

June 24, 1952

P. H. DEMING

2,601,599

METHOD OF RECOVERING LIQUEFIABLE HYDROCARBONS FROM GASES

Filed Nov. 26, 1948

4 Sheets-Sheet 1

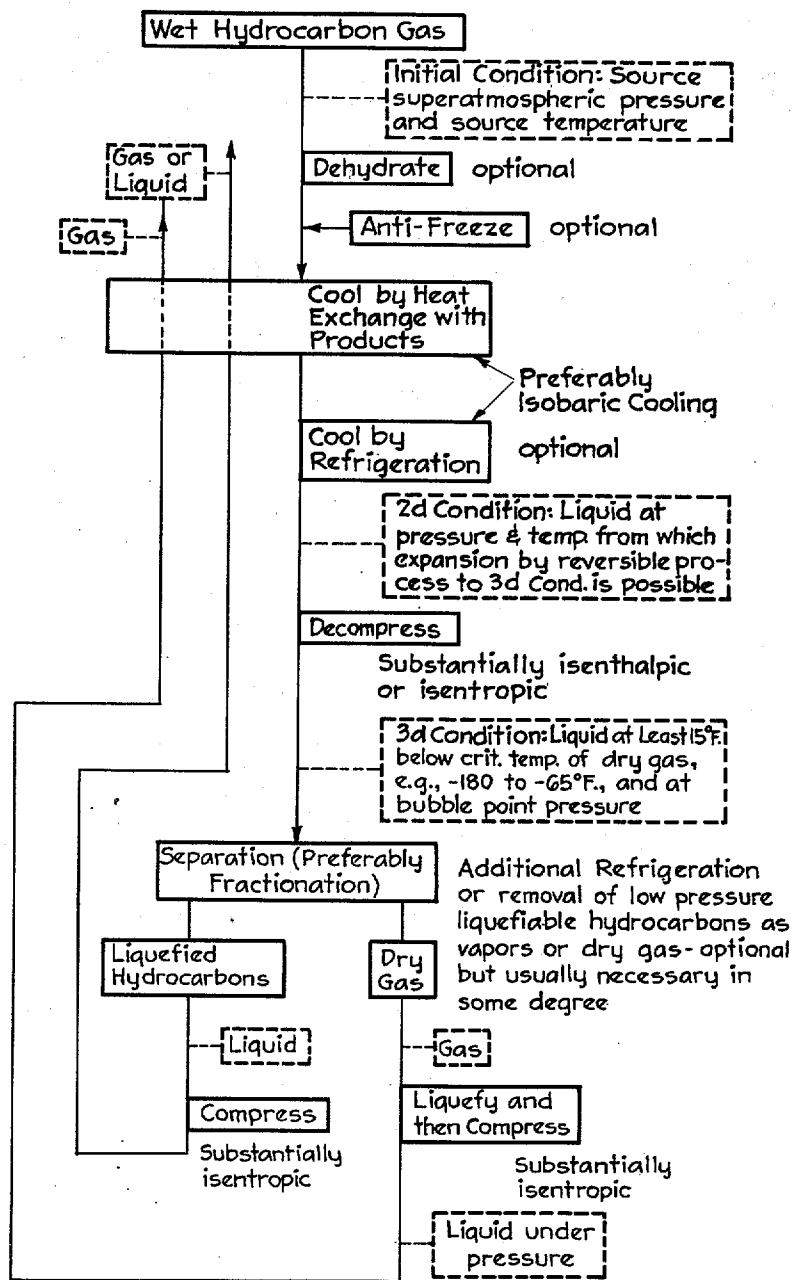


Fig. 1

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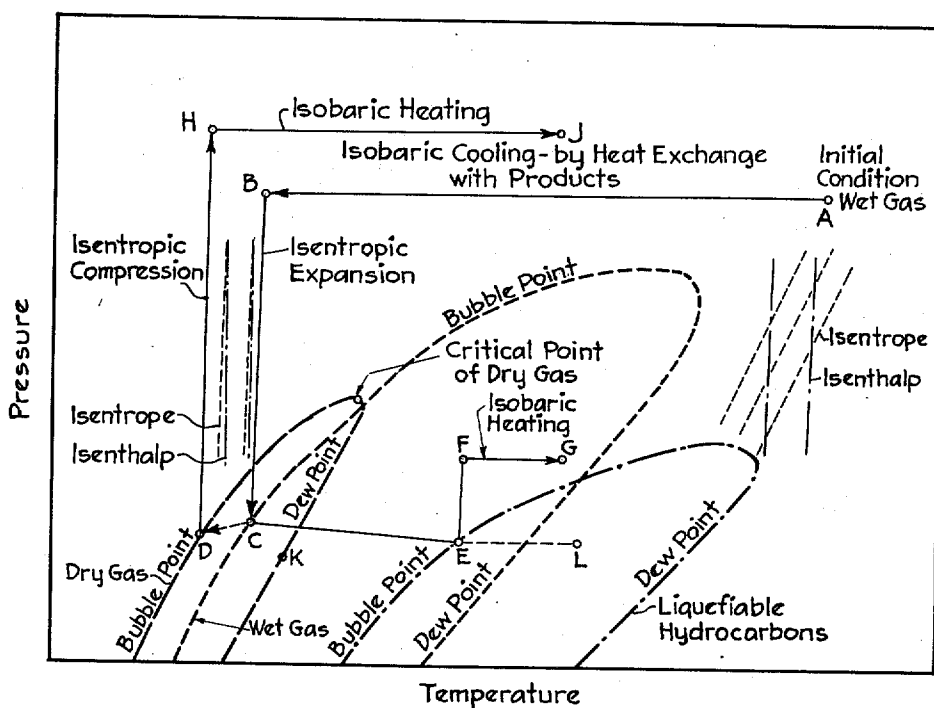
