

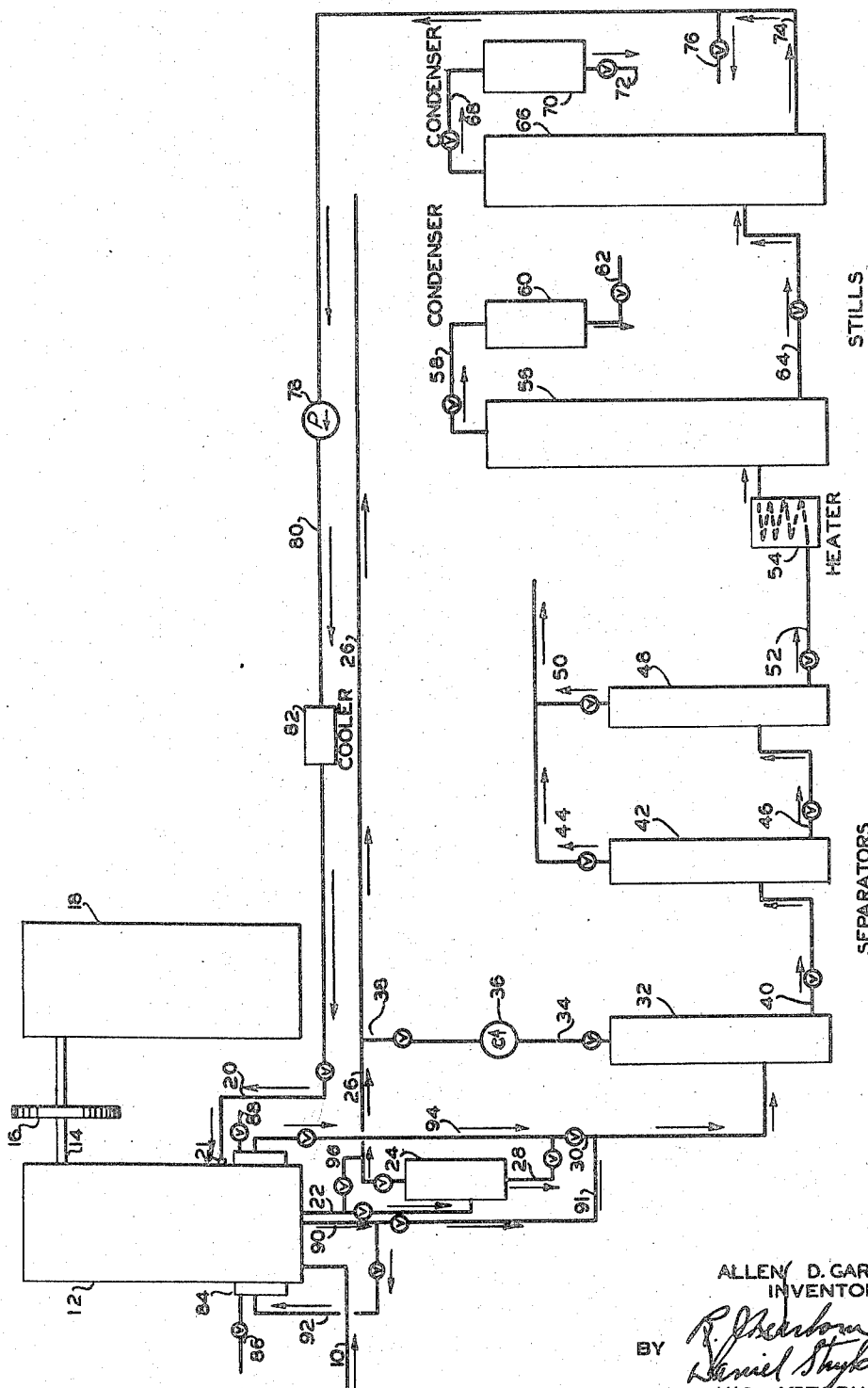
July 26, 1949.

