamber, however, is in a horizontal position and the upper wall is relatively heated, whereas the lower wall is relatively cooled. To supply a means for circulating the liquid in the chamber countercurrently, since this cannot be achieved thermally in a horizontal chamber, the patentee proposed to utilize an endless tape moving countercurrently through the chamber and thereby in effect dragging a fraction accumulating adjacent the upper hot wall toward one extremity of the chamber and a fraction accumulating adjacent the lower cold wall toward the opposite end of the chamber for separate removal.

It has now been determined that the methods and apparatus described in these patents have an inherent disadvantage in that the portion of a given fraction which reaches the end of a separation chamber but is not withdrawn is forced, by displacement, to reverse its direction of movement along the opposite chamber-forming wall surface. This displacement of the non-withdrawn portion of the fraction constitutes an inherent source of inefficiency in that further energy must be expended to move the component concentrated in that portion toward the first chamber-forming surface. Thus, for example, when a fraction that becomes progressively more concentrated in a given component as it descends along the cold wall of a vertical separation chamber is only partially withdrawn upon reaching the lower end of the chamber, the balance of the fraction must turn around and begin an ascent along the hot wall. In order to drive said given component in this turned around and ascending fraction back to the descending fraction adjacent the cold wall, a further amount of heat is required to impart the necessary additional kinetic energy of translation to the molecules thereof. Substantially the same is true when only part of the ascending stream adjacent the hot wall is withdrawn at the top of a vertical separation chamber or when only part of a fraction accumulating adjacent the hot or cold wall of a horizontal separation chamber of the Beams type is withdrawn at one end or the other.

The present invention is directed specifically to the problem of avoiding this inherent inefficiency in hitherto proposed vertical and horizontal countercurrent flow thermal diffusion methods.

In accordance with the method of the invention, the liquid mixture to be subjected to separation into liquid fractions containing dissimilar components is confined in a thermal diffusion separation chamber, subjected to a temperature gradient to separate the liquid mixture into two countercurrently moving fractions, one adjacent each of the opposed chamber-forming walls. At least one of the fractions is continuously withdrawn substantially completely from the outer end of the chamber toward which the fraction in question moves. Fresh liquid mixture is continuously introduced into the chamber at a location intermediate the outer ends and additional liquid mixture, which may be identical with the fresh liquid mixture or may contain the same dissimilar components in different concentrations, is introduced as auxiliary feed into the end or ends of the chamber from which a fraction or fractions is or are substantially completely withdrawn without substantially diluting said fraction or fractions.

The apparatus of the present invention in essence comprises at least two smooth, substantially parallel walls having surfaces closely spaced apart to form at least one thermal diffusion separation chamber, means for relatively heating and cooling the opposed wall surfaces, an inlet for the chamber remote from at least one of the ends of the chamber, an outlet at each end of the chamber, an auxiliary inlet at at least one of the ends of the chamber, and means for avoiding substantial intermixing, at one or both ends of the chamber, between liquid

introduced through the auxiliary inlet or inlets and the fraction or fractions withdrawn through the outlet or outlets of the same end or ends of the chamber.

