Dec. 31, 1935. S. C. CARNEY 2,026,019

RECTIFICATION PROCESS AND APPARATUS

Filed May 8, 1931 2 Sheets-Sheet 1

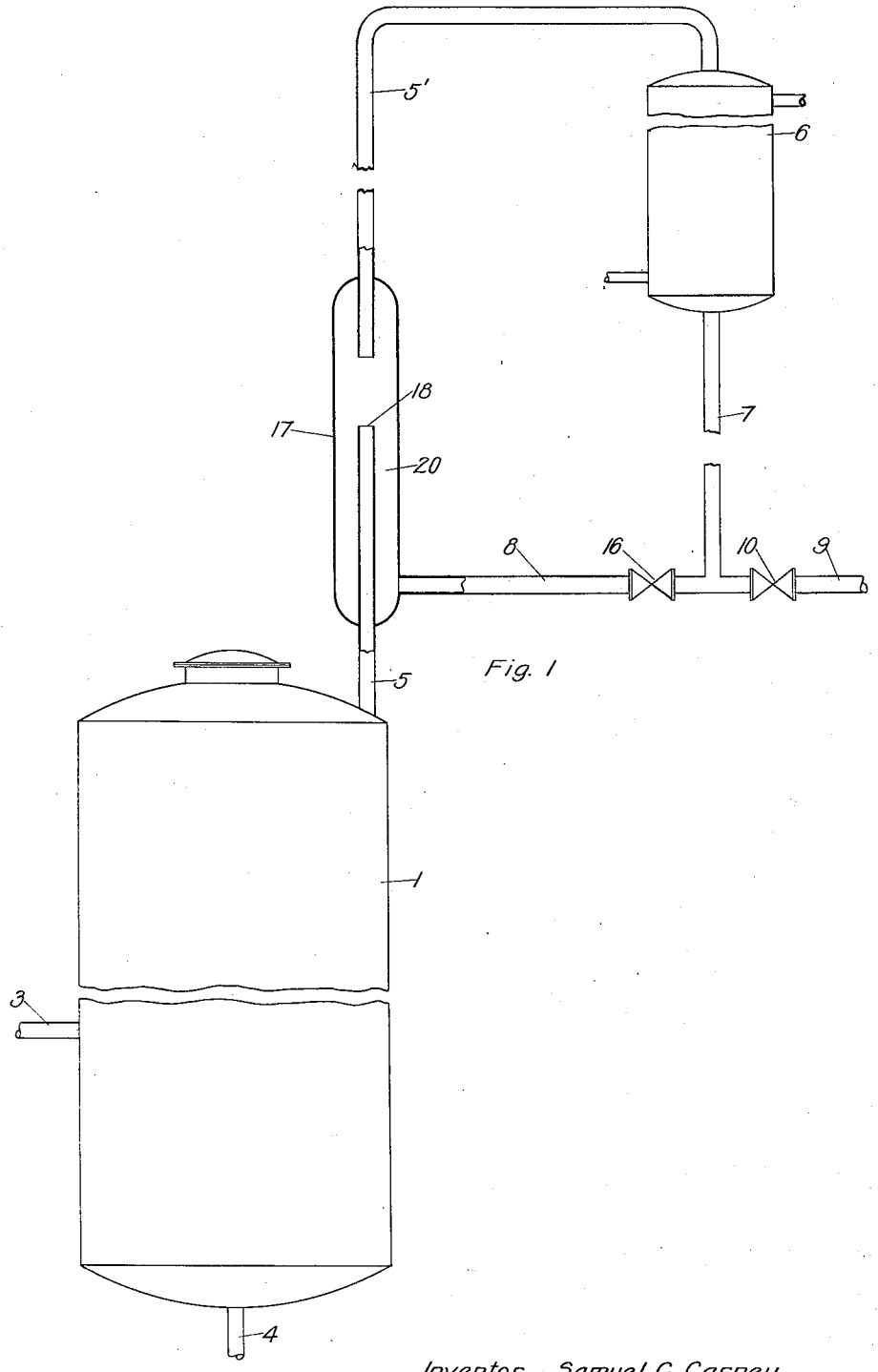


Fig. 1

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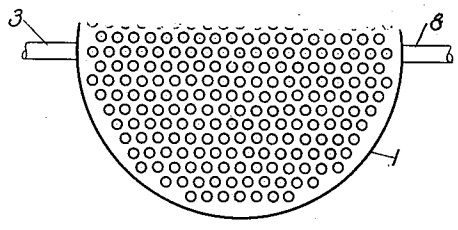


Fig. 3

Fig. 2

Fig. 3.