A. D. GARRISON
RECOVERY OF HYDROCARBONS

2,477,367

Filed May 15, 1943

3 Sheets-Sheet 1



— 5 —

ALLEN D. GARRISON
INVENTOR
BY *R. Pearson*
Naniel Snyder
HIS ATTORNEYS

July 26, 1949.

A. D. GARRISON
RECOVERY OF HYDROCARBONS

2,477,367

Filed May 15, 1943

3 Sheets-Sheet 2

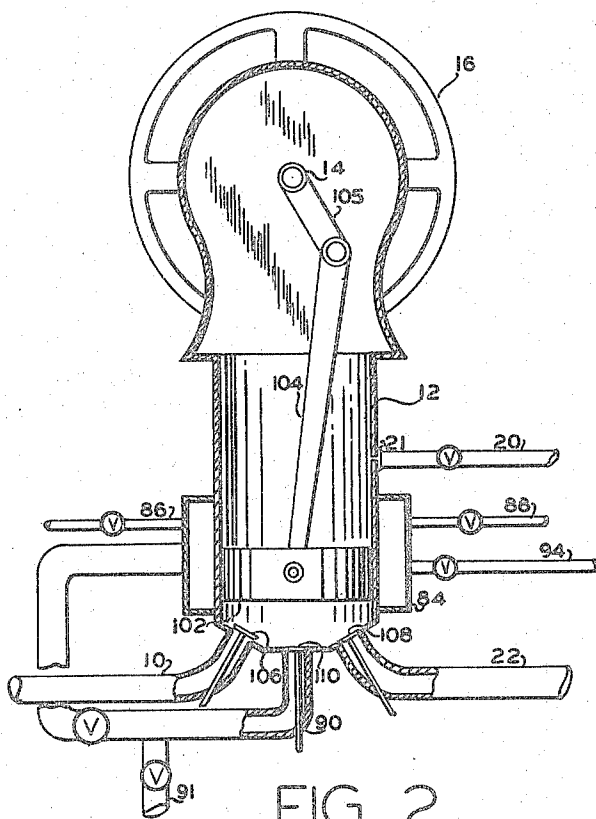


FIG. 2

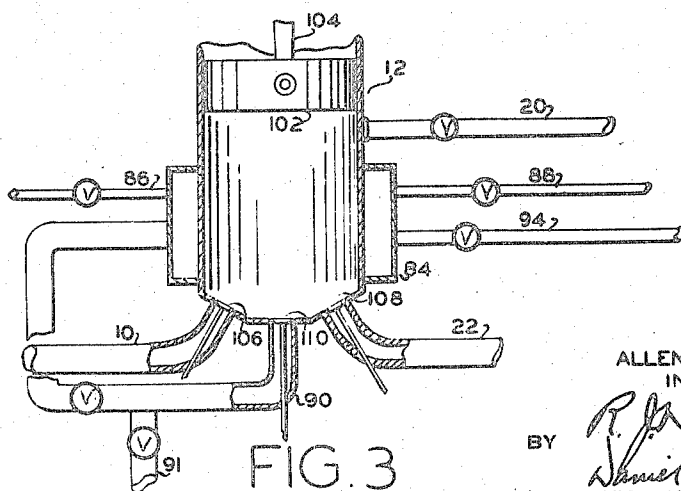


FIG. 3

ALLEN D. GARRISON
INVENTOR

BY

R. J. Anderson
Samuel Styer
HIS ATTORNEYS

July 26, 1949.

