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METHOD OF SEPARATING LIQUIDS AND GASES

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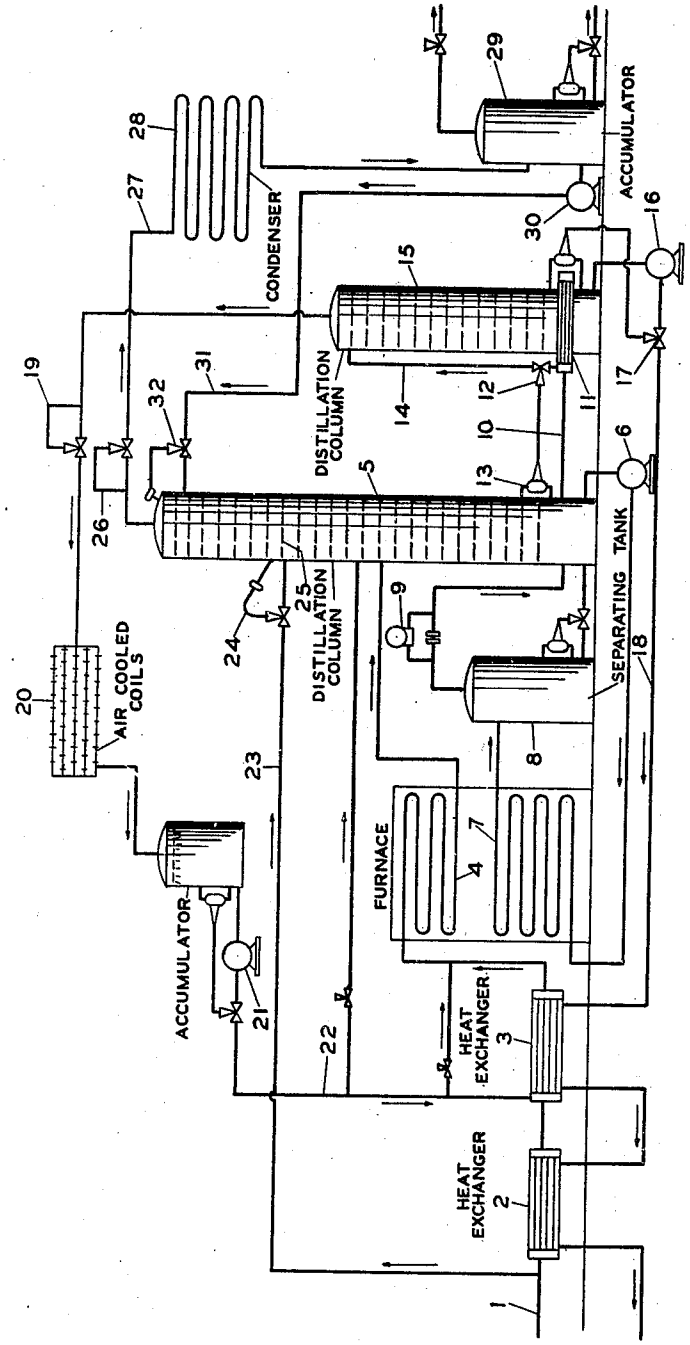

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METHOD OF SEPARATING LIQUIDS AND GASES

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4 Claims. (Cl. 196—8)

This invention relates to the separation of a light fraction and a heavy fraction which are in solution. More particularly, this invention relates to the distillation of rich absorption oil using sub-atmospheric pressure generated by condensation in which only liquids and not vapors are moved from the lower to the higher pressure.

A primary object of the present invention is to provide an improved method of separating light and heavy fractions in solution in which the distillation is performed in a plurality of steps of decreasing pressure with the heavy fraction being partially vaporized at reduced pressure.

A further important object of the present invention is to provide an improved method for separating a light fraction and a heavy fraction by distillation, the heavy fraction being decomposable by high temperature in which the distillation is carried out in a plurality of steps of decreasing pressure with the heavy fraction being partially vaporized in a final step at sub-atmospheric pressure.

A further object of the present invention is to permit operation of a direct fired still on absorption oil at a temperature lower than otherwise necessary, thus minimizing the danger of cracking the oil being distilled.

A further object of the present invention is to permit operation of a direct fired still on absorption oil instead of steam and at the same time deliver the vapor product to its condenser at the pressure customary in steam still operation.

Other objects of the present invention are: to use air cooling more effectively; to remove part of the heat from the distilled oil by its evaporation rather than by liquid cooling; and to complete the stripping of product from the solvent oil at a favorably low pressure without the use of compressors on the vapors so distilled off.