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2,026,019

RECTIFICATION PROCESS AND APPARATUS

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Application May 8, 1931, Serial No. 535,915

14 Claims. (Cl. 202—40)

This invention relates to the process of rectification and fractionation of liquids and vapors.

My invention consists more particularly in the maintenance of operating equilibrium during such process. By the application and use of my invention a more stable operation is obtained allowing a greater thruput than has heretofore been considered possible. It is understood that the appended claims are to be accorded the range and scope of equivalents consistent with the state of the prior art.

Conventional rectifying columns are usually equipped with a series of bubble trays and since with only minor differences, the pressure is uniform throughout the column, the differences in composition of liquid and vapor on various trays set up variations of temperature in a gradient of increasing temperatures from top to bottom of the column. Because of the unknown and constantly varying composition of the vapors and liquids in the lower parts of the column, the ultimate operating control of all practical rectifying columns is directed towards the control of temperature and pressure at the top of the column where the composition and properties of the desired top product are reasonably well known. The control of the temperature and pressure present difficulties that very seriously affect the efficiency of the column. In the following discussion some of these difficulties are briefly outlined and as a means of presenting a more concrete discussion of the matter the fractionation of a mixture of hydrocarbons will be considered. It will be assumed for the sake of the discussion that propane is the lightest fraction in the mixture and that the desired overhead product is to be pure propane. If through any variations of operating control a small amount of isobutane comes into the top part of the column, there is a rise in the temperature of the vapor first, but as this isobutane is condensed and mixes with the propane already there, there is a decline in pressure. Though the entrance of isobutane as an impurity into that region vital to operating control, may in theory be manifested either by a rise in temperature or a decline in pressure, in actual columns it is in fact chiefly manifested by a decline in pressure, with also some rise in temperature if a considerable amount of the impurity enters the top. This happens because a practical reflux condenser always has some excess capacity and a rise in temperature, by increasing the mean temperature difference in the condenser increases the rate at which heat is removed by the condenser.

Thus since the effect of entrance into the top of the column of an impurity is chiefly to reduce the pressure, this reduction in pressure starts increased boiling on the lower plates, increases vapor velocity throughout the column and thus facilitates entrance to the top of a greater amount of the impurity. Thus unless the tendency to form an impure top product is resisted by conscious act of the operator or the action of an automatic device which he has arranged, an imperfection in the operation does not tend to correct itself but tends to grow worse at least until the sensible heat stored in the material in the kettle and lower plates of the column which is released by the reduction of pressure (causing a sudden generation of vapor) is dissipated by the reflux condenser and the system reaches a new dynamic equilibrium at the lower pressure and correspondingly lower purity of top product.

The means used in the present art, either manual or automatic, to stop such a pressure decline and to bring the system back to a proper condition, are correct in tendency and consist in effect of stopping or reducing the rate of taking product until conditions are again normal. But neither a manual nor an automatic corrective can be applied until a certain change sufficient to be detected has occurred, and until a certain amount of heavier material has passed overhead thus contaminating the propane.

Operating a column to any precise condition in the present state of the art is therefore a matter of maintaining an unstable equilibrium which if disturbed tends to get worse. The equilibrium must be maintained by operating skill, since it is known that the most perfect rectifying system if operated with an entire lack of skill, will perform no separation at all.

The reflux condensate returned to the top of the column is always cooled substantially below its boiling point. This subcooling of the reflux results from the fact that the reflux condenser must have a cooling capacity in excess of that necessary to condense the average flow of vapor in order to handle greater amounts of vapor under varying conditions and to assure flexible operation. This continual flow of sub-cooled reflux to the top plate tends to cool the material thereon and further disturb its equilibrium. Thus for ideal operation the reflux liquid should be returned to the top plate at its boiling point which is impossible with the present column.