A. D. GARRISON
RECOVERY OF HYDROCARBONS

2,477,367

Filed May 15, 1943

3 Sheets-Sheet 3

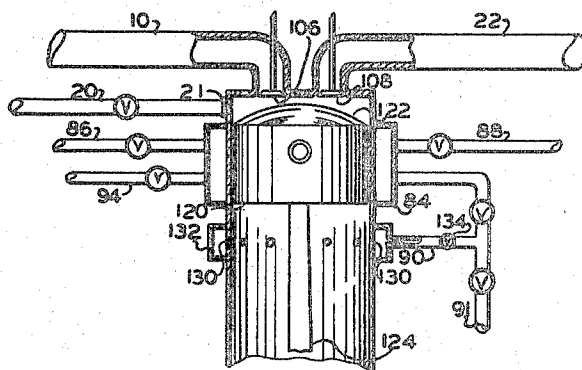


FIG. 4

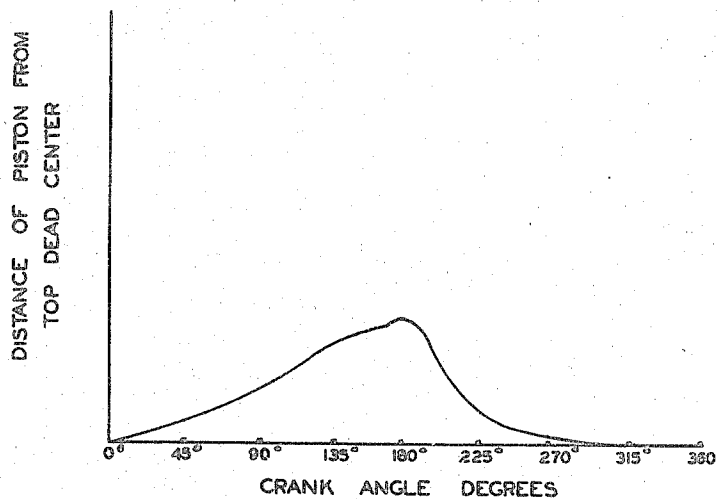


FIG. 5

ALLEN D. GARRISON
INVENTOR
BY *R. J. [Signature]*
Samuel [Signature]
HIS ATTORNEYS

UNITED STATES PATENT OFFICE

2,477,367

RECOVERY OF HYDROCARBONS

Allen D. Garrison, Houston, Tex., assignor to
Texaco Development Corporation, New York,
N. Y., a corporation of Delaware

Application May 15, 1943, Serial No. 487,105

5 Claims. (Cl. 62—123)

1

This invention relates to a process of recovering liquefiable hydrocarbons from high pressure hydrocarbon fluids. More particularly, the invention relates to a process of recovering liquefiable hydrocarbons from fluids flowed from high pressure wells of the distillate or condensate type.

A number of processes have been proposed for the recovery of liquefiable hydrocarbons from high pressure hydrocarbon fluids of the type flowed from distillate or condensate wells. For example, liquefiable hydrocarbons have been recovered from such fluids by processes in which the condensation of desired hydrocarbons is accomplished principally by reducing the pressure on the fluids and subjecting the fluids to cooling. These processes in general have the disadvantage that the percentage of recovery of desired hydrocarbons is relatively low and, further, the residual gases, which ordinarily must be returned at a high pressure to an underground formation, are obtained at low pressures. Various types of absorption processes have also been practiced and these processes have found considerable favor because of the high recovery of desired hydrocarbons. However, again the pressure of absorption is often low relative to the pressure required for returning residual gases to a formation, and the costs of compressing residual gases represent an important part of the costs of operating these processes.

It has also been proposed as a variation of the first type of process to accomplish the expansion of the high pressure hydrocarbon fluid in an expansion engine. By this procedure it is possible to achieve increased cooling of the fluid during expansion and to obtain useful work which may be employed in compressing residual gases. From the standpoint of recovery, however, this proposed process stands in the position of other processes wherein recovery is accomplished solely by reducing the pressure on the fluid and cooling.

It is a principal object of the present invention to provide a novel and efficient process for the recovery of liquefiable hydrocarbons from high pressure hydrocarbon fluids, particularly high pressure hydrocarbon fluids which are under conditions in the critical area and such that they are subject to retrograde condensation. A more specific object of the invention is to provide a

2

process for the treatment of a hydrocarbon fluid removed from a distillate or condensate well whereby desired liquefiable hydrocarbons may be recovered efficiently and residual gases may be obtained at a high pressure at a minimum cost.

Other objects of the invention in part will be obvious and in part will appear hereinafter.