It is apparent from the foregoing that a number of flow patterns and structures are contemplated in the method and apparatus, respectively of the present invention. Thus, for example, the countercurrent movement of the fractions separated within the chamber by thermal diffusion, and the chamber itself, may be vertical or horizontal. When the flow pattern and the apparatus are vertical, thermal circulation is ordinarily sufficient to impart the desired countercurrent movement to the dissimilar fractions. If the flow pattern and apparatus are horizontal, in which case thermal circulation is not a factor, the desired countercurrent movement of the separated fractions must be promoted by other means such as the moving tape means proposed in the Beams patent. Where the flow pattern is vertical, the fresh liquid is introduced at a location intermediate the upper and lower ends of the chamber, preferably at about the midpoint thereof, and (*a*) substantially the entire ascending fraction may be withdrawn from the top, in which case additional liquid mixture will be introduced at the upper end of the chamber through an auxiliary inlet without substantially diluting the ascending fraction, (*b*) substantially the entire descending fraction may be withdrawn at the lower end of the chamber, in which case an additional amount of liquid mixture will be introduced through an auxiliary inlet at the lower end of the chamber without substantially diluting the descending fraction, or (*c*) both the ascending and descending fractions will be substantially completely withdrawn at the upper and lower ends, respectively, of the column, in which case additional liquid mixture will be introduced through auxiliary inlets at the upper and lower ends of the column without substantially diluting the ascending and descending fractions, respectively. While the various flow patterns within the scope of the invention have been described with reference to a vertical separation chamber, it is to be understood of course that the same flow patterns are possible in a horizontal separation chamber in which the upper wall is the hot wall and the lower wall is the cold wall.

The apparatus of the invention may be modified depending upon the particular flow pattern desired. Thus, for example, where it is desired to withdraw substantially the entire ascending fraction in a vertical separation chamber and to introduce additional liquid mixture through an auxiliary inlet at the upper end of the chamber, means such as a baffle or the like are provided at the upper end of the chamber between the outlet and the inlet to avoid substantial dilution of the ascending fraction by the entry of the liquid mixture. Similarly, if substantially the entire descending fraction is to be withdrawn at the lower end of the chamber, such means are provided between the outlet and the auxiliary inlet at the lower end. If both the ascending and descending fractions are to be substantially completely withdrawn, such barrier means are provided at both ends of the chamber. Similar modifications are contemplated for the various embodiments wherein the separation chamber is in the horizontal position.

In the preferred embodiment of the invention, liquid mixture is confined in a substantially vertical separation chamber because of the inherently greater simplicity of structures that do not require moving parts. The width of the separation chamber, i. e., the spacing between the hot and cold walls, should be no greater than about 0.15 inch and preferably between about 0.02 and 0.06 inch.

The primary advantage of the method and apparatus of the invention is in avoiding nullification of a substantial amount of the separation that takes place within a thermal diffusion chamber by displacing components concentrated adjacent the hot wall toward the cold wall and vice versa, and thereby increasing the inherent efficiency and yield without any corresponding increase in dimensions of the apparatus or in the amount of heat required.

This and other advantages, as well as the utility, of the invention will become apparent from the following detailed description made with reference to the accompanying drawing, wherein:

Figure 1 is a schematic cross-section through one embodiment of the apparatus of the invention;

Figure 2 is a schematic view in cross-section taken on section line 2—2 of Figure 1;

Figure 3 is a flow diagram schematically illustrating the flow pattern produced in the apparatus form shown in Figures 1 and 2;

Figures 4 to 6, inclusive, schematically illustrate other flow patterns within the scope of the invention; and

Figure 7 is a schematic illustration of a cascade type flow pattern involving the use of a number of thermal diffusion separation chambers, the flow pattern of each of which corresponds to that illustrated in Figure 4.

As shown in Figures 1 and 2, a typical form of the apparatus of the invention comprises two wall members 10 and 11 having smooth and substantially parallel surfaces 12 and 14 closely spaced by any suitable means such as a gasket 16 to form a thermal diffusion separation chamber 17. The wall member 10 is provided with a coil 19 for the passage of a heating medium, an inlet 20 and associated conduit 21, an auxiliary inlet 22 and associated conduit 24, and an outlet 26 and associated conduit 27. The wall member 11 is provided with a coil 29 for passage of a cooling medium therethrough or equivalent cooling means, and an inlet 30 and associated conduit 31, and an outlet 32 and associated conduit 34. Barriers or the like 36 and 37 are provided at the upper and lower ends of the chamber 17 between the opposed outlets and auxiliary inlets 26 and 30, on the one hand, and 22 and 32, on the other.