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METHOD OF RECOVERING LIQUEFIABLE HYDROCARBONS FROM GASES

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4 Sheets-Sheet 2



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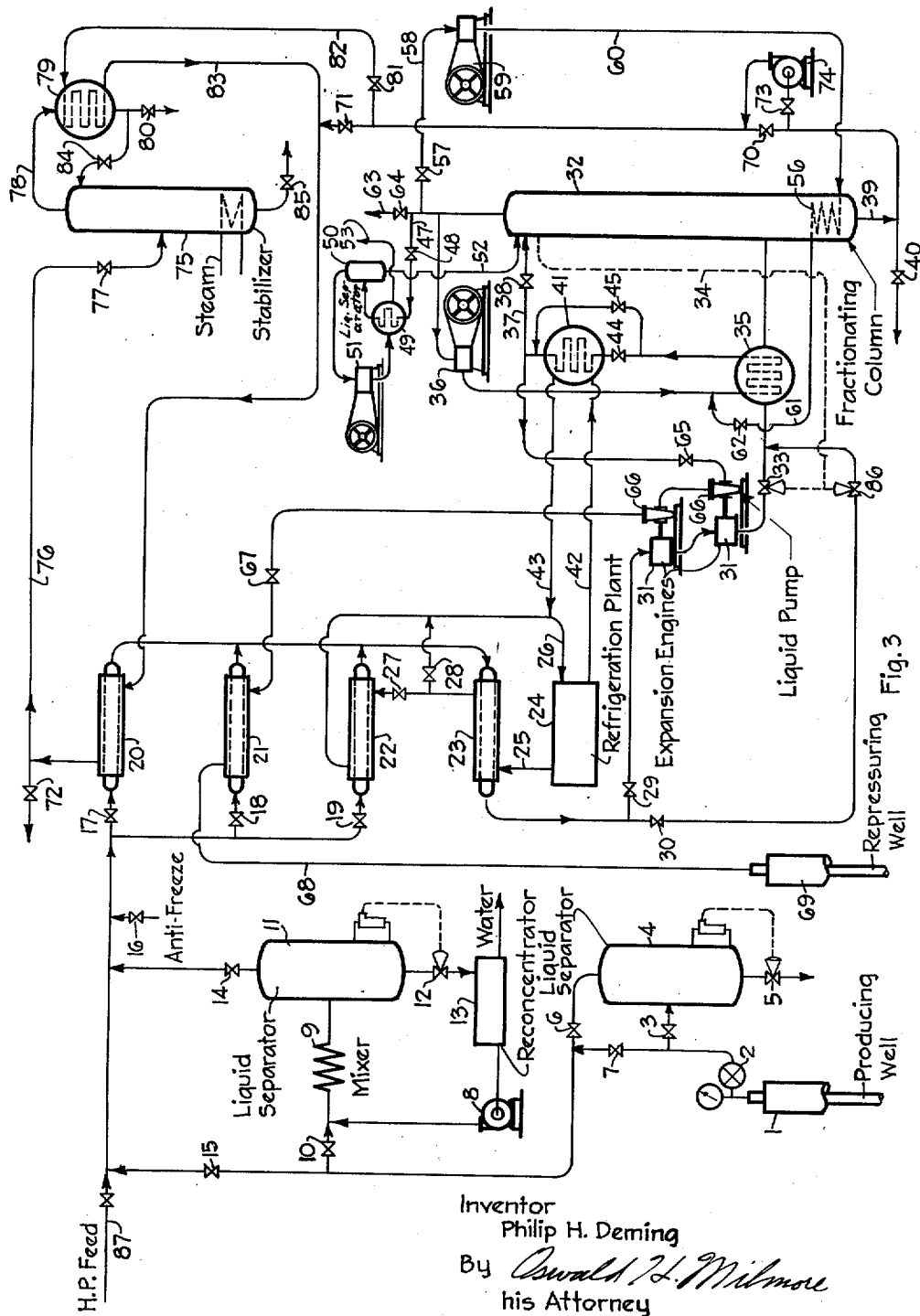
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4 Sheets-Sheet 4

