

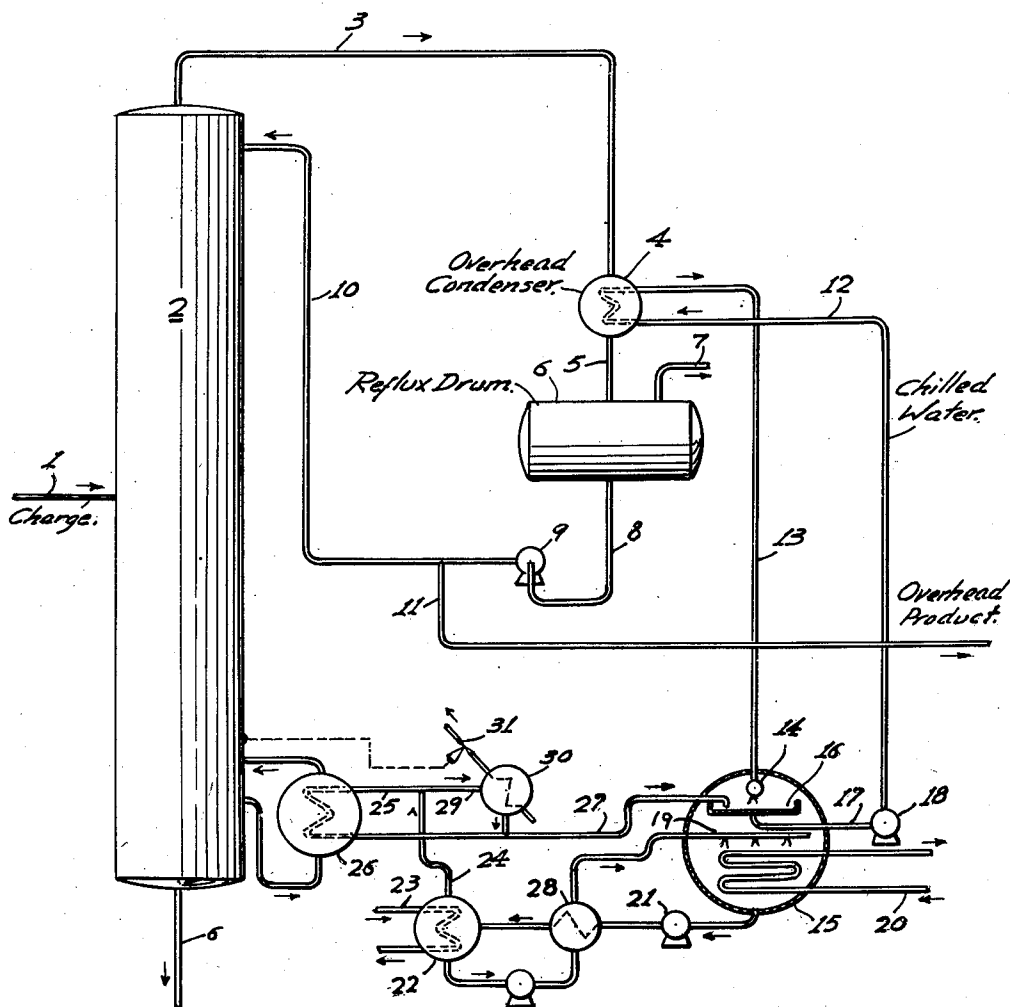
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PROCESS AND APPARATUS FOR SEPARATING FLUID MIXTURES

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PROCESS AND APPARATUS FOR SEPARATING FLUID MIXTURES

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This invention relates to fractional distillation and more particularly to a method and apparatus for the fractional distillation of mixtures of narrow boiling range.

Mixtures of narrow boiling range present a difficult separation problem. A conventional method of fractionating such mixtures involves the use of high temperatures and pressures in the fractionating column and the cooling of the overhead product by available cooling water. Because of the relatively high temperature of normal cooling water, e. g. 85° F., it is necessary for the fractionating column pressure to be relatively high in order to condense the overhead product. Also, a high reflux ratio is required in separating a narrow boiling point mixture at high temperature and pressure, and this contributes to the excessive cost of such operation. It has been recognized that the refrigeration of the overhead condenser would be desirable for separating narrow boiling range mixtures so that the column could be maintained at low temperatures and pressures, but the use of conventional compression refrigeration equipment to obtain a lower condensing temperature than ordinary cooling water provides is not usually economically practicable.