In Figures 3–7, the letters C and H designate hot and cold walls, respectively; P_c and P_h indicate the cold and hot wall fractions, respectively; and F and AF stand for feed of fresh liquid mixture and auxiliary feed of liquid mixture, respectively.

In operation, fresh liquid mixture is continuously introduced into the chamber 17 by way of conduit 21 and inlet 20 with the result that the central portion of the chamber 17 constitutes a mixing zone in which the proportions of the dissimilar components are substantially the same as the proportions thereof in the fresh liquid mixture. As the liquid moves away from the central mixing zone, it becomes resolved, by virtue of the temperature gradient imposed across it from the hot wall to the cold wall, into two fractions, one fraction being progressively more concentrated in a first dissimilar component of the liquid mixture and ascending adjacent the hot wall, and the other fraction being progressively more concentrated in a second dissimilar component, or progressively less concentrated in the first dissimilar component, and descending along the cold wall. When the ascending fraction reaches the upper end of the chamber 17, it is substantially completely withdrawn through outlet 26 and associated conduit 27. Similarly, when the fraction descending along the cold wall reaches the lower end of the chamber, it is substantially completely withdrawn through outlet 32 and associated conduit 34. Additional liquid mixture is introduced into the chamber 17 at the upper end by way of conduit 31 and auxiliary inlet 30 and at the lower end by way of conduit 24 and auxiliary inlet 22. The barrier or divider 36 is effective in avoiding substantial dilution of the ascending fraction withdrawn through outlet 26 by the liquid mixture introduced through auxiliary inlet 30 and the barrier or divider 37 is similarly effective in avoiding substantial dilution of the descending fraction withdrawn by way of outlet 32 by the additional liquid mixture introduced through the auxiliary inlet 22.

By removing the lower barrier or divider 37 and utiliz-

ing either or both the ports **22** and **32** as outlets for a portion of the descending fraction, the apparatus schematically illustrated in Figure 1 may readily be converted to produce the flow pattern schematically illustrated in Figure 4. In this embodiment, the fresh liquid mixture is introduced into the chamber **17** by way of inlet **20**, substantially the entire ascending fraction is continuously removed by way of outlet **26**, additional liquid mixture is introduced at the upper end by way of auxiliary inlet **30** without substantial intermixing of the ascending fraction due to the action of barrier or divider **36**, and a portion of the descending fraction is continuously withdrawn at the lower end of the chamber through ports **32** and **22** or both.

By eliminating the barrier or divider **36** of the apparatus illustrated schematically in Figures 1 and 2 and utilizing one or both the ports **26** and **30** as outlets for a portion of the ascending fraction, the apparatus may readily be converted to produce the flow pattern shown in Figure 5. In this modification, the fresh liquid mixture is introduced by way of inlet **20**, a portion of the ascending fraction is withdrawn at the upper end of the chamber **17** by way of ports **26** or **30** or both, substantially the entire descending fraction is withdrawn at the lower end of the chamber by way of outlet **32**, and additional liquid mixture is introduced at the lower end of the chamber by way of auxiliary inlet **22**, substantial dilution of the descending fraction by the auxiliary feed being avoided by the action of barrier or divider **37**.

Figure 6 illustrates schematically a flow pattern corresponding to that illustrated in Figure 4, turned on it side. This flow pattern is considered the equivalent, in a horizontal separation chamber of the Beams type, of the vertical flow pattern illustrated in Figure 4 and may readily be obtained by modifying the Beams type apparatus in a manner similar to that described with reference to Figures 1 and 2. It is to be understood, of course, that flow patterns corresponding to those shown in Figures 3 and 5 are likewise possible in the Beams type apparatus and come within the scope of the present invention.