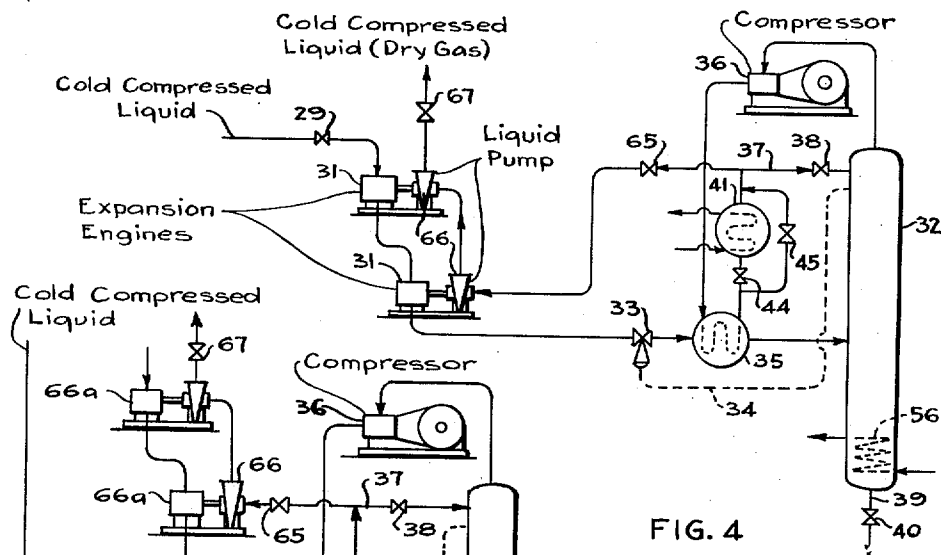


FIG. 4

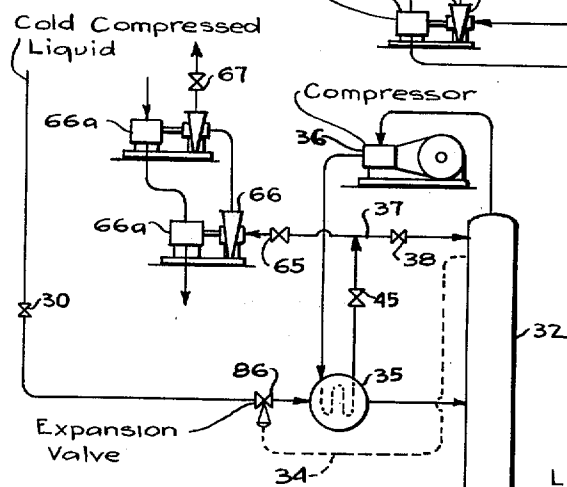


FIG. 5

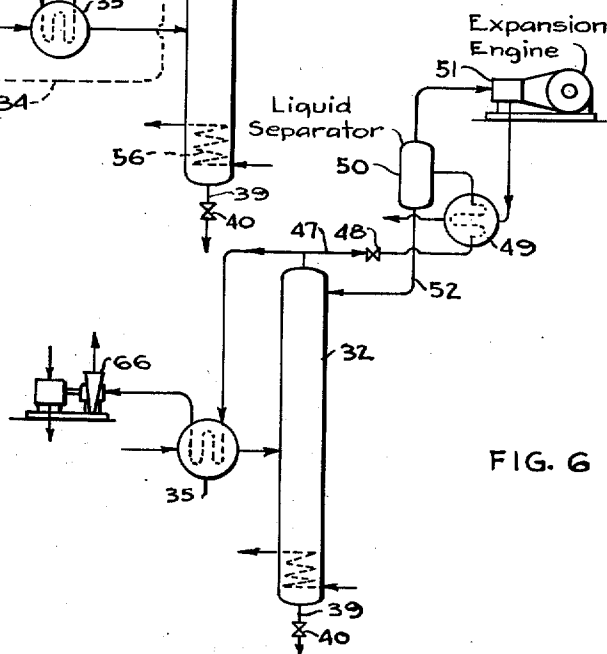


FIG. 6

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METHOD OF RECOVERING LIQUEFIABLE
HYDROCARBONS FROM GASES

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17 Claims. (Cl. 166—21)