The present invention makes it possible to refrigerate the overhead condenser of a fractionating column at operating costs not exceeding those of columns using cheap cooling water. As a consequence, the fractionation of narrow boiling range mixtures such as propylene-propane or isobutane-n-butane is greatly improved because of the lower permissible temperatures and pressures in the fractionating column which increase the differences in relative volatilities of the lighter to heavier components and thus decrease the required work of separation.

A detailed description of the invention can be given by reference to the accompanying drawing which is a diagrammatic representation of a preferred embodiment of the apparatus of the invention in which the process of the invention can be carried out.

In the apparatus of the drawing, material to be fractionated is continuously introduced through line 1 into fractionating column 2 provided with suitable liquid-vapor contacting means, e. g. bubble cap trays or perforated trays, and is subjected to conventional fractionation therein. The more volatile fraction of the charge mixture is continuously withdrawn as a vapor from the top of the column through line 3. The overhead product vapors are continuously cooled and at least partially condensed in a refrigerated overhead product condenser by indirect heat exchange with an evaporating refrigerant. The drawing shows the preferred embodiment of my apparatus in which I employ a conventional overhead condenser 4 and refrigerate this condenser by passing through its tubes a stream of chilled liquid delivered from a refrigerant evaporating zone.

The condensate from condenser 4 and any remaining uncondensed material pass through line 5 into reflux drum 6 in which uncondensed material is disengaged

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from the condensate. The non-condensable vapors, if any, are vented from reflux drum 6 through line 7 and disposed of as desired. Condensate is withdrawn through line 8 and pump 9. A portion of the condensate, sufficient for refluxing, is returned via line 10 to the top of the fractionating column 2 while the remainder is withdrawn via line 11 as overhead product.

In accordance with my preferred procedure, the same liquid is used both as the evaporating refrigerant and as the chilled liquid for passage through condenser 4. It is also preferred that this liquid be water. The advantages of using water for both of these purposes will be apparent from the further description of the process and apparatus of the drawing in which water is used for both purposes.

The chilled water introduced by line 12 for refrigerating condenser 4 is returned by line 13 for rechilling and is sprayed through header 14 into the evaporation zone in the upper portion of shell 15. At the start of the process a partial vacuum is imposed on the shell 15 by any suitable vacuum producing means such as a steam jet, not shown in the drawing, so as to promote the vaporization of the water introduced into the evaporation zone of shell 15. A portion of the water sprayed into the upper portion of shell 15 flashes into vapor and thus chills the remaining liquid down to a temperature nearly corresponding to the temperature of water with vapor pressure equal to the pressure in the shell. The water chilled in this manner collects in evaporator tank 16 from which it drains by line 17 and is returned by chilled water pump 18 to the overhead condenser 4.

A concentrated salt solution, preferably an aqueous solution of lithium bromide, is introduced through sprayer 19 into the lower portion of the low-pressure shell 15. The water vapor flashed in the evaporation zone of shell 15 moves down and is absorbed by the concentrated salt solution so that the shell pressure remains below the vapor pressure of the water introduced through header 14 and continuous evaporation of the water occurs. To assist in the maintenance of the proper low pressure in shell 15, the steam jet used for producing the original vacuum in the shell can function to purge the shell of any non-condensables which might enter the shell by leakage.

Since the heats of condensation and dilution resulting from the absorption of water vapor in the lithium bromide solution tend to raise the temperature of the salt solution and reduce its absorptive power, it is preferred to provide cooling means in the shell 15 such as the coil 20, over which the salt solution is sprayed. Through coil 20 is passed a coolant such as cooling water to absorb the heat released in the vapor absorption.