Temperature variations in a column are very difficult to control as temperature at any plate is a function of the composition of the liquid on

that plate, pressure remaining constant, and it is usually varied indirectly by varying the amount of heat supplied at the bottom of the column or the amount of heat removed at the top. If the condenser and upper plates of the column contain pure propane in both the liquid and vapor phase a slight decline in temperature or a slight admixture of butane will cause the vapor phase to disappear and the liquid level on the plate will build up. This produces the condition usually known in the art as "flooding". Liquid cannot leave the closed space above the plate through the sealed down pipe as there is no vapor to replace it and the column is temporarily inoperable. It sometimes takes a number of hours to relieve the conditions and get a flooded column in operation again. In usual rectification the complete disappearance of the vapor phase in the condenser rarely occurs due to the complexity of the vapor and to the fact that as condensation progresses the remaining lighter vapor will only condense with increased difficulty. However, this condition is capable of existing in varying degrees and due to the inherent instability of the process may develop so rapidly that the operator can often control it only after considerable effort and loss of time. When this unstable condition is induced due to internal variations of temperature and pressure, any overhead fraction will not be of sharp cut and will be of little value where a pure product is desired. The purity of the product at any given time will vary with the degree to which the unstable conditions have progressed and as these conditions are only indicated to the operator by his instruments or automatic controls after they are already under way, much damage can be done before the column can be brought back to correct operation. To guard against these variations and to protect the product, the conventional method is always to operate the column at a very low thruput. In this manner a greater degree of safety is maintained at the expense of output and cost of operation.

The usual way of attacking this problem has been to design instruments of increased accuracy and efficiency in detecting changes in operating conditions, so that they could more quickly be either automatically or manually corrected. These refinements in control have met with a certain amount of success but they are at best only corrective and do not operate until an undesirable condition already exists in the column. An ideal column would be one in which slight variations of operating conditions cannot affect the purity of the overhead product, and which will naturally tend to correct themselves rather than get worse.

I have discovered the principles on which such an ideal can be attained and have incorporated them as improvements and additions to the conventional column whereby its operation is made inherently stable. In so doing I have recognized the phase rule and the three dependent variables concerned in rectification, temperature, pressure and composition, and have designed my improved column to take advantage of the fact that when any one varies either of the others, or both, will also change to a compensating degree. The previous art has been concerned with relatively ineffective attempts in trying to fix either temperature or pressure as an operating control and then draw off an overhead of fixed composition. The principle of the present invention is in allowing the temperature and pressure to vary naturally and in compensating degree in maintaining an overhead product of fixed composition. In so doing the column works evenly and freely and without the danger of variations in composition of the product. It does not need the careful attention necessary to the conventional column nor does it require the high margin of operating safety; consequently its throughput is greatly increased.

I have also discovered that the proper place for effecting the inherent control and stability of the column is that point at which liquid of the precise composition of the top product being removed will at the existing temperature of that point, when in contact with the vapor, exert the existing pressure of the system. Since any working apparatus must have material in motion the ideal is the approach to a proper dynamic equilibrium as contrasted with the scientific ideal of a static equilibrium which the present art attempts to approach by providing intimate contact of liquid and vapor, and for exact and close separation, slowing down the rate of operation until conditions approach the static.

The drawings by way of illustration show a preferred example of an apparatus suitable for carrying out my invention. However, it will be understood that numerous other modifications and adaptations are possible within the scope of my invention and it is not limited to any specific construction.

Fig. 1 shows an elevation of a conventional rectifying column fitted with an apparatus embodying the elements of my invention shown in section.

Fig. 2 shows an elevation of a conventional rectifying column with a portion broken away showing a section of the top bubble plate and an additional plate above it illustrating another embodiment of my invention.

Fig. 3 is a horizontal sectional view taken on the line 3—3 of Fig. 2.

Referring to the drawings, like numbers representing like parts, the columns diagrammatically illustrated consist of the shell or container 1, which may contain a series of any conventional type of fractionating trays. 3 represents a feed inlet pipe, 4 a liquid draw-off line, 5 a vapor exit line and 6 a condenser of any suitable construction. Line 7 leaves the bottom of the condenser and passes to the T connection branching into lines 8 and 9. Line 9 passes to any suitable storage container (not shown) and is equipped with the valve 10. Any suitable heating element is installed at the base of the column.

Referring to Fig. 1 the enclosed chamber 20 is formed by jacket 17 which surrounds line 5 as it rises vertically from the column. Line 5 ends at 18 whereat it opens into the chamber 20. Line 5' opens into the top of chamber 20 and passes to the condenser 6. Line 8 controlled by valve 16 enters the bottom of the chamber.