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This invention relates to the recovery of liquefiable hydrocarbons from gases containing them and occurring initially under high pressure. More particularly, it is concerned with a recovery method in which the dry gas, stripped of the desired liquefiable hydrocarbons, may be again brought to a high pressure for any purpose. An example of an application of the process is in the operation of high pressure oil and gas wells, in which hydrocarbons of gasoline boiling range or lighter hydrocarbons, such as butane, propane, and ethane are recovered from a gas flowing from a production well and the residual gas is again introduced into the oil reservoir through the same or a different well, known as a repressuring well, to maintain the pressure therein. The method may, however, be applied to hydrocarbon gas mixtures from any source, such as products of high pressure pyrolysis, and it is not necessary that the residual gas be used for repressuring an oil reservoir.

It has become increasingly common to encounter deep producing formations in which the petroleum occurs under high pressures, such as 2000 to 5000 pounds per square inch or higher. When the well fluids are recovered in a gaseous state they frequently contain methane, ethane, and appreciable though lesser amounts of hydrocarbons heavier than ethane, such as, for example, constituents suitable for use as motor fuels, gasoline, butane and propane. These heavier constituents are in the vapor phase due to the well known phenomenon of vaporization of higher-boiling constituents in gas at high pressures, sometimes referred to as retrograde vaporization, described by Katz and Kurata in Industrial and Engineering Chemistry, volume 32, pages 817-827, June 1940.

When the pressure within an oil reservoir falls some of the heavier hydrocarbons are condensed, i. e., are separated from the gaseous solution just described. This phenomenon is known as "retrograde condensation" and is objectionable because the condensed hydrocarbons cannot be recovered from the formation with the gas. This loss of liquefiable hydrocarbons is commonly referred to as "retrograde loss."

In the recovery of such heavier constituents as condensate from high pressure gas fields, dry gas is recycled to the gas-bearing structure to prevent retrograde loss by maintaining the well pressure and to store the natural gas for future use. The recovery method normally employed involves the expansion of the wet gas withdrawn from the well to recover the condensate, (which

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expansion may involve retrograde condensation) and the reduction of the pressure to such a level that absorption methods may be conveniently employed to recover the balance of the butanes and heavier fractions in the wet gas, it being impossible to recover all of the liquefiable constituents by mere retrograde condensation. The dry gas remaining is then recompressed for return to the producing structure.

10 An inherent difficulty in such a process is the irreversibility of the expansion of the wet gas. This irreversible expansion is compensated for by installing mechanical compressors and by absorption and stripping of the gas for the recovery of condensate. It has been proposed to reduce pumping costs by expanding the gas in an engine to produce mechanical or kinetic energy, and to utilize such energy to drive the compressors in the recompression stage; however, such proposals have dealt with gases at relatively high temperatures at which the gases have comparatively low densities, thereby requiring large volumetric capacity and, consequently, heavy capital outlays. Expansion and compression of gas are not, as carried out in practice, thermodynamically reversible processes, and such operations are not very efficient. The operation of such bulky equipment incident to the handling of such large volumes of gases and the great capital costs prevented economies to be realized from the use of such expansion engines.

Another object is to provide a method of operating high pressure wells in which the energy available in expanding the high pressure gas-vapor mixture to the pressure required for the facile recovery of the heavier constituents may be more effectively used to produce mechanical energy which may be used to recompress the residual, dry gases to the pressure required for return to the formation at a low temperature, or as a work credit to reduce net recompression costs. Further, it is an object to provide a method of this type wherein the expansion and compression approach more closely reversible processes; and wherein expansion and compression are effected under conditions at which small mechanical installations can be utilized, thereby eliminating high capital outlays and making the realization of economies possible.

Another object of the invention is to provide a recovery method of the type described in which the residual gas is recompressed under conditions requiring a lower expenditure of energy.

Still another object is to provide a method of

recovering heavier constituents from gaseous hydrocarbon mixtures occurring initially at high pressures in which the quantitative recovery of the desired constituents is improved.