In accordance with the present invention a mixture of hydrocarbons at a high pressure and a temperature such that the mixture is subject to retrograde condensation upon a reduction in pressure is treated by a process comprising expanding the mixture while doing work to a pressure at which desired condensation of liquefiable hydrocarbons takes place, contacting the mixture while in the expanded condition with an absorption oil to sweep out or collect condensed hydrocarbons and absorb additional hydrocarbons, compressing at least the residual gases while utilizing the work created in the expansion, and recovering the liquid hydrocarbons from the mixture.

The pressure to which the mixture is expanded, of course, will depend upon the characteristics of the mixture, but in general will not be below about 700 pounds per square inch and ordinarily will be within the range from about 1200 to 2200 pounds per square inch. This pressure is generally within the retrograde condensation range of the hydrocarbon mixture and may be the pressure at which maximum condensation of liquid takes place at the existing temperatures. While this pressure is sometimes referred to as the critical pressure, it is probably more accurately termed the pressure at the bottom of the retrograde condensation range, the term critical pressure being reserved for the pressure at the critical point for the mixture. See the article by D. L. Katz and F. Kurata, *Industrial and Engineering Chemistry*, vol. 32, No. 6, June 1939, pages 817 to 827.

The process may be carried out by expanding the hydrocarbon mixture and compressing at least the residual gases in the same zone or chamber, although separate expansion and compression chambers may be used, if desired. The liquid hydrocarbons are preferably removed from the expansion zone at the end of the expansion step. The process also preferably involves utiliz-

ing the liquid hydrocarbons removed from the expansion step for cooling the chamber in which the expansion and compression steps are carried out when these are both accomplished in the same chamber or for cooling the compression chamber when separate chambers are employed.

An embodiment of the invention comprises expanding the fluid relatively slowly, especially towards the end of the expansion, introducing the absorption oil a sufficient period before the start of compression to permit settling of liquid hydrocarbons, removing liquid hydrocarbons before compression is begun, and compressing the residual gases rapidly.

The process involves the advantage among others that it utilizes the expansion of the hydrocarbon mixture to create work and reduce the temperature of the mixture and at the same time accomplishes a high recovery of desired hydrocarbons. Thus, it is more efficient than the previously proposed processes which rely principally on reducing the pressure and cooling for recovery because a better recovery of desired hydrocarbons, particularly light hydrocarbons such as C₃ and C₄ hydrocarbons, is possible. As compared with conventional absorption processes, the process is advantageous in that it is thermodynamically sounder, requiring less fuel for compression and also less for circulation of absorption oil. The use of separated cold liquid hydrocarbons for cooling the zone in which expansion and compression is accomplished is effective not only to improve condensation but also to bring these liquid hydrocarbons to a desirable temperature for release of absorbed and condensed light hydrocarbons.

The invention will now be described in connection with the accompanying drawings in which Figure 1 is a flow sheet illustrating one manner in which the present process may be incorporated in a complete recovery system; Figure 2 is a diagrammatic view with parts in section of one form of expansion chamber which may be employed in the practice of the process; Figure 3 is a similar view of a part of the expansion chamber illustrated in Figure 2, showing the piston location at the end of the expansion step; Figure 4 is a similar view of another form of expansion chamber, this view showing the location of the piston at the end of the compression step; and Figure 5 is a graph illustrating the piston movement in one embodiment of the invention.

Referring to Figure 1, a suitable hydrocarbon mixture under a high pressure, for example a pressure of 1500 to 4000 pounds per square inch, enters the system through a line 10. When this fluid is a distillate well fluid it will ordinarily have been passed through a preliminary separator to remove hydrocarbons condensed due to the drop in pressure and temperature from the formation to the separator. Also, when the hydrocarbon mixture contains undesirable amounts of water which might cause difficulty because of hydrate formation, the mixture will have been subjected to dehydration by conventional means. The hydrocarbon mixture is conducted by means of line 10 to a combined expansion and compression engine represented generally at 12. This engine may be of the type disclosed in Figures 2 and 3 or Figure 4, which will be described hereinafter.