While the liquid mixture introduced into the separation chamber by way of one or more auxiliary inlets may be identical with the fresh liquid mixture, it need not necessarily be identical in both composition and relative proportion of the dissimilar components. A flow pattern in which this is illustrated is shown in Figure 7 in which the letters, A, B, C and D designate four separation chambers similar to that illustrated in Figures 1 and 2, but modified as described to the flow pattern of Figure 4. The letters C and H are utilized to indicate cold and hot walls of the separation chambers, respectively; F indicates the feed of fresh liquid to be subjected to separation by thermal diffusion; P_h designates the hot wall fraction; and P_c designates the cold wall fraction. In thermal diffusion chamber A the primary feed of liquid mixture at the center of the chamber and the auxiliary feed at the upper end are identical. In chambers B, C and D, however, the auxiliary feed in each instance corresponds to the portion of the cold wall fraction removed from the lower end of the previous chamber in series. The cascade type of flow pattern illustrated in Figure 7 is particularly advantageous in instances in which the primary interest is in concentrating a component that tends to accumulate adjacent the cold wall of a thermal diffusion column. It is to be understood, of course, that if the primary interest is in concentrating a component that tends to accumulate adjacent the hot wall, a similar cascading type of flow pattern, wherein the flow pattern of each individual separation chamber is similar to that of Figure 5, will be more applicable.

A determination was made, for comparative purposes, of the results obtainable by subjecting a 50:50 mixture of cetane and monomethyl naphthalene to thermal diffusion, utilizing, on the one hand, the vertical flow pattern of Figure 4, and on the other hand, the continuous vertical countercurrent flow method heretofore proposed, i. e., with the auxiliary feed at the upper end of the column eliminated. All other conditions, such as the width, length and breadth of the chamber, and the temperature gradient, were the same. In run No. 2, the auxiliary feed was the same as the primary feed. The results of these comparisons are tabulated immediately below:

Table

Run No.	1	2
Primary Feed Rate, ml./hr.	1,800	1,800
Secondary Feed Rate, ml./hr.		900
Total Feed Rate, ml./hr.	1,800	2,700
Top Product Rate, ml./hr.	900	1,800
Percent, by volume, of Cetane in:		
Feed	50	50
Hot Wall Fraction	57.3	56.3
Separating Efficiency, percent	57.3	75.0

While the degree of separation of the cetane fraction removed from the upper end of the chamber is slightly reduced by the use of an auxiliary feed, it is important to note that the volume of the fraction withdrawn from the upper end of the chamber is doubled while the total feed rate is increased by a factor of only 1.5. This means that for the flow pattern of Figure 4, essentially the same concentration of components, in the fraction withdrawn from the upper end of the chamber, can be obtained with half the heat consumption. Since the cost of heat is the greaest operating cost in a thermal diffusion operation, the reduction in heat consumption represents a significant reduction in direct operating costs. Furthermore, it appears that the separating efficiency of run No. 2, illustrated schematically in the flow pattern of Figure 4, is 31% higher than that of the flow pattern in run No. 1, with which it was compared, the separating efficiency being defined as the ratio of the product of the volume of the hot wall fraction and the concentration of the desired component therein to the product of the volume of the feed and the concentration of the desired component in the feed.

It is to be expected that various modifications will readily occur to those skilled in the art upon reading this description. All such modifications are intended to come within the scope of the invention as defined in the accompanying claims.

I claim:

1. A method for continuously separating, by thermal diffusion, two fractions containing dissimilar components that are normally liquid under the conditions of separation and which are included in a mixture normally liquid under the conditions of separation, which comprises confining the liquid mixture in a uniformly narrow separation chamber having substantially smooth walls and two outer ends; imposing a temperature gradient across the liquid by maintaining one wall at a temperature higher than the temperature of the other wall, thereby concentrating one of said dissimilar components in the mixture in a first fraction adjacent one wall and another of said dissimilar components in a second fraction adjacent the other wall; moving said first and second fractions countercurrently and endwise within the chamber toward the outer ends thereof; continuously withdrawing the first fraction from one outer end of the chamber; continuously withdrawing the second fraction from the other outer end of the chamber; continuously introducing a first liquid mixture into one of the outer ends of the chamber without substantially diluting the fraction advancing toward said one of said outer ends; and continuously introducing a second liquid mixture into the chamber at a location intermediate said outer ends.