A specific object of the invention is to provide an improved method for recovering relatively heavier constituents from a mixed hydrocarbon gas containing the same together with fixed gases, such as methane and/or ethane, in which the initial gas is cooled and expanded to the pressure and temperature requisite for efficient separation of the heavier constituents substantially by reversible processes, and the residual gas is again heated and recompressed substantially by reversible processes, whereby the cooling, heating and pumping costs are greatly reduced. A further object is to provide a process wherein lighter constituents, e. g., ethane and/or propane, may be recovered.

Still a further specific object is to provide an improved method for recovering relatively higher constituents from a mixed hydrocarbon gas of the type described in which the separation of the desired constituents is effected at a temperature below the critical temperature of the dry gases, i. e., below retrograde condensation range, whereby liquefaction of such gases and the more efficient fractionation of the mixture become possible.

The feed mixture treated according to the method described herein is, in keeping with common usage, designated as "wet gas," it being understood that such material is usually a well fluid produced from a distillate or condensate well, but may be obtained from crude oil wells or even from refinery operations. It is usually produced at pressures above the critical pressure of the dry gas from wells tapping a distillate reservoir. It should be noted, however, that "wet gas," as understood in the art, occurs not only as a true gas but occurs variously at temperatures above the critical temperatures of the wet gas and/or at pressures above the critical pressure of the wet gas, under some of which conditions the designation of the hydrocarbon fluid mixture as a "gas" is not always rigidly significant. The term "wet gas" is, therefore, intended to include all mixtures commonly designated in the art as such, i. e., not only hydrocarbon fluid mixtures occurring at temperatures corresponding to or higher than their dew points and below their critical pressures, but also all hydrocarbon fluid mixtures occurring at temperatures above their critical temperatures regardless of pressure, as well as those occurring near to or above their critical pressures but above the critical temperature of the dry gas contained therein, even though their temperatures are somewhat below the critical temperatures of the fluid mixture. Wet gas consists predominantly of dry gas and minor amounts, usually less than 20%, of liquefiable hydrocarbons, and usually contains upwards of 75% methane.

The "dry gas" is the more volatile part of the wet gas, remaining after the desirable heavier constituents have been separated therefrom and usually consists predominantly of methane or ethane or their mixture; it may contain minor amounts of heavier hydrocarbons, such as propane and even higher-boiling materials, depending upon the efficiency of the separation. Dry gas usually contains from 75% to 95% methane. The critical temperature of such dry gas is usually between about -50 and -115° F.

The invention will be described by reference

to the accompanying drawings forming a part of this specification, wherein:

Fig. 1 is a process flow chart indicating the main steps according to a preferred form of the invention;

Fig. 2 is a pressure-temperature diagram showing dew point and bubble point curves for typical hydrocarbon materials occurring in the process and indicating qualitatively one possible set of operating conditions; and

Fig. 3 is a schematic flow diagram illustrating one possible application of the method.

Figs. 4, 5 and 6 are schematic flow diagrams illustrating alternate processes shown in Fig. 3, the numeral designations in the different figures referring to equivalent elements.

According to the present invention, as indicated in Fig. 1, an initial wet gas is liquefied by cooling it to a temperature below the critical temperature of the dry gas to be ultimately rejected therefrom, and the liquid is expanded or decompressed in a decompression stage while in the liquid state substantially to the bubble point of the liquefied wet gas. Dehydration and/or addition of anti-freeze to the wet gas may precede cooling. There may not be, and in the usual case wherein the wet gas is above its critical pressure there will not be, any change in phase observed during the liquefaction process. The resulting liquefied and expanded wet gas is then treated to form a vapor phase (i. e., a phase less dense than the said resulting wet gas) and a new residual liquid phase, by further decompression to a pressure below the bubble point pressure and/or by the addition of heat. The further decompression, when used, may be effected in a separate stage (as by flow through an expansion nozzle) or may be effected in the above-mentioned decompression stage by continuing the decompression therein to a lower pressure. The decompression may even be carried so far beyond the bubble point pressure as to result in substantially complete vaporization of the liquid; in this case the residual liquid phase is formed by condensing part of the vapor by refrigeration. The resulting vapor phase, regardless of how it was formed, contains the dry gas and is separated in a separating zone from the residual liquid phase which contains the heavier constituents to be recovered from the gas. Such heavier constituents are commonly known as "liquefiable hydrocarbons."