Leading from the side of the engine is a shaft 14 to which is attached a flywheel 16. This shaft is coupled to a suitable source of auxiliary power represented generally at 18. This source may be an internal combustion engine of any suitable

type. The hydrocarbon mixture is expanded in engine 12 to a desired pressure within the retrograde condensation range of the mixture while doing work. This results in condensation of hydrocarbons in the form of a mist or droplets because of the decrease in both pressure and temperature. At or near the end of the expansion step absorption oil is introduced into the chamber through valved line 20. This line is provided at its end with a nozzle indicated generally at 21 whereby the absorption oil is introduced in the form of a spray. The absorption oil spray acts to sweep the condensed hydrocarbons from the residual gases in the expansion chamber and also to absorb, to a certain extent, additional hydrocarbons.

In accordance with one embodiment of the invention, the resulting mixture, including residual gases and condensed liquid hydrocarbons with absorption oil, is compressed in the chamber 12 to a pressure in excess of that at which the mixture entered the engine. This embodiment is based upon the fact that while the condensation resulting from a reduction in pressure is reversed upon the pressure being raised, the condensation and vaporization do not proceed at the same rate. Thus, while the condensation takes place substantially instantaneously, a time interval is required for vaporization. Also, vaporization is retarded by the relatively heavy hydrocarbons in the absorption oil, which is usually a hydrocarbon mixture boiling within a range above the boiling range of the bulk of the liquefiable hydrocarbons. The heterogeneous mixture is removed from the engine through valved line 22 which leads to a separator 24. This separator may be a vessel provided with baffles or other means of separating liquids and gases, or it may be a precipitator such as a Cottrell precipitator. The separator should be located close to the engine in order to reduce or eliminate revaporization of liquid hydrocarbons. The residual gases are removed from the separator through a valved line 26 and may be returned to a distillate formation for the purpose of maintaining pressures. The liquid is removed from the bottom of separator 24 through valved line 28, and passes into valved line 30 and into a separator 32.

This separator is maintained at some pressure below the pressure on the hydrocarbon liquid at the time of separation from residual gases, for example a pressure of about 1000 pounds. At this pressure light gases pass overhead through valved line 34. These gases, which consist mainly of methane and ethane, may be compressed by means of compressor 36 to the same pressure as the residual gases in line 26. At the raised pressure they are passed through valved line 38 and combined with the gases flowing in line 26. The liquid is removed from the lower portion of separator 32, through valved line 40 and is passed into a lower pressure separator 42. In this separator the pressure may be of the order of 500 pounds per square inch and additional light hydrocarbons are evolved. These light hydrocarbons may be subjected to absorption in known manner, or, as shown, they may be passed overhead and combined with gases from a lower pressure separator to be described.

The liquid is then removed from the lower portion of separator 42, passed through valved line 46 leading to a third separator 48, which may be at a low pressure of the order of 50 to 80 pounds per square inch. Here additional light hydro-

5

carbons are evolved and are passed overhead through valved line 50 and combined with the gases from separator 42. These combined gases may be subjected to additional absorption or they may be employed for fuel without treatment. The liquid removed from the separator 48 is passed through valved line 52 to a heater 54 where it is heated to a sufficiently high temperature for distillation. The heated oil is introduced into a still 56 which may be maintained at a pressure of the order of about 60 pounds per square inch. In this still liquefiable hydrocarbons boiling, for example, below 320° F. are vaporized and removed overhead through valved line 58. The vapors are condensed in condenser 60 and passed to storage through valved line 62.

The remaining liquid is removed from the bottom of still 56 through valved line 64 and is passed to another still 66. The remainder of the condensed and absorbed hydrocarbons are vaporized in this still, which is maintained at a lower pressure than still 56. The vapors are removed overhead through valved line 68, condensed in condenser 70 and passed to storage through valved line 72. The remaining liquid, which constitutes a suitable absorption oil, is removed from the bottom of the still through line 74. A portion of this liquid may be removed from the system through valved line 76. Line 74 leads to a pump 78 which serves to raise the pressure on the liquid to a pressure slightly above the pressure in the expansion step in the expansion engine. The liquid at the higher pressure passes through line 80 to a cooler 82, wherein the temperature of the absorption oil is reduced to a suitable temperature for injection into the expansion chamber, this being accomplished by flowing the oil through line 20, as previously explained. When operating in accordance with the present procedure the expansion chamber may be cooled by means of a cooling jacket 84, which is supplied with a cooling liquid such as water through valved line 86, the water passing out through a line 88.

