

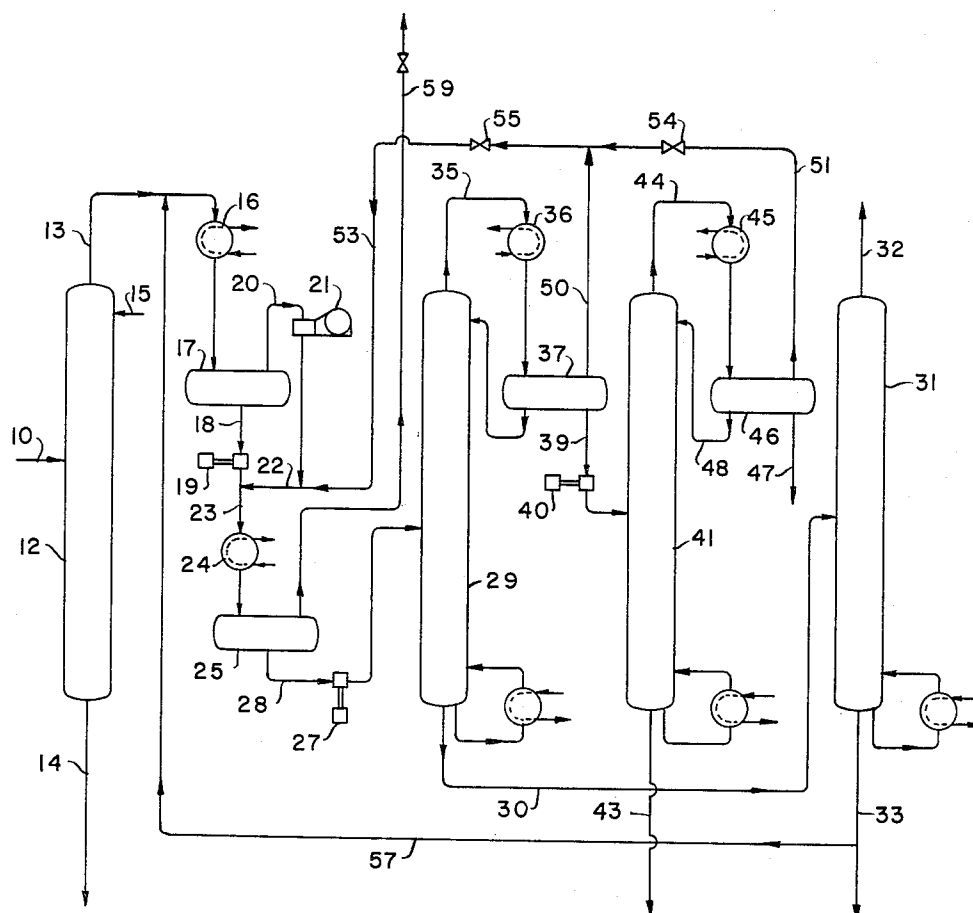
Sept. 18, 1962

H. FORBES ET AL

3,054,745

LIQUID RECOVERY FROM GASEOUS STREAM

Filed June 15, 1959



INVENTORS:

HENRY FORBES

HUBRECHT VAN DER MAREL

GODFRIED J. VAN DEN BERG

BY *J. Reid Anderson*

THEIR ATTORNEY

1

3,054,745

LIQUID RECOVERY FROM GASEOUS STREAM
Henry Forbes, Hubrecht van der Marel, and Godfried J.
van den Berg, all of The Hague, Netherlands, assignors
to Shell Oil Company, a corporation of Delaware
 Filed June 15, 1959, Ser. No. 820,285
 Claims priority, application Netherlands Oct. 7, 1958
 5 Claims. (Cl. 208—340)

This invention relates to the recovery of liquid from vaporous hydrocarbon stream containing normally gaseous components and in particular provides an improved method for further increasing the amount of liquid recovered.

It has been conventional practice in working up of a hydrocarbon mixture containing normally gaseous components to employ two or more distillation columns in series, with the feed of each succeeding one being produced by the partial condensation of the top product of the preceding one. A process of this general type is described in Petroleum Refiner, April 1950, pages 97-100. In the process described there the gases remaining from the partial condensation are further worked up by means of additional equipment since these gases still contain valuable components which are lost when the gases are discharged and burned.