The cooling mentioned above is the cumulative effect of indirect cooling and expansion, i. e., it is not essential that the indirect cooling step alone be sufficient to lower the temperature to the required separation temperature. Provided that liquefaction to the specified temperature is attained, the expansion may be effected simultaneously with indirect cooling or may even wholly or in part precede it. In the preferred embodiment, however, the cooling is effected substantially isobarically by indirect heat exchange, utilizing the dry gas being discharged from the process to absorb at least a part of the heat. The recovered liquefied hydrocarbons may also be used to cool the wet gas when the amount thereof is sufficient to justify their use economically. Additional refrigeration may be optionally employed, either before or, preferably, following heat exchange of the wet gas with the outgoing products. The expansion preferably follows the indirect cooling step, whereby important operating economies are effected. The separation of the liquid phase from the vapor

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phase formed after expansion may be a simple flash separation, but in the preferred embodiment the use of a packed column or bubble tray or equivalent fractionation column is employed. It is an important feature of this invention that the separation is effected under conditions permitting the use of a fractional distillation or rectification unit, whereby greater quantitative recovery of the heavier constituents of the wet gas may be achieved. Additional refrigeration and/or removal of some of the products, e. g., dry gas or recovered constituent, at a pressure below its partial pressure in the feed to the separator is optional, but is usually necessary in some degree in the separating stage.

Separation of the vapor containing the dry gas and the liquid containing the liquefiable hydrocarbons is possible in the method according to this invention because temperatures below the critical temperature of the dry gas and the correspondingly low pressures are used. At higher pressures complete rectification of hydrocarbon mixtures is not possible. (See the article "High-Pressure Rectification" by L. W. T. Cummings, vol. 23. *Industrial and Engineering Chemistry*, pages 900-902, August 1931).

To permit effective separation by fractionation it is desirable to cool the wet gas to at least 15° F. below the critical temperature of the dry gas, and temperatures below the critical temperature of methane are preferred. Accordingly, the upper limit of the desirable operating range depends upon the critical temperature of the dry gas and may be between -65° F. and -130° F. for the gases most commonly encountered, but the preferred temperature is below -115° F. The lower limit is dependent upon the limits of the refrigerating equipment and may be below about -180° F.

All or part of the separated vapor or dry gas may be recompressed for return to the well. In the preferred embodiment, the separated vapor is recompressed at a temperature below its critical temperature, and is compressed in the liquid state, thereby reducing compression costs by a smaller expenditure of kinetic energy and the handling of a smaller volume of fluid, and permitting the use of a smaller mechanical installation. The cool, re-pressured dry gas is flowed in heat exchange relation to the incoming wet gas in a continuous process.

To achieve maximum operating efficiency I prefer to operate the method by cooling the initial wet gas by a substantially reversible process substantially to a temperature from which decompression or expansion by another reversible process to the conditions for separation (described below) is possible; thereafter expanding the cooled fluid by a substantially reversible process until a vapor phase, i. e., a phase less dense than the fluid being expanded, is formed at a temperature below the critical temperature of the dry gas; separating the resulting vapor phase or dry gas from the liquid phase in a separation zone; liquefying and recompressing the separated dry gas to the ultimately required pressure; and passing the recompressed and liquefied dry gas in heat exchange relation to additional quantities of wet gas.

The method outlined in the foregoing paragraph is conveniently effected by cooling the wet gas isobarically in heat exchangers, wherein at least a part of the heat is transferred to the recompressed dry gas, to a temperature from which expansion by a reversible process to the

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conditions for separation is possible. The decompression or expansion is effected either substantially isentropically (as by permitting the wet gas to do work of expansion in an expansion engine) or substantially isenthalpically (as by simple adiabatic expansion). Any type of expansion at the low temperatures contemplated according to this invention, while not truly isentropic and reversible, is nearly so, it being noted that on a pressure-temperature diagram of Fig. 2 the lines of equal entropy as well as the lines of equal enthalpy are closely parallel to the pressure axis at these temperatures.

With the temperature lowered sufficiently so that an isenthalpic expansion is nearly isentropic, or isentropic expansion develops relatively little work, the wet gas at a pressure which may be at, substantially above, or somewhat below the critical pressure of the dry gas, is expanded to a pressure well below the critical pressure of the dry gas. The dry gas is conveniently again compressed at the same or approximately the same temperature, whereby comparatively little work is required to attain the pressure required for return of the dry gas to the field. When the wet gas was expanded through an expansion engine the work done by the expanding wet gas may be utilized in the recompression stage. The final pressure of the dry gas is often near to or considerably above its critical pressure. This final pressure is usually, but not necessarily, somewhat higher than the pressure from which the wet gas was expanded. This circumstance, and the unavoidable friction losses, usually make it necessary to employ a source of mechanical energy for recompression in addition to that developed in the expansion of the wet gas, except when only a portion of the dry gas is re-pressured or the dry gas is further refrigerated before recompression. The use of the kinetic energy developed by expansion of the wet gas for recompression of dry gas may, however, be omitted because of the comparatively small amount of work involved under the conditions contemplated in this method.