The advantages of the present method over steam stills currently used are, primarily, the elimination of steam and the difficulty and expense involved in its use. The advantages of the present fire still over fire stills proposed are: the product vapors are delivered at reasonably high pressure while final stripping of the oil is accomplished at low pressure; the low pressure is attained without use of vacuum pumps on vapors; the vacuum is attained while condensing at such high temperature that air cooling in finned tubes may be employed at high efficiency, both because of the temperature and of the fact that condensation, and not liquid cooling, is being done in the air cooled unit; and the vacuum employed has the additional advantage that part of this cooling of the heated solvent oil is done by the evaporation of some of it, such evaporation being also used in the distillation process.

Other objects and advantages will appear from the more detailed description of the invention following hereinafter.

This application discloses an improvement over my co-pending application Serial No. 270,683 filed April 28, 1939, which has issued as Patent No. 2,277,070 on March 24, 1942.

In order to more clearly understand the reasons for the cycle employed, it is useful to consider the known art of stripping or exhausting a lighter hydrocarbon from its solution in a heavier. It is known to be of prime importance in the art, to completely remove from the solvent oil even an additional fraction of a per cent of even the heaviest hydrocarbon derived from the gas treated in the absorber. In fact, it is with respect to this aspect of distillation that direct fired apparatus, though commonly used in refineries, is viewed least favorably by operators of absorption plants, where the current practice is to use large volumes of open steam to attain this highly important final denuding of the solvent oil.

In the current mathematics of the art, the completeness with which a given component of the gasoline dissolved, is removed from its solution is expressed by the "Stripping factor S". It is known, for example, that when S equals 1.4 for a given component of the dissolved gasoline, and usually the heaviest present is considered, for example heptane, about 98% of the amount present will be removed from solution by a distillation with that stripping factor, and 98% of the amount present will be removed whether its concentration in the feed be 1%, 2%, or 10%. In other words, completeness of stripping depends on stripping factor alone and is independent of the original concentration in the feed. It is similarly known, for example, that a stripping factor S equalling 0.7 will result in the removal of about 70% of the amount present, still regardless of its original concentration.

It is neither necessary nor desirable, for the present purpose, to go further into a discussion of the stripping factor S, but only to state that it is accepted in the art as completely defining that phase of distillation having to do with the removal of the solute from the solvent. It is also accepted in the art that the stripping factor S is itself completely defined by the expression.

$$S \text{ equals } K\frac{V}{L}$$

The term K in the above equation expresses the ratio, for the component under consideration, between "mol fractions in vapor phase" in equilibrium with "mol fractions in liquid phase."

In its meaning are included the effects of temperature and pressure on that individual hydrocarbon and for the present purpose it may be considered as expressing the ease with which a component may be distilled overhead, that being easier if K is large, and raising temperature or lowering pressure always increases it. These K's for the different hydrocarbons at the various combinations of temperature and pressure are known and whether quite accurately known or not, the fact remains that they attempt to express inflexible physical laws that we cannot change, as the stripping factor S expresses a mathematical relation which one also cannot change.

This leaves the terms V and L which mean only quantities, V being mols of vapor travelling upward through the plates of a column and L being mols of liquid travelling downward over the same plates.

These quantities, an inventor, operator or designer may change, and it is the intention here to shown how to change them favorably.

Returning to the equation

$$S \text{ equals } K\frac{V}{L}$$

S is a mathematical relation, K is a constant, and L is nothing more than the amount of rich oil we have to distill, which is a fixed quantity. V is the amount of vapor one has to make and not only make, but condense also. It represents almost the entire cost of the operation. Solving for V, we have

$$V \text{ equals } \frac{LS}{K}$$

Since V represents the cost, it is desirable to reduce its size or else the cost of keeping it at the necessary size. From the equation above, it is clear that V is reduced in direct proportion as S is reduced or K increased. Conversely, V becomes greater in direct proportion as either L or S is increased or K reduced. It is to be noted that all the changes are in direct, simple proportion. As previously stated, an S of 1.4 strips, 98% and an S of 0.7 strips, not 49%, but 70%. This is an advantage that may be used.

But if one reduces S, the solvent will not be denuded. This brings out the further point that if the operation be done in one piece of equipment which necessarily has but one final temperature and one pressure, neither K nor S can be changed, and since L is constant, no improvement is possible. The art really stands that way today, with absolutely no freedom to reduce V except by raising the temperature or lowering pressure which reduces it by increasing K.