The column illustrated by Figures 2 and 3 is equipped with a series of bubble plates such as the top one shown at 2. It is also equipped with the tray 11 above the highest bubble plate 2. Line 8 from the condenser enters the column at a point just above tray 11. Line 8 is controlled by valve 16. The circumference of tray 11 is fastened and sealed to the shell 1 in the same manner that another bubble plate might be added above plate 2. Tray 11 is drilled with small and equally spaced holes 12 and the vertical tubes 13 are sealed therein, thus forming a structure of

heat exchanger type, i. e. a structure possessing a relatively great heat exchange area.

In operating the apparatus illustrated in Fig. 1, which embodies the basic principles of my invention, say as mentioned above for recovering propane, the hydrocarbons are fed to the column thru line 3. As fractionation progresses on the various plates, the column is so adjusted that the top plate contains pure propane in both the liquid and vapor phase. The vapor from the column then passes out thru line 5, thru the chamber 20, and into the condenser 6, where condensation takes place. By proper manipulation of the valves 10 and 16 the condensed propane is passed down pipe 7 thru line 8 and into chamber 20. The condensate rises to the point 18 and then runs down the inside of line 5 countercurrent to the rising vapors. The valves 10 and 16 are now adjusted so as to maintain the necessary flow of liquid product as reflux to chamber 20, and the remaining propane is continuously drawn off thru pipe 9 to storage.

Any of the usual internal temperature and pressure variations during operation are automatically adjusted within the system without allowing contamination of the overhead product reaching the condenser. For instance whenever any fractions heavier than propane get into the liquid on the top plate, it will change the equilibrium thereon as propane can exist in two phases only under certain conditions of temperature and pressure and if either is disturbed, one of the phases will begin to disappear. The addition of butane or heavier fractions on the top plate will cause a lowering of the vapor pressure of the mixture and a condensation of vapor resulting in a decrease of pressure and increased boiling and flow of vapor from below bringing up more butane. The butane vapor is at a higher temperature and its heat on condensation and mingling with the propane has a tendency to make the latter boil. This effect however is offset by the lowering of the vapor pressure of the mixture due to the physical admixture of butane with propane thus causing the condensation. It is at this point that the advantages of my invention become apparent for without it butane vapors would begin passing overhead and would continue to do so until the operator was again able to bring the column back to normal operating conditions. When the butane reached the condenser, condensation and "flooding" would quite probably occur. This is prevented by my invention because the new vapor formed from the top plate will be at a higher temperature as it contains the higher boiling butane fractions. As this vapor enters the portion of line 5 in chamber 20 it will undergo a rapid heat exchange with the countercurrent flow of descending propane and also thru the tube walls with the propane in the chamber. The butane fractions will condense in the countercurrent flow of liquid and run back to the top plate and the heat liberated from the condensation will be absorbed in boiling propane around the tube in chamber 20. This evolution of propane vapor will tend to bring the pressure back to normal and stop the flow of butane from below to the top plates. The butane at first cannot mix with the propane in chamber 20 and consequently its heat effect of increasing vaporization is utilized, while its effect of reducing pressure cannot act. Any large variations of operating conditions can be counteracted by the operator's control and in the meantime the propane in chamber 20 is acting to maintain the correct pressure in the column thus assuring stable operation as the temperature varies. The reflux maintained in chamber 20 is inactive just as long as the column is functioning properly but when there occurs a temperature difference between the vapor rising in tube 5 and the boiling propane reflux in the chamber there immediately occurs an evolution of vapor from the reflux and the conditions which caused the temperature difference are relieved. The chamber reflux works inherently to the required degree to restore equilibrium because the hotter the rising vapors are, the more rapid the evolution of vapor in the chamber and the sooner normal conditions are restored. It does not, of course, maintain this equilibrium indefinitely and will never permit the removal as product of more propane than currently enters the column in the feed.