The foregoing conditions are indicated on Pressure-Temperature diagram (Fig. 2), which shows the two-phase regions by means of curves marked "bubble point" and "dew point" for wet gas, dry gas, and recovered liquefiable hydrocarbons. It further shows in a qualitative way the inclinations of the isentropes and isenthalps for wet gas in different regions of the diagram. It will be noted that at high temperatures, above the critical temperature of the dry gas, the isentropes (dotted lines) are inclined considerably with respect to the isenthalps (dotted and dashed lines) so that a considerable change in entropy is involved when carrying out isenthalpic expansion or compression. At lower temperatures these lines are almost parallel, and isenthalpic expansions are practically isentropic.

In accordance with the instant invention wet gas, at the conditions shown by point A, is cooled to point B by heat exchange with dry gas and recovered liquefied hydrocarbons; added refrigeration may be used if necessary. It is then decompressed or expanded from point B to a point near point C, e. g., exactly to point C, the bubble point of the wet gas. This point is at a lower temperature than the critical temperature of the dry gas, indicated on the drawing. The expansion from B to C is by a substantially reversible process, e. g., isentropic, or isenthalpic; in the latter case it is nevertheless substantially isen-

tropic because the isenthalps and isentropes are almost parallel. In Fig. 2 isentropic expansion is indicated.

When point C is reached a less dense phase is separated from the expanding wet gas either by further reduction in pressure and/or the addition of heat; just before reaching point C the wet gas is, therefore, a liquid and hence may be regarded as having been liquefied in cooling form A, although no two-phase system may have occurred.

At point C the wet gas is fractionated to produce dry gas, indicated at D, and liquefied hydrocarbons, indicated at E. The fractionation may be effected by a further expansion within the fractionation column (i. e., at a pressure below point C) and/or by adding heat, and further refrigeration involving either external refrigeration or removal of a portion of the low pressure products, as described hereinafter may be used to provide reflux and offset work import due to compression. The liquefied material E is compressed isentropically or substantially isentropically to state F and flowed in heat exchange with the incoming wet gas, thereby raising its temperature to state G, at which it is discharged from the process. The dry gas is liquefied at point D and repressured or "compressed" isentropically or substantially isentropically as a liquid to state H, preferably at a pressure high enough to permit introduction into a well for repressuring; it is then flowed in heat exchange with incoming wet gas, thereby raising its temperature to state J, at which it is discharged from the process.

A total work-heat balance is achieved in the method by any of the following steps or by a combination of any two or all three:

- a. Installation of a refrigeration plant.
- b. Vaporization of the recovered products.
- c. Removal of fractions of the wet gas at lower than their partial pressure before expansion. For example, a portion of the dry gas can be removed at low pressure as a product.

This method involves several important advantages over prior methods of treating wet gas. Aside from the saving in compression costs resulting from the expansion and compression of the gas in a cycle which is nearly isentropic, isenthalpic and isothermal, as considered above, this method makes it possible to separate the fractions of the wet gas at their partial pressures in a reversible process without consumption of work (except for unavoidable friction losses). Not only may heavier components of gasoline and higher boiling range be recovered quantitatively, but butane, propane, and even ethane may be recovered in the liquid phase in the separation zone by a proper selection of the operating temperature.

For convenience, all of such relatively heavier hydrocarbon components which it is desired, in any particular process, to recover from the wet gas are herein designated as "liquefiable hydrocarbons" it being understood that such components as butane, propane and ethane are to be included only when the recovery thereof is contemplated.

By operating in accordance with this method the high pressure absorption, reabsorption and stripping operations usually practiced are obviated and the separation may be effected in a separation zone involving straight fractionation at low pressure and temperature. The method is not, however, restricted to operations in which the dry gas is returned to the well without passage through an absorption unit.

The instant process is capable of utilizing work credits available through the discharge from the process of products at pressures lower than their partial pressures. Thus, during the later phases of a recycling project on a well the greater work requirements can be met by a greater off-take of low pressure dry gas. Further, nitrogen, if present in the wet gas at partial pressures higher than atmospheric pressure, can be rejected with a work credit.

The invention described above can be carried out in many different embodiments and the arrangement of the heat exchangers, expansion valves and engines and compressors, as well as the flow for the separation zone will depend in part upon the size of the plant and economic considerations, and in part upon the nature of the heavier constituents which it is desired to recover. Thus, it is possible to operate the separating zone under conditions to recover substantially only gasoline and heavier hydrocarbons. In other situations the quantitative recovery of propane and/or ethane is desired, and the separating zone may comprise double columns of the type used in the Linde air fractionation system.