My invention proposes doing the distillation in two stages, and this affords freedom in changing all these terms. In the first column at 20# gauge, we operate with S for heptane equals 0.3, thus reducing V there in the ratio 1.4 to 0.3 or making V only 21.4% as great, but in order to do this, we must feed back to the first column an amount equalling about 30% of the original feed which increases L making the effective V 1.3 times 21.4% or about 28% of its original value.

In the second column at 10# absolute, the K for heptane is twice as great at 60° F. lower temperature, and there we leave the S at 1.4, completing the stripping with half the V required in the first column, because of the double value of K for heptane. And the reduction in temperature furnishes the heat to make the required vapor, at the same time cooling the solvent oil by that much.

The foregoing has been only for illustration, and since the cycle may be operated through a broad range of conditions, the advantage in vapor volume may be either greater or less than indicated.

For the purpose of more fully disclosing my invention but as merely illustrative of the application thereof, the features of my process and apparatus embodying and suitable to the practice of my invention are described in connection with the accompanying drawing which discloses a diagrammatic elevation of an apparatus suitable for carrying out the present invention.

Referring to the drawing in detail, the rich oil coming from absorber (not shown) through pipe 1, flows through heat exchangers 2 and 3 in series, then to a direct fired preheater 4, entering a first column at 5, the primary feed plate. The oil flows downward over the plates of the exhausting section, being stripped of its lighter components down to, for example, removal of ⅔ its pentane content. A pump 6 circulates a suitable flow from the bottom of the column through a direct fired heater 7 in which it is re-boiled and both liquid and resulting vapor are discharged into a separating tank 8. Vapor from this tank is measured by a meter 9, in accordance with the vapor flow through which the amount of heat supplied at heater 7 is regulated. Both vapor and liquid from tank 8 are discharged into the base of the first column below its lowest plate. Oil from the base of the first column flows through a pipe 10 to a heat exchange element 11 located in the base of a second column. Its flow is governed by an automatic valve 12 actuated by a level control 13 attached to the first column. In element 11, the hot oil gives up a part of its heat to what is really the same oil flowing down over the plates of the second column. Because of the reduced pressure in the second column, part of the oil is vaporized by its own sensible heat thus reducing its temperature. It flows downwardly through the second column, counter current to the vapor developed at the reduced pressure by the heating element 11, and from its base is pumped by a pump 16, controlled by a level control valve 17 through a line 18 back to the heat exchangers 3 and 2 in series.

Vapors from the top of the second column flow through a back pressure regulator 19 to a condenser 20 which may be suitably air cooled at a temperature around 200° F. or by any other suitable means. The vapor, consisting chiefly of vapors of the solvent oil, and substantially free from butane and lighter constituents due to the action of the first column, totally condenses at a low pressure and a high temperature and the condensate is pumped by a pump 21 through a pipe 22 to join the incoming liquid feed passing through the heat exchanger 3. Various practical methods of operation may make it desirable that the condensate in line 22 should not flow to heat exchanger 3 as shown, but in some cases to heater 4 direct, or in other cases to a suitable plate in the first column, this to be determined by the composition and temperature of the material.

A small part of the rich oil, as controlled by a thermostatic valve 24, flows through a line 23 to a secondary feed plate 25 of the first column.

Vapors from the first column flow through a back pressure regulator **26** and a line **27** to a condenser **28**. Uncondensed vapor and condensate are separated in a tank **29**, from which tank a pump **30** pumps through a line **31** reflux as controlled by a thermostatic valve **32**, said reflux entering the top plate of the first or high pressure column.

The temperature at the base of both columns is left free to float, control in both cases being by means of the application of a substantially constant amount of heat instead of by fixing the temperature. In the first column, this is measured by measuring the vapor; in the second column, constant conditions will result in a constant heat input which tends to vary correctly if oil flow varies.

It is old to flash off vapor by reducing pressure, but it is new to condense that vapor and return it to the first column. It is also known that condensing a suitably heavy vapor will develop pressures below atmospheric. As an example of the low pressure that may be reasonably attained at 200° F., consider the vapor from the second column of composition as follows:

Per cent		Vapor pressure at 200° F.	Partial pressure
		Pounds.	*Pounds.*
Butane	2	200	4.
Pentane	5	73	3.65
Decane	93	2	1.86
	100		[1] 9.51

[1] Absolute.

Such a material is as rich as many rich oils and it would require very light stripping at fire still temperatures in the first column to produce from the second a vapor as condensable as the above.

The mols returned to column **5** increase only proportionately the stripping vapor required there for a given result on hexane. But by taking this increase in mols of feed, one gains three important advantages in column **5**.

1. Gasoline concentration above the feed plate is increased, thus requiring less reflux or heat removal at the top by whatever means used.