The modification of my invention illustrated in Figs. 2 and 3 operates according to the same principles above outlined. The propane vapor rising from plate 2 passes upward thru the tubes 13 which correspond to line 5 in chamber 20 of Fig. 1. The vapor leaving the tubes passes out of the column thru line 5 to the condenser 6 and a part of the liquid product is returned as reflux thru lines 7 and 8 to the chamber formed by tray 11 and the walls of the column. The reflux overflows down the insides of tubes 13 and falls to plate 2. The vapors rising from plate 2 thru the tubes 13 are cooled by the countercurrent flow of reflux and any heavier fractions of the vapor are condensed in the reflux and fall directly back to plate 2. The heat released by such condensation is absorbed as before by the propane in the chamber and produces an evolution of vapor from tray 11 proportionate to the amount of heavy material in the vapor, thus maintaining a stable equilibrium as before. The reflux on entering the chamber thru line 8 is somewhat subcooled and it is very quickly brought to its boiling point by heat exchange thru tubes 13 with the rising vapors, and on running down to plate 2 after overflowing from the chamber into the tubes will be at substantially the temperature of the liquid on the plate. Thus it cannot disturb the equilibrium of the liquid on the plate as is usual in the conventional column.

By maintaining a part of the product, in the described example propane, on tray 11 and, of course, supplementing its action by the operator's general control of the column, the advantages of the present invention are attained. During actual runs the temperature of the vapors ascending from plate 2 has varied as much as 20° F., with the corresponding inherent pressure variations supplied by the propane from tray 11 to maintain the purity of the overhead product. Such variations would be disastrous to the operation of the ordinary column. As the temperature rose heavier material would soon reach the condenser and an impure product would result with probably also flooding of the condenser. Flooding is prevented by my invention because heavy material is condensed and cannot reach the condenser. Because of this improvement the column can be run at all times to obtain nearly its maximum thruput which is a great advance over the present art of rectification and makes a great saving on the operating cost of such equipment possible. The thruput of my improved column can be, with perfect safety, about twice that of the conventional column.

Obviously many modifications of my invention are possible. In place of the tubes 13 it may,

under certain conditions, be more advantageous to use other types of heat exchanging surfaces. For instance a honeycomb construction could be used, or any other means would be applicable which prevented contact between the vapor and liquid until they had passed over a sufficient heat exchanging surface to condense any heavier fractions of the vapor and bring reflux liquid to its boiling point. Such surfaces must be chosen however as will not restrict the flow of vapor sufficiently to cause any marked pressure gradient on opposite sides thereof.

My invention can be operated solely in closed systems, whose pressure is that of the contained vapors, this operating pressure being that of the boiling liquid product when substantially in equilibrium with its own vapor; or, when the product is taken as a vapor, that of the boiling reflux when substantially in equilibrium with such vaporous product.

It is of course understood that the rectification of a hydrocarbon fraction has been discussed only as an illustrative example and not as a limitation as my process is of great value and readily adaptable to any rectification process producing any possible fractionation or separation of volatile liquids.

Many useful materials, such for instance as byproducts of numerous industries, which it has heretofore been impractical to recover due to the relatively high cost of the operation, can be obtained by the use of my invention on a commercial and profitable scale. The expression "indirect heat exchanging relationship" or its equivalent as used in the appended claims is defined as meaning a heat exchange thru a separating surface and without physical contact between the materials involved.

I claim as my invention:

1. An apparatus for rectification of liquids, comprising: a rectifying column and a reflux condenser in cooperation therewith, a special plate at the top of the column, a vapor space above said plate in a vapor flow communication with the condenser, means for returning reflux condensate from the condenser to said special plate, a heat exchanging means on said plate adapted to direct liquid overflowing the plate to the column and to conduct vapor from the space below to the space above the said plate in a heat exchange relationship with the reflux condensate thereon, in order to condense a portion of the ascending vapor, and to evaporate a portion of the reflux condensate.

2. An apparatus for rectification of liquids, comprising: a rectifying column and a reflux condenser in cooperation therewith, a special plate at the top of the column, a vapor space above said plate in vapor flow communication with the condenser, means for returning reflux condensate from the condenser to said special plate, and a heat exchanging means on said plate adapted to conduct vapor from the space below to the space above the said plate and to conduct the overflowing reflux from said plate in a reverse flow to that of the vapor.