In accordance with another embodiment, also illustrated in Figure 1, at the end of the expansion step and before compression is accomplished in the expansion engine, liquid hydrocarbons, including those condensed from the gases and the absorption oil, are removed from the expansion chamber through line 90. This liquid may be passed directly into separator 32 through a line 91 and line 30. In accordance with the preferred procedure, however, this liquid is passed through valved line 92 and through jacket 84 where it is employed for cooling the expansion and compression chamber 12. The hydrocarbon liquid is removed from the cooling jacket 84 through valved line 94, which leads to line 30, through which the liquid hydrocarbons enter separator 32. When operating in this way the compressed gases leaving the chamber 12 through line 22 will be substantially denuded of liquid phase material and the use of separator 24 may be eliminated. Thus, the gases may be passed through valved line 96 and directly into line 26.

Referring now to Figure 2, this figure illustrates a simple form of apparatus adapted for use in the expansion and compression steps. In the figure, unnecessary details have not been illustrated in order to simplify description of the process. The reference numerals refer to corresponding parts of Figure 1. The apparatus illustrated comprises a familiar type of engine provided with a piston 102, connecting rod 104

6

connected to the crank 105, intake valve 106, exhaust valve 108 and a valve 110 for removal of liquid hydrocarbons. The engine is shown in the position it will occupy at the beginning of the expansion step, shortly after the beginning of the upward movement of the piston. Assuming that the high pressure hydrocarbon fluid is received at a pressure of about 3000 pounds per square inch, the gas at this pressure enters through the intake valve 106 causing the piston to do work. The introduction of the high pressure fluid is controlled so as to attain the final desired pressure at the end of expansion, for example, a pressure of 1500 pounds per square inch. When the amount of fluid required to accomplish this result has been introduced the intake valve is closed and the expansion allowed to proceed.

At the end of the expansion the piston will be in the position shown in Figure 3. Just prior to the end of the expansion stroke the desired amount of absorption oil, for example, 2 to 5 gallons per 1000 cubic feet of high pressure fluid at standard conditions, is introduced through line 20, preferably so as to fall in a spray within the chamber. As previously described, the resulting liquid hydrocarbons, including the condensed hydrocarbons and the absorption oil may remain in the mixture during the compression step. In this case all of the valves are closed until the pressure desired on the residual gas is reached, at which point the exhaust valve 108 is opened a regulated distance and the compression stroke is continued while forcing out mixed gases and liquid hydrocarbons at the high pressure. In the example under consideration, this pressure may be about 3500 pounds per square inch.

It is preferred, however, to open valve 110 for a brief period, prior to substantial compression in order to remove from the chamber the hydrocarbon liquid formed due to the reduction in temperature and pressure and due to the introduction of the absorption oil. After the liquid has been removed, the valve 110 is closed and the compression proceeds as described above. Thus, in this case, the residual gases are obtained at a high pressure apart from the condensed and absorbed hydrocarbons.

The engine is designed so as to contain only a small amount of high pressure gas at the end of the compression step, and the introduction of the high pressure hydrocarbon fluid through the inlet valve is started when the pressure below the piston is but slightly less than the pressure of the inlet gas.

Reviewing the operation of this embodiment in the engine shown in Figures 2 and 3, it will be noted that the inlet valve is opened when the piston is a little above bottom dead center and the pressure in the cylinder is slightly below the pressure of the inlet gas. The absorption oil is introduced shortly before the piston reaches top dead center so that the oil may act on the condensed hydrocarbons and the gases during the time interval between the introduction of the absorption oil and the reaching of top dead center by the piston. The valve for removal of liquid hydrocarbons may be opened at about top dead center and is closed before any substantial compression. The exhaust valve will be opened when the residual gases reach the desired pressure, which pressure will be obtained in a gas where the pressure is to be about double the expansion pressure, when the piston is just shortly past the middle of the compression stroke. The exhaust valve will then be closed at about bottom dead center.