2. Because the stripping factor for the complete stripping has a greater value than 1, its reduction to a reasonable value, say on hexane, reduces heat requirement faster than the increased feed, which applies lineally, increases it.

3. By definition, temperature at the base of column **5** is the boiling point of what flows out there. The gasoline constituents retained, but chiefly the lighter solvent fraction added to the feed, reduces operating temperature there.

As to the second column, plants already have two columns and pumping is the cheapest thing in a plant. By dropping the pressure and thus adding to the pumping load, we gain:

1. In any possible fire still the oil must be heated to its boiling point, neither more nor less, regardless of how much of it is evaporated and recondensed at that temperature. Here we use part of that necessary sensible heat for completing the stripping under favorable low pressure conditions.

2. Something is saved in oil cooling by dissipating that much heat in a condenser instead of in a heat exchanger or cooler and at a temperature high enough to permit air cooling.

3. The second column strips without any reflux to hinder it, requiring that only this overhead, not 1½ to 3 times the overhead be condensed, and that condensation, which reduces the heat load on the more difficult condensation at the top of the first column, is done at favorably high temperature.

So far as heat utilization is concerned, operating control consists in the maintenance of the relation between vapor volume through meter **9** and the absolute pressure on column **15** within certain reasonable limits. A definite vapor volume for exhausting is required in column **15** which is less with lower pressure. Since the temperature of the oil leaving column **5** is chiefly governed by the pressure and is changed but little by the amount of latent heat applied at the base of column **5**, the pressure drop must be sufficient to permit sensible heat from this relatively fixed temperature to flash off the necessary exhausting vapor.

The ability of the condenser **20** to establish a pressure sufficiently low for this requirement of the second column depends in turn on the vapor volume through meter **9**, as secondarily affected by primary feed temperature at plate **5**. The minimum requisite, and that is the desirable operating condition, is that column **5** shall remove propane to pentane with sufficient thoroughness to result in an easily condensable total vapor from column **15**. That this may reasonably be done may be seen from the fact that heptane has a vapor pressure of but 18# absolute at 200° F., the oil vapors less than 2# absolute, and even 1% propane in the 200° F. condensate contributes but 5# absolute. So really what the first column has to do, as a minimum, is to cut well into the pentane. It is essential, too, that pressure as condenser **20** be sufficiently lower than that of column **15** so that regulator **19** may hold a constant pressure on column **15** thus freeing it from pressure fluctuations due to weather conditions affecting the condenser, which would otherwise result.

It will be clear that all the pentane, hexane and heptane will finally get into the product out of the top of the first column despite the fact that the minimum requirement of the first column is the removal of pentane and lighter with sufficient thoroughness to develop the low pressure in condenser **20**. All the heavier material will get into the product by reason of the fact that a given vapor ratio through meter **9** removes a certain per cent of each component, depending solely on its K and not on its concentration. If, for example, in the first time through, ⅓ of the hexane be removed, hexane will be returned from the second column until the hexane in the feed to column **5** becomes three times as great as in the oil leaving the absorber. Taking ⅓ of this increased amount will obviously send the entire current production overhead from column **5** and recycle the remaining ⅔. It will also be seen that the size of this recycle will vary inversely with vapor volume through meter **9** and is thus under operating control. Consideration of it will also make it clear to an experienced operator, without any calculations, that reflux control of end point at top of column **5** very plainly becomes easy because product is distilled easily without forcing, from an oil artificially enriched in heavier components of the gasoline. The limit in size of this recycle is also easily seen to be in the necessity of having a vapor from column **15** totally condensable at its pressure. Column **15** being set to strip totally will just as well strip

an increased concentration and an increase in the hot condenser load at condenser **20** is a small price to pay for a much greater reduction in load at condenser **28**, especially since all the heat to condenser **20** comes from hot oil which must be cooled anyway.

The cycle is not limited to two stages, and in a case where large amounts of ethane or propane are to be recovered, the same principles may indicate the desirability of distillation in three stages, the first at higher pressure producing polymerization feed stock. Also, it may be desirable to do part of the oil cooling of denuded oil from the second column by means of further reduction in pressure.

Consideration of the characteristics of surface condensers as used for condensing steam after turbines, indicates that a similar method might be advantageous for fire still oil cooling. For after the oil is stripped, a surface condenser could reduce the pressure to a very low value, so low for example, that the denuded oil would boil at 200° F., leaving only the heat below this to be dissipated in heat exchangers and coolers. Such oil vapors have a molar latent heat nearly as great as steam, but weigh around eight times as much per mol. Such a condenser could be cooled first by the rich oil on the way to the still. This could be followed by an air cooled condenser or one cooled by the residue gas, or such vapors would lose a lot of heat if merely moved around a little through a plurality of bare pipes.