An object of the invention is to provide a simpler method for reducing this loss and in particular a method which does not require the use of complex equipment. These and other objects will become more apparent from the following description of the invention taken in conjunction with the drawing which is a schematic representation of a preferred system for performing the process of the invention.

It has now been discovered that in the working up of a vaporous hydrocarbon mixture containing normally gaseous components utilizing a process of the type involving two or more distillation zones (with the feed of each succeeding zone being supplied by condensing the top product of the preceding zone) that the amount of liquid recovered from the hydrocarbon mixture may be significantly increased by returning the off gas from the partial condensation of the top product from the second distillation zone (likewise if more than two zones are employed, the off gas of those additional zones may also be returned) to the top product of the first distillation zone at a point preceding its separation into condensate and gas. In the preferred embodiment of the process, the returned gas is combined with the top product of the first distillation following the partial condensation of that product. Preferably, the combined stream of returned gas and partially condensed first top product is cooled before being separated into condensate and gas. It is possible to further increase liquid recovery and thereby reduce the amount of gas lost from the process by returning a portion of the liquid product of the second distillation zone to combine with the top product of the primary zone.

The only gases that are generally withdrawn from the process of the invention are the primary ones, i.e., the gases left from the condensation of the top product of the primary distillation zone. It is correct that the quantity of primary gases is greater than the quantity formed when there is no combination or return of the later off gases to the primary top product, but this quantity is less than the total quantity of primary and secondary gases which are withdrawn in conventional practice. Hence, there results with the practice of the process of the invention a net gain of liquid product which would otherwise be lost in gaseous form. The primary top product (i.e., from the primary distillation) is conveniently combined with the return gases at a point where the primary top

2

product has not yet been finally separated but beyond its partial condensation. The resulting mixture of returned gases and partially condensed primary top product is then preferably cooled again before being separated so that a further condensate formation may occur.

A quantity of the bottom product or a heavy side stream derived from the second distillation or from an additional distillation of these heavy streams may also be combined with the top product of the primary column. This leads to a further restriction of the quantity of primary gas withdrawn.

The process of the invention may be used with an advantage under conditions in which total condensation of the top product formed in the primary distillation is impossible, or is attended with difficulties. This may be the case, for example, when the primary column is operated at substantially atmospheric pressure and the feed thereto contains components (e.g., hydrogen) which are gaseous at normal temperatures and pressures. The feed may consist, for instance, of a hydrocarbon mixture from a reforming process or from a hydrodesulfurization treatment.

With reference to the drawing a desulfurized hydrocarbon oil having a relatively high content of normally gaseous components is introduced via line 10 to a central section of a primary distillation column 12 operated at atmospheric pressure. The feed is separated into a light fraction which contains gasoline and lighter components which are discharged overhead through a line 13 and into a heavy fraction containing kerosene and gas oil which is withdrawn through a line 14. In the present case, circulating reflux is used for the column 12, being supplied through a line 15, although conventional refluxing may also be employed. The cutting point in this first distillation is, for instance, at 165° C. The gasoline and gas fraction taken overhead in the line 13 passes to a cooler 16 where a partial condensation occurs and from there the stream is passed to an accumulator 17. The accumulator operates under a pressure of approximately 1.1 atmospheres absolute and at a temperature of about 45° C. The partly gaseous and partly liquid effluent from the cooler is phase separated in the accumulator 17.

The liquid product of the accumulator is removed via a line 18 and passed to a liquid pump 19. The gaseous product from the accumulator leaves in the line 20 going to a gas compressor 21 where it is pressurized to substantially the same pressure as the liquid leaving the pump 19. The pressurized gas exits from the compressor 19 in a line 22 and is combined with the pressurized liquid in a line 23 and passed to a second partial condenser 24. The partly gaseous and partly liquid product from the cooler 24 is collected in an accumulator 25. The pressure of this second accumulator is approximately 5 atmospheres absolute and the temperature is around 40° C. In this accumulator a partly gaseous and partly liquid product is again collected, since complete condensation of the top product of the primary distillation column 12 is not possible even at this relatively high pressure and relatively low temperature. The failure to completely condense may be attributed in part to the relatively high content of low boiling components in the feed to the distillation column 12.