7

In Figure 4 there is illustrated another form of apparatus for carrying out the invention. Figure 5 illustrates the manner in which the expansion and compression steps are accomplished in another embodiment of the invention. Although the type of engine shown in Figure 4 can be used in a process as illustrated in Figures 2 and 3, it will be particularly described in connection with the embodiment illustrated in part by Figure 5. This embodiment comprises expanding the high pressure hydrocarbon fluid relatively slowly, introducing the absorption oil just before the end of the expansion, removing hydrocarbon liquid at the end of the expansion step, and then quickly compressing the residual gases. By expanding and introducing the absorption oil in this way, time is allowed for condensation and collection of condensed hydrocarbons by the absorption oil. The relatively short compression period is advantageous in that problems of heat dissipation are reduced and the efficiency of compression is increased.

The engine of Figure 4 is provided with a piston 120 having a convex face 122. A connecting rod 124 serves to transmit force to and receive force from the piston. The valve for removal of liquid hydrocarbons from the chamber at the end of the expansion takes the form of ports 130 which are opened and closed by the motion of the piston. The liquid passing through the ports enters a ring 132 and is removed through line 90 as previously described. In this case, however, the line 90 is provided with a check valve 134 which prevents return of fluid through the ports when the piston is in the upper portion of the cylinder.

Figure 4 illustrates the position of the piston and valves at the end of the compression stroke and after closing of exhaust valve 108. After the piston has moved down to reduce the pressure in the chamber to a pressure slightly less than the pressure of the incoming hydrocarbon fluid, inlet valve 106 will be opened to admit the high pressure fluid into the chamber.

An engine such as shown in Figure 4 is well adapted for operating the process so as to vary and control the expansion and compression steps. This manner of operating will be understood by referring to the graph of Figure 5. The introduction of the fluid is begun at a point past bottom dead center (0 crank angle degrees) at which the pressure in the cylinder is about equal to the pressure on the fluid and is continued until an amount is introduced adapted to yield the desired final pressure. The graph shows that the introduction of fluid and expansion are accomplished over about 175 crank angle degrees. The ports 130 will remain closed until about this point is reached and then will be opened for about 5 degrees of rotation, through bottom dead center, to permit removal of liquefiable hydrocarbons and absorption oil from the engine. These liquid products will have settled on the convex face of the piston and will have flowed to the ports. In general, the introduction of absorption oil should be started at about 160 to 165 degrees of rotation from top dead center.

After the piston has reached bottom dead center the compression is accomplished quickly. As the piston moves upward the ports 130 are first closed, and then the compression is accomplished substantially entirely over about 110 crank angle degrees. Exhaust valve 108 is opened when the pressure on the residual gases has reached the de-

8

sired point and these gases are used as before described.

It will be understood that the invention in its broader aspects is not limited to any of the foregoing specific ways of operating, and that the devices described are presented primarily for the purposes of illustrating the operation of the process rather than highly developed mechanisms. Thus, the piston movement disclosed in Figure 5 may be accomplished by any suitable mechanism for controlling the movement of pistons, several of which are known. It will also be understood that when controlling the expansion and compression as shown in Figure 5, it is not necessary to remove the liquid products at the end of the expansion. For example, an engine such as illustrated in Figure 3 may be operated so as to accomplish controlled expansion and compression, and the entire mixture of liquid products and residual gases may be removed from the cylinder at a high pressure and separated at this pressure.