While I have described my invention as applied to the distillation of rich absorption oil, it will be apparent that it is equally applicable to any distillation problem wherein a light fraction is to be separated from a heavy fraction.

The terms "vapors" and "gases" are used interchangeably in this disclosure and when the term "liquid" is used it describes the condition at the pressure and temperature present.

I claim:

1. The process of removing the desirable constituents from an enriched absorption oil in the absence of steam or other stripping media which comprises heating the enriched absorption oil to the desired temperature in a fire still, passing the enriched absorption oil to the feed zone of a first distillation column from which the absorbed constituents are taken off as a vapor, condensing said vapor and returning a part of the same to the top of the column as reflux, diverting a portion of the liquid effluent of the first distillation column to a heater to vaporize a portion of the same, contacting the enriched absorption oil in the first distillation column with a controlled amount of vapor evolved from the diverted portion of the liquid effluent, passing the remainder of the liquid effluent of the first distillation column to a second column operating at a lower pressure than the first column to evolve a portion of the absorption oil as vapors therefrom, removing the vapors evolved in the second column and substantially completely condensing the same, and passing the condensate from the second column to the first distillation column, entering the same into the first distillation column at a point within the feed zone substantially below the reflux entrance.

2. The process of removing the desirable constituents from an enriched absorption oil in the absence of steam or other stripping media which comprises heating the enriched absorption oil to the boiling point in a fire still, passing the enriched absorption oil to the feed zone of the first distillation column from which the desirable constituents are taken off as a vapor, condensing said vapor and returning a part of the same to the top of the column as reflux, diverting a portion of the liquid effluent of the first distillation column to a heater to vaporize a portion of the same, returning the unvaporized liquid to the first distillation column, contacting the enriched absorption oil in the first distillation column with an amount of the vapor evolved from the diverted portion of the liquid effluent quantitatively controlled relative to the feed to give a stripping factor for heptane greater than .3 in the first distillation column, passing the remainder of the liquid effluent of the first distillation column to a second column operated at subatmospheric pressure to evolve a portion of the absorption oil as vapors therefrom, removing the vapors evolved in the second column and substantially completely condensing the same, passing the condensate from the second column to the first distillation column and entering the same into the first distillation column at a point within the feed zone substantially below the reflux entrance.

3. The process of removing the desirable constituents from an enriched absorption oil in the absence of steam or other stripping media which comprises heating the absorption oil in a fire still to the boiling point of the absorption oil, passing the enriched absorption oil to the feed zone of a first distillation column from which the desirable constituents are taken off as a vapor, condensing said vapor and returning a part of the same to the top of the column as reflux, diverting a portion of the liquid effluent of the first distillation column to a heater to vaporize a part thereof, passing the vapor and unvaporized liquid to the first distillation column, contacting the enriched absorption oil in the first distillation column with the vapor evolved from the diverted portion of the liquid effluent of the first distillation column to remove the desirable constituents, controlling the amount of vapor entered into the first distillation column quantitatively to eliminate substantially all propane from the liquid effluent of the first column, passing the remainder of the liquid effluent of the first distillation column to a second column operated at subatmospheric pressure to evolve as vapors therefrom a quantity of the absorption oil sufficient to permit condensation of said vapors at a superatmospheric temperature, removing the vapors evolved from the second column and substantially completely condensing the same, passing the condensate from the second column to the first distillation column and entering the same into the first distillation column at a point within the feed zone substantially below the reflux entrance.

4. The process of removing the desirable constituents from an enriched absorption oil in the absence of steam or other stripping media which comprises heating the absorption oil in a fire still to the boiling point of the absorption oil, passing the enriched absorption oil to the feed zone of a first distillation column from which the desirable constituents are taken off as a vapor, condensing said vapor and returning a part of the same to the top of the column as reflux, diverting a portion of the liquid effluent of the first distillation column to a heater to vaporize a part thereof, passing the vapor and unvaporized liquid to the first distillation column, quantitatively controlling the amount of vapor evolved from

the diverted portion of the liquid effluent to give a stripping factor for heptane greater than .3 in the first distillation column, passing the remainder of the liquid effluent of the first distillation column to a second column operated at subatmospheric pressure to evolve as vapors therefrom a quantity of the absorption oil sufficient to permit condensation of said vapors at a superatmospheric temperature, removing the vapors evolved from the second column and substantially completely condensing the same, passing the condensate from the second column to the first distillation column and entering the same into the first distillation column at a point within the feed zone substantially below the reflux entrance.

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