Liquid is pumped from accumulator 25 by a pump 27 through a line 28 to a central section of a secondary distillation column 29 where it is separated into butane-free gasoline and fraction containing butane and lower boiling components. The butane-free gasoline is obtained as bottom product and is led through a line 30 to a distillation column 31. This column fractionates the gasoline feed into a light gasoline discharged overhead through a line 32 and into a heavy gasoline (naphtha) which is withdrawn in a line 33.

The top product of the secondary distillation column 29 is withdrawn through a line 35, cooled in a partial condenser 36 and collected in an accumulator 37. The pressure in the distillation column and in the accumulator 37 is approximately 12 atmospheres absolute and the temperature in the accumulator about 45° C. Some of the liquid separating in the accumulator 37 is pumped through a line 39 under the force of a pump 40 to the central section of a distillation column 41.

In the column 41, the condensate feed from the preceding column is separated into C₄ hydrocarbons and into a lower boiling fraction. The C₄ fraction is discharged through a line 43 and the top product is removed via a line 44 to a cooler 45 and from there to an accumulator 46. In this latter vessel a liquid consisting substantially of propane separates and is withdrawn through a line 47. A portion of the propane is returned as reflux to the column 41 via line 48. The pressure in the distillation column and accumulator 46 is approximately 24 atmospheres absolute and with the temperature of the accumulator being normally 45° C.

The gases condensing in the accumulators 37 and 46 are not withdrawn from the process as in conventional practice but recycled to the accumulator 25, this being done in the present case through lines 50, 51 and 53 which are provided with the necessary pressure reducing valves 54 and 55. In the case illustrated the recycling gases are first mixed with the compressed gas in the line 22 and then mixed with the pressurized liquid from pump 19.

If desired a portion of the naphtha fraction withdrawn through the line 33 may be recycled via a line 57 to the top product line 13 from the primary distillation column 12. The recycled naphtha may be mixed either upstream or downstream of the cooler 16 with the fraction supplied by the top product line 13. In this manner the loss of gases through the line 59 (the vent line to the primary accumulator 25), is still further reduced.

EXAMPLE

A crude oil is separated by distillation into a fraction boiling below 350° C. and a fraction boiling above 350° C. The former fraction is subjected to a hydrodesulfurization treatment in which a cobalt oxide/molybdenum oxide/alumina catalyst is used. After cooling the reaction product is subjected to an expansion in stages to separate the bulk of the dissolved gases and vapors. The liquid finally obtained (486 tons per 1,000 tons of crude oil), in which small quantities of light components such as hydrogen, hydrogen sulfide and normally gaseous hydrocarbons are still dissolved, is then separated by distillation into a number of fractions with the use of the plant shown in the drawing.

In the primary column 12 (for which circulating reflux is exclusively used again) a bottom product boiling above 165° C. is obtained at about atmospheric pressure (1.1 atm. abs.); the feed components boiling below this temperature pass overhead as primary top product (184.15 tons per 1,000 tons of crude oil) and are led through the line 13 and the cooler 16 where they are cooled to 45° C., into the accumulator 17 where the pressure is 1.1 atm. abs.

The liquid and the vapor are pumped, as shown in the drawing, to the accumulator 25 where the pressure is 5 atm. abs.; the temperature in this vessel is 40° C. The liquid collecting in this vessel is separated in the secondary distillation column 29 at elevated pressure into butane-free gasoline on the one hand and butane+lighter components on the other. The top product is obtained with the use of a conventional reflux system, as indicated in the drawing. The pressure and temperature in the accumulator 37 is 12 atm. abs. and 45° C., respectively. The bottom product is separated in the column 31 into a top product boiling below 93° C. and a bottom product boiling between 93° C. and 165° C.