2. A method for continuously separating, by thermal diffusion, two fractions containing dissimilar components

that are normally liquid under the conditions of separation and which are included in a mixture normally liquid under the conditions of separation, which comprises confining the liquid mixture in a uniformly narrow and substantially vertical separation chamber having substantially vertical and smooth walls and an upper and a lower end; imposing a temperature gradient across the liquid by maintaining one wall at a temperature higher than the temperature of the other wall, thereby concentrating one of said dissimilar components in the mixture in a first fraction ascending adjacent the wall maintained at the higher temperature and another of said dissimilar components in a second fraction descending adjacent the other wall; continuously withdrawing the first fraction from the upper end of the chamber; continuously withdrawing the second fraction from the lower end of the chamber; continuously introducing a first liquid mixture into one of the upper and lower ends of the chamber without substantially diluting the fraction withdrawn from said one of said upper and lower ends; and continuously introducing a second liquid mixture into the chamber at a location intermediate said upper and lower ends.

3. A method for continuously separating, by thermal diffusion, two fractions containing dissimilar components that are normally liquid under the conditions of separation and which are included in a mixture normally liquid under the conditions of separation, which comprises confining the liquid mixture in a uniformly narrow and substantially vertical separation chamber having substantially vertical and smooth walls and an upper and a lower end; imposing a temperature gradient across the liquid by maintaining one wall at a temperature higher than the temperature of the other wall, thereby concentrating one of said dissimilar components in the mixture in a first fraction ascending adjacent the wall maintained at the higher temperature and another of said dissimilar components in a second fraction descending adjacent the other wall; continuously withdrawing the first fraction from the upper end of the chamber; continuously withdrawing the second fraction from the lower end of the chamber; continuously introducing a first liquid mixture into the upper end of the chamber without substantially diluting the first fraction; and continuously introducing a second liquid mixture into the chamber at a location intermediate the upper and lower ends.

4. A method for continuously separating, by thermal diffusion, two fractions containing dissimilar components that are normally liquid under the conditions of separation and which are included in a mixture normally liquid under the conditions of separation, which comprises confining the liquid mixture in a uniformly narrow and substantially vertical separation chamber having substantially vertical and smooth walls and an upper and a lower end; imposing a temperature gradient across the liquid by maintaining one wall at a temperature higher than the temperature of the other wall, thereby concentrating one of said dissimilar components in the mixture in a first fraction ascending adjacent the wall maintained at the higher temperature and another of said dissimilar components in a second fraction descending adjacent the other wall; continuously withdrawing the first fraction from the upper end of the chamber; continuously withdrawing the second fraction from the lower end of the chamber; continuously introducing a first liquid mixture into the upper end of the chamber without substantially diluting the first fraction; and continuously introducing a second liquid mixture into the chamber at a location intermediate the upper and lower ends.

5. A method for continuously separating, by thermal diffusion, two fractions containing dissimilar components that are normally liquid under the conditions of separation and which are included in a mixture normally liquid under the conditions of separation, which comprises confining the liquid mixture in a uniformly narrow and substantially vertical separation chamber having substantially vertical and smooth walls and an upper and a lower end; imposing a temperature gradient across the liquid by maintaining one wall at a temperature higher than the temperature of the other wall, thereby concentrating one of said dissimilar components in the mixture in a first fraction ascending adjacent the wall maintained at the higher temperature and another of said dissimilar components in a second fraction descending adjacent the other wall; continuously withdrawing the first fraction from the upper end of the chamber; continuously withdrawing the second fraction from the lower end of the chamber; continuously intorducing a first liquid mixture into the upper and lower ends of the chamber without substantially diluting the first and second fractions; and continuously introducing a second liquid mixture into the chamber at a location intermediate the upper and lower ends.

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