The absorption of water vapor in the salt solution lowers its salt concentration and thus reduces its absorbing power. Diluted salt solution is continuously drained from shell 15 and is delivered by dilute solution pump 21 to generator 22. In generator 22, a heating medium such as exhaust steam passing through coil 23 heats the solution and boils off the water vapor previously condensed in the adsorption zone of shell 15, thus restoring the solution to its original concentration. It is preferred to impose a partial vacuum on the generator 22 so that generation of vapors from the diluted absorbent solution will not require an excessively high temperature. The partial vacuum can be imposed in any suitable manner, for example as in shell 15, by means of a conventional steam jet.

Water vapor boiled out of the solution in generator 22 passes via lines 24 and 25 into the tubes of reboiler 26 and liquid from the bottom of column 2 is passed through the reboiler shell. In this manner, by heat ex-

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change between the generated water vapor and the column bottom liquid the water vapor from generator 22 is condensed and the reboiling of column 2 is effected. Condensed water vapor is returned to the evaporator tank 16 via line 27. Preferably, as shown in the drawing, a heat exchanger 28 is placed between the pump 21 and the generator 22 to cool the hot concentrated solution withdrawn from the bottom of generator 22 and to heat the cooler diluted solution entering generator 22.

In the preferred embodiment of my invention the heat balance in the column 2 is maintained through the use of the balancing condenser 30. The coolant line passing through condenser 30 is provided with a flow control valve 31. The valve 31 is operated by a pressure controller at the lower end of column 2. When the pressure in column 2 tends to rise above a predetermined pressure level, the pressure controller operates valve 31 to increase the rate of flow of coolant through the tubes of condenser 30. As a result the rate of flow of vapor from line 24 through line 29 into the condenser 30 increases so that the flow of vapor through the reboiler decreases and the temperature of column 2 drops. Likewise, when pressure tends to drop in column 2 the temperature of the condenser 30 is increased by a decrease in the coolant rate, and the vapor flow increases through line 25 to the reboiler and therefore the temperature in the bottom of column 2 rises.

From the foregoing description it can be seen that my invention makes it possible to refrigerate the overhead condenser of a fractionating column and obtain the important advantages resulting therefrom at operating costs not exceeding the operating costs for a fractionating column which uses normal temperature cooling water in its overhead condenser. The apparatus of my invention is operated by the same heat, e. g. exhaust steam, as would be supplied to a conventional fractionating column, but the heat is supplied to the generator 22 of the refrigeration equipment rather than directly to the fractionating column reboiler as in conventional columns. Then, since the column temperature can be low as a result of refrigeration of the overhead condenser, the reboiler temperature can be lower so that for this purpose the heat supplied by condensing the vapor from generator 22 is sufficient. Thus, for substantially the same operating cost as conventional fractionation, it is possible to operate a fractionating column in accordance with my invention at a considerably lower temperature and pressure than conventional columns. The resulting advantages are numerous.

One advantage is that my invention makes it possible to use existing fractionating columns for fractionations which by conventional practice would take place at pressures higher than the existing equipment could withstand. For example, a conventional depentanizer which uses cooling water in its overhead condenser operates at about 25 pounds per square inch gauge. A conventional debutanizer column also using cooling water in its overhead condenser operates at about 100 pounds per square inch gauge and must, of course, be of considerably heavier construction than the depentanizer column. My invention makes it possible to use an existing depentanizer column as a debutanizer since the debutanizer can operate at pressures as low as about 25 pounds per square inch gauge when the overhead condenser is refrigerated with chilled water in accordance with my invention. Another advantage is that with lower pressure and temperature the same degree of separation of a narrow boiling range mixture can be obtained with a much lower reflux ratio than is required in a column of higher temperature and pressure. Because of the lower reflux ratio, a smaller column can handle the same amount of charge.