The liquefied top product of the column 29 is separated in the column 41 into a bottom product consisting of butanes, and into a more volatile top product. The latter is again obtained with the use of a conventional reflux system, the pressure and the temperature in the reflux accumulator 46 being 24 atm. abs. and 45° C., respectively. The condensed top product consists substantially of propane and is withdrawn through the line 47.

Gases not condensing in the reflux accumulators are recycled through the lines 50, 51 and 53 to line 22 and ultimately find their way into the accumulator 25 whence the components of the feed supplied through the line 10 which in the process described cannot be condensed, are withdrawn through the line 59.

It is found that in this process of the invention the losses of vaporous material escaping through the line 59 are about 14.4 tons per 1,000 tons of crude oil. More detailed figures relating to the composition of this product are listed in column A of the table. These figures relate to the case in which there is no partial recycling of the bottom product of the column 31 through the line 57. With the use of this recycling the losses are further reduced; in the case in which 27.2 tons (per 1,000 tons of crude oil) of the bottom product of the column 16 (consisting of heavy gasoline), is recycled through the line 57, only approximately 13.8 tons of vaporous product per 1,000 tons of crude oil escapes through the line 59. More detailed figures relating to the composition of the vaporous product in this case are shown in column B of the table.

For comparison, corresponding figures are given in column C of the table which relate to the distillation hitherto known in which (1) the uncondensable gases and vapors from the reflux accumulators 37 and 46 are not recycle but withdrawn as such in a separated state; and (2) no recycling takes place through the line 57.

Column C of the table indicates the total losses of gases and vapors escaping from the accumulators 25, 37 and 46 in this case. An approximate total of 18.9 tons of gases and vapors are lost per 1,000 tons of crude oil, viz. considerably more than is the case with the use of the process according to the invention, even when in the latter process there is no recycling of heavy gasoline through the line 57. Hence in particular the losses of the valuable components butane and propane are greatly reduced.

Table

	A t./1,000 t. of crude oil	B t./1,000 t. of crude oil	C t./1,000 t. of crude oil
H ₂	0.023	0.022	0.023
CH ₄	0.446	0.438	0.440
C ₂ H ₆	2.847	2.803	3.172
H ₂ S.....	2.047	1.988	2.061
C ₃ H ₈	4.809	4.694	8.889
C ₄ H ₁₀	2.602	2.355	4.065
C ₅ +.....	1.673	1.635	0.236
Total.....	14.447	13.835	18.866

We claim as our invention:

1. In the processing of a hydrocarbon mixture containing normally gaseous components to recover liquid therefrom, wherein the top product of a first distillation zone is partly condensed and separated into a condensate and gas, and said condensate at least in part is introduced to a second distillation zone from which there is removed a liquid product and a second top product that is partly condensed to provide a second condensate and a second gas, the improvement comprising returning the second gas at least in part to the first top product at a point preceding its separation into condensate and gas, thereby significantly increasing the liquid recovered from the hydrocarbon mixture.

2. A process in accordance with claim 1 wherein the second condensate is subjected at least in part to a third distillation to provide a third top product which on partial

5

condensation and separation supplies a third condensate and a third gas, which gas is returned at least in part to the first top product at a point preceding its separation into condensate and gas.

3. A process in accordance with claim 1 wherein the returned gas is combined with the first top product following its partial condensation. 5

4. A process in accordance with claim 3 wherein the combined stream of returned gas and partly condensed first top product is cooled before being separated into condensate and gas. 10

5. A process in accordance with claim 1 wherein a portion of the liquid product of the second distillation zone is combined with the first top product to further increase liquid recovery. 15

6

References Cited in the file of this patent

UNITED STATES PATENTS

1,552,980	Blaise	Sept. 8, 1925
2,327,896	Houghland	Aug. 24, 1943
2,736,688	Kraft	Feb. 28, 1956

OTHER REFERENCES

Petroleum Refiner, II, September 1949, page 232.
 Petroleum Refiner, III, vol. 28, No 9, September 1949,
 pages 213, 216, 217, 220, 221, 225, 229, 232, 233, 236,
 237, and 240.
 Petroleum Refiner, April 1950, pp. 97 to 100.