3. An apparatus for rectification of liquids, comprising: a rectifying column, a series of horizontally disposed plates spaced one above the other in the column arranged for fractionally condensing rising vapors, a reflux condenser, an enclosed chamber located higher than the uppermost of said plates and provided with liquid sump and with a vapor space above the said sump, said vapor space being in vapor flow communication with the sump, and with the condenser, means for returning reflux condensate from the condenser to said sump, a heat exchange means in said chamber arranged to direct liquid overflowing the sump to the uppermost plate of the column and to conduct vapor from the space immediately above said plate in a heat exchange relationship with the liquid in the sump to condense a portion of the ascending vapor and to vaporize a portion of the liquid in the sump without physical contact between the ascending vapors and the liquid in the sump.

4. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, and passing the uncondensed portion of the vapors to the condenser for producing a condensate.

5. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, returning the condensed portion to the column, and passing the uncondensed portion of the vapors to the condenser for producing a condensate.

6. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, and evaporating a portion of said body of reflux, and passing the uncondensed portion of the vapors to the condenser for producing a condensate.

7. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors,

and evaporating a portion of said body of reflux, and passing the uncondensed portion of the vapors together with the evaporated reflux to the condenser for producing a condensate.

8. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, passing the uncondensed portion of the vapors to the condenser for producing a condensate, and returning at least a portion of the produced condensate to the body of reflux in the heat exchanger.

9. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, passing the uncondensed portion of the vapors to the condenser for producing a condensate, returning at least a portion of the produced condensate to the body of reflux in the heat exchanger, and returning a portion of the body of boiling reflux from the heat exchanger to the column.

10. In a process of rectification of liquids by means of a distillation column containing a series of plates and provided with a condenser and a heat exchanger positioned between said plates and the condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux in the heat exchanger in a vapor flow communication with contents of the column, boiling said body of reflux by conducting vapors from the column through the heat exchanger in indirect heat exchange relationship with said body of reflux and without mixing therewith, thereby condensing a portion of the vapors, passing the uncondensed portion of the vapors to the condenser for producing a condensate, returning at least a portion of the produced condensate to the body of reflux in the heat exchanger, and returning a portion of the body of boiling reflux from the heat exchanger to the column together with the condensed portion of the vapors.

11. In a process of rectification of liquids by means of a distillation column containing a series of bubble plates and a heat exchange plate above the top bubble plate, and provided with a condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux on the heat exchange plate in vapor flow communication with the contents of the column below said heat exchange plate, boiling said body of reflux by conducting vapors from the column through the heat exchange plate in indirect heat exchange relationship with said body of reflux without mixing therewith, thereby condensing a portion of the vapors, and passing the uncondensed portion of the vapors to the condenser for producing a condensate.

12. In a process of rectification of liquids by means of a distillation column containing a series of bubble plates and a heat exchange plate above the top bubble plate, and provided with a condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux on the heat exchange plate in vapor flow communication with the contents of the column below said heat exchange plate, boiling said body of reflux by conducting vapors from the column through the heat exchange plate in indirect heat exchange relationship with said body of reflux without mixing therewith, thereby condensing a portion of the vapors, returning the condensed portion to the bubble plate zone of the column, and passing the uncondensed portion of the vapors to the condenser for producing a condensate.

13. In a process of rectification of liquids by means of a distillation column containing a series of bubble plates and a heat exchange plate above the top bubble plate, and provided with a condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux on the heat exchange plate in vapor flow communication with the contents of the column below said heat exchange plate, boiling said body of reflux by conducting vapors from the column through the heat exchange plate in indirect heat exchange relationship with said body of reflux without mixing therewith, thereby condensing a portion of the vapors, and evaporating a portion of said body of reflux and passing the uncondensed portion of the vapors together with the evaporated reflux to the condenser for producing a condensate.

14. In a process of rectification of liquids by means of a distillation column containing a series of bubble plates and a heat exchange plate above the top bubble plate, and provided with a condenser, the steps of counterflowing vapors and liquid reflux through the column, maintaining a body of reflux on the heat exchange plate in vapor flow communication with the contents of the column below said heat exchange plate, boiling said body of reflux by conducting vapors from the column through the heat exchange plate in indirect heat exchange relationship with said body of reflux without mixing therewith, thereby condensing a portion of the vapors, passing the uncondensed portion of the vapors to the condenser for producing a condensate, returning at least a portion of the produced condensate to the body of reflux in the heat exchanger, and returning a portion of the body of boiling reflux from the heat exchange plate to the bubble plate zone of the column.

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