My invention affords still other advantages in certain separations. For example, in separating a mixture of isobutane and n-butane in accordance with my inven-

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tion, the bottoms from the fractionating column is obtained at a considerably lower temperature than in conventional towers, namely at about 85° F., so that it is unnecessary to cool the bottoms product before using or storing it. This makes it possible to eliminate one of the heat exchanges of conventional towers. Also, in the separation of this mixture to obtain isobutane for alkylation, the isobutane overhead product is chilled by the overhead condenser to a rather low temperature, about 45° F., so that further chilling of the isobutane as required in columns in which the overhead condenser employs ordinary cooling water, is unnecessary before charging the isobutane to the alkylation unit.

As an illustration of the type of results obtainable with the process and apparatus of my invention the following example can be given.

Example

To a fractionating column of the type shown in the drawing is charged a mixture comprising n-propane, 1 percent by volume; isobutane 22 percent by volume; n-butane 76 percent by volume and isopentane 1 percent by volume. Exhaust steam at 230° F. is delivered to the generator 22 of the refrigerating equipment. An aqueous solution of lithium bromide is employed as the refrigerating system absorbent. The concentration of the lithium bromide solution varies from about 60 to about 65 percent during the operation. The temperature of overhead condenser 4 is maintained at about 50° F. by circulating through its tubes chilled water delivered from the refrigeration equipment at about 41° F. The condenser temperature of 50° F. permits temperatures in the fractionating column ranging from 60° F. at the top of the column to 85° F. in the reboiling section at the bottom of the column. The pressure is maintained at about 40 pounds per square inch absolute at the bottom of the column. With a 9 to 1 reflux ratio the overhead product of the column has the composition: n-propane, 3.8 volume percent; isobutane 91.3 volume percent; and n-butane 4.9 volume percent. The bottoms product has the composition: isobutane 2.3 volume percent; n-butane 96.7 volume percent; and isopentane 1.0 volume percent.

In the conventional fractionation of the same C₄ mixture, the overhead condenser would be cooled by available cooling water at about 85° F. and the overhead condenser temperature would be about 105° F. The conditions of operation of the column in order to obtain a degree of separation comparable to the separation in my process would include the following: temperature at the top of the tower, about 135° F. and at the bottom of the tower in the reboiling section, about 230° F.; pressure, about 115 pounds per square inch absolute; reflux ratio, about 12 to 1. From these figures it can clearly be seen that the conventional process would require a much more expensive fractionating column to withstand the considerably higher pressure and to afford the capacity for the considerably higher reflux ratio.

In the detailed description of the process and apparatus of my invention, it has been stated that the process of the invention employs water as the refrigerant and as the liquid medium for heat exchange between the evaporation zone and the overhead condenser. It should be understood, however, that while this is the preferred method of operation, other procedures can be used. Thus, for example, it is possible to condense the overhead product in tubes passing through the evaporation zone, in effect making the evaporation zone serve directly as the overhead condenser and eliminating the need for delivering a chilled liquid from the evaporation zone to a separate overhead condenser.

Another possible modification of the process is the employment of a heat exchange medium other than water for refrigerating the separate overhead condenser. Thus it is possible to provide coils in the evaporation zone through which brine or other heat transfer medium is

flowed and, after chilling, delivered to the overhead condenser. In such case the brine stream would be a separate closed system and the cooling effect would be obtained by evaporation of condensate returned to the evaporation zone by line 27.

It is also possible in my process to employ substances other than the preferred lithium bromide as the absorbent. It is, of course, important that the absorbent be a solid which has little or no vapor pressure of its own and most of the suitable solids are salts. The absorbent should form a low viscosity solution so as to minimize the work of pumping and the solution should, of course, be of low corrosivity. The absorbent should have a low heat of dilution and concentration and should have good heat transfer characteristics such as high thermal conductivity and high specific heat. A primary requirement of the absorbent is a strong absorbing affinity for the refrigerant liquid used in the process. Compounds having the indicated desired properties includes the various halides of alkali metals and alkaline earth metals.