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

I claim:

1. The process of recovering liquefiable hydrocarbons from a hydrocarbon mixture which is substantially in a single phase at a high pressure such that the mixture is subject to retrograde condensation upon a reduction in pressure, which comprises expanding the hydrocarbon mixture in an expansion and compression chamber substantially within the retrograde condensation range while doing work, the resulting reduction in pressure and temperature causing the formation of liquefiable hydrocarbons in the liquid phase, intimately contacting the expanded mixture in said chamber with absorption oil to collect the hydrocarbons in the liquid phase, withdrawing liquefied condensate and absorption oil from said chamber separately from expanded gases compressing at least the residual gases in said chamber while utilizing the work created in the expansion, and recovering said hydrocarbons in the liquid phase from the withdrawn liquefied condensate and absorption oil.

2. The process of recovering liquefiable hydrocarbons from a hydrocarbon mixture which is substantially in a single phase at a high pressure such that the mixture is subject to retrograde condensation upon a reduction in pressure, which comprises expanding the hydrocarbon mixture in an expansion and compression chamber substantially within the retrograde condensation range while doing work, at least the latter portion of the expansion step being at a relatively slow rate, the resulting reduction in pressure and temperature causing the formation of liquefiable hydrocarbons in the liquid phase, intimately contacting the expanded mixture in said chamber toward the latter part of the expansion step with absorption oil to collect the hydrocarbons in the liquid phase, removing liquid hydrocarbons from the expanded mixture in said chamber while in the expanded state leaving residual gases, and compressing said residual gases at a relatively rapid rate in said chamber while utilizing the work created in the expansion.

3. The process of recovering liquefiable hydrocarbons from a hydrocarbon mixture which is substantially in a single phase at a high pressure

such that the mixture is subject to retrograde condensation upon a reduction in pressure, which comprises expanding the hydrocarbon mixture substantially within the retrograde condensation range while doing work, the resulting reduction in pressure and temperature causing the formation of liquefiable hydrocarbons in the liquid phase, intimately contacting the expanded mixture with absorption oil to collect the hydrocarbons in the liquid phase, removing liquid hydrocarbons at a low temperature from the expanded mixture while in the expanded state leaving residual gases, compressing said residual gases while utilizing the work created in the expansion, and passing said liquid hydrocarbons into indirect heat exchange relationship with the residual gases during compression.

4. The process of recovering liquefiable hydrocarbons from a hydrocarbon mixture which is substantially in a single phase at a high pressure such that the mixture is subject to retrograde condensation upon a reduction in pressure, which comprises expanding the hydrocarbon mixture in an expansion and compression chamber substantially within the retrograde condensation range while doing work, the resulting reduction in pressure and temperature causing the formation of liquefiable hydrocarbons in the liquid phase, intimately contacting the expanded mixture in said chamber with absorption oil to collect the hydrocarbons in the liquid phase, removing liquid hydrocarbons at a low temperature from the expanded mixture while in the expanded state in said chamber leaving residual gases, compressing said residual gases while utilizing the work created in the expansion, and passing said liquid hydrocarbons into indirect heat exchange relationship with the residual gases during compression.

5. The process of recovering liquefiable hydrocarbons from a hydrocarbon mixture which is substantially in a single phase at a high pressure such that the mixture is subject to retrograde condensation upon a reduction in pressure, which comprises expanding the hydrocarbon mixture in an expansion and compression chamber substantially within the retrograde condensation range while doing work, the resulting reduction in pressure and temperature causing the formation of liquefiable hydrocarbons in the liquid phase, introducing at a predetermined period in the expansion step a spray of absorption oil into the expanded mixture in said chamber to collect the hydrocarbons in the liquid phase, discharging liquid condensate and absorption oil from said chamber at substantially the end of said expansion step while confining residual gases within said chamber compressing the residual gases in said chamber while utilizing the work created in the expansion, exhausting the recompressed residual gases from said chamber at a high pressure, and then repeating the cycle.

ALLEN D. GARRISON.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,405,155	Paris	Jan. 31, 1922
1,437,102	Garner et al.	Nov. 28, 1922
1,463,782	Armstrong	Aug. 7, 1923
2,309,075	Hill	Jan. 19, 1943
2,313,681	Steedman	Mar. 9, 1943
2,364,660	Reid	Dec. 12, 1944
2,374,104	Kirkbride	Apr. 17, 1945