While water is greatly preferred as the liquid refrigerant because of its cheapness and its many desirable properties, the invention also includes the use of other liquids. Ethylene glycol is an example of a liquid which is suitable with certain absorbent salts.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof; therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process which comprises subjecting a narrow boiling range fluid mixture to fractionation in a fractionating column, continuously removing overhead the more volatile fraction of the mixture as a vapor, cooling and at least partially condensing such vapors by heat exchange with a stream of chilled liquid refrigerant delivered from an evaporation zone, imposing a pressure in said evaporation zone below the vapor pressure of said liquid refrigerant, chilling said liquid refrigerant stream by partial evaporation of the liquid in said evaporation zone, maintaining the pressure in said evaporation zone below the vapor pressure of the liquid refrigerant by continuously absorbing the vapors of said refrigerant in a stream of absorbent salt solution, thus diluting said solution, passing said stream of diluted absorbent salt solution from the zone of absorption to a generating zone, heating the diluted absorbent salt solution in said generating zone to generate refrigerant vapor and reconcentrate said solution, returning the reconcentrated solution to the zone of absorption, exchanging heat between at least a portion of said refrigerant vapor and the bottom liquid of said fractionating column whereby to condense said refrigerant and reboil said column, passing another portion of said refrigerant vapor into heat exchange with a coolant in a separate heat exchanging zone, controlling the rate of flow of coolant to said separate heat exchanging zone in accordance with pressure variations within said fractionating column whereby to increase the rate of flow of coolant to said separate heat exchanging zone when the pressure in said fractionating column tends to rise above a predetermined pressure level, and returning the condensed refrigerant to the zone of evaporation.

2. In a fractional distillation apparatus, the combination of a fractionating column and a heat operated absorption refrigeration apparatus, means for condensing the overhead vapors from said fractionating column by indirect heat exchange with chilled refrigerant from said re-

frigeration apparatus, means for delivering chilled liquid from a refrigerant evaporator to said condensing means, means for returning liquid refrigerant from said condensing means to said evaporator for partial vaporization of said refrigerant, means for introducing an absorbent solution in the region of said evaporator to absorb the vaporized refrigerant thus diluting the absorbent solution, means for delivering diluted absorbent solution to a refrigerant generator, means for heating said generator to form refrigerant vapor and reconcentrate said solution, means for delivering refrigerant vapor from said generator to the reboiler of said fractionating column for indirect heat exchange with the bottoms liquid of said column, means for delivering a portion of the vapors from said generator to a condensing means, means for delivering a coolant to said condensing means and having a flow control valve, and pressure responsive means in the lower end of said fractionating column for controlling said valve to increase the rate of coolant passing through said condensing means when the pressure in said column tends to rise above a predetermined maximum.

3. The process which comprises subjecting a fluid mixture to fractionation in a fractionating column, continuously removing overhead the more volatile fraction of the mixture as a vapor, cooling and at least partially condensing such vapor by heat exchange with an evaporating refrigerant, absorbing the vapors of said refrigerant in an absorbent solution, thus diluting the solution, heating the diluted solution to generate refrigerant vapor and reconcentrate said solution, exchanging heat between at least a portion of said refrigerant vapor and the bottoms liquid of said fractionating column whereby to condense said refrigerant and reboil said column, passing another portion of said refrigerant vapor into heat exchange with a coolant in a separate heat exchanging zone, and controlling the rate of flow of coolant to said separate heat exchanging zone in accordance with pressure variations within said fractionating column whereby to increase the rate of flow of coolant to said separate heat exchanging zone when the pressure in said fractionating column tends to rise above a predetermined pressure level.

4. In a fractional distillation apparatus, the combination of a fractionating column and a heat operated absorption refrigeration apparatus, means for condensing the overhead vapors from said fractionating column by indirect heat exchange with chilled refrigerant from said refrigeration apparatus, means for reboiling said column by indirect heat exchange between the bottoms liquid of said column and regenerated refrigerant vapors from said refrigeration apparatus, a separate condensing means, means for delivering a portion of the generated refrigerant vapors from said refrigeration apparatus to said separate condensing means, means for delivering a coolant to said separate condensing means and having a flow control valve, and pressure responsive means in the lower end of said fractionating column for controlling said valve to increase the rate of coolant passing through said condensing means when the pressure in said column tends to rise above a predetermined maximum.

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