The embodiment of the process shown in Fig. 3 will be described to illustrate a possible method of applying the method according to this invention, and not by way of limitation. Referring to Fig. 3, wet gas produced from a well 1 is permitted to flow freely through the main control valve 2 and branch valve 3 and into a liquid separator 4 wherein liquids entrained in the gas are separated. There is usually an unavoidable pressure drop between the formation and the top of the well resulting frequently in the condensation of moisture and/or heavier petroleum hydrocarbons. These are separated and withdrawn through the liquid level-controlled valve 5; wet gas, freed from condensed liquids, is withdrawn through valve 6. When the valve 3 is open the valve 7 is closed.

When the amount of liquid in the wet gas is not sufficient to require the use of the separator 4, the valve 3 is closed and valve 7 is opened and the separator is by-passed. The wet gas, in either case, may be treated to remove water therefrom to prevent the clogging of the system by freezing or by the formation of solid hydrates. Instead of removing the moisture or removing all of the moisture, an agent which will inhibit the formation of solids upon cooling may be injected into the wet gas.

In the flow diagram illustrated, a reagent such as alcohol, ethylene glycol, diethylene glycol, calcium chloride, and the like, is introduced by means of a liquid pump 8 and mixed in a mixer 9 with the wet gas supplied through valve 10. The liquid reagent, together with dissolved water, is separated from the gas in the liquid separator 11 and withdrawn at the bottom through a valve 12 which may be controlled by a liquid level controller. The reagent is fed into a reconcentrator 13, which may be of any suitable type, wherein the water is separated and the concentrated reagent is stored for recycling through the pump 8. The wet gas, freed from moisture, is withdrawn through valve 14. When the treatment with the reagent is not necessary the valve 10 is closed and valve 15 is opened.

Instead of, or in addition to the treatment in the mixer 9 and separator 11, the wet gas may be mixed with a fluid which will inhibit the formation of solids. For example, ammonia may be injected into the stream through a valve 16.

The wet gas, still substantially at the well pres-

sure, is sub-divided into three streams, flowing through valves 17, 18, and 19, respectively, arranged to regulate the relative volumes without appreciably lowering the pressure. The first two streams are cooled isobarically by flow through heat exchangers 20 and 21, respectively, wherein they flow in indirect and counter-current heat exchange relation with liquid recovered from the wet gas, and cold dry gas, respectively. The heat exchangers may comprise several stages arranged in series, so as to cool the wet gas to as near the temperature of the dry gas or liquid introduced at the other end as practicable. Preferably, the sizes of the streams flowing through the valves 17 and 18 are adjusted in relation to the heat absorbing capacities of these cold fluids, so that the cooled wet gas issues at about 5° C. to 15° C. above the initial temperature of the cold fluids; the excess of wet gas is flowed through the valve 19 as the third stream and cooled in heat exchanger 22 by means of any refrigerant. It is, however, possible (although thermodynamically less efficient) to eliminate the heat exchanger 22 and pass all of the wet gas as only two streams through the exchangers 20 and 21. The three streams are combined after being cooled and further cooled in the heat exchanger 23. The refrigerant for the heat exchangers 22 and 23 may, for example, be any material which is a fluid at the temperatures involved, e. g., about -50° F. to -170° F. It may be cooled by a refrigeration plant 24, provided with a cold refrigerant outlet 25, return line 26 and flow lines having valves 27 and 28, and driven by any source of power. The refrigerant may also be cooled by evaporating one or more of the products from the separation zone.

The wet gas is brought to the state of a compressed liquid in the heat exchangers 20 to 23. In Fig. 2, this cooling is represented by the line A-B. Referring to Fig. 4 as well as to Fig. 3, valve 29 being open and valve 30 closed, this liquid is passed through an expansion engine, which may operate on one or more stages, as for example, four stages. A two-stage engine is schematically indicated at 31. This engine may have a reciprocating piston with any suitable valve gear, or may be of the rotary or of any other type. The last stage of the engine may be regulated by any suitable means to maintain the desired pressure in the fractionating column 32. It is, however, usually more convenient to operate the engine to expand the liquid to a pressure slightly above the desired fractionating pressure and effect a final expansion in a pressure release valve 33, controlled by the pressure in the fractionating column through a pressure control line 34.

As a result of the expansion in the engine 31 and the valve 33 the liquefied wet gas is expanded as a liquid from state B to state C in Fig. 2. The final pressure may be somewhat below that of point C, resulting in the formation of a vapor phase, and the fluid issuing from the valve 33 is in this case a mixture of liquid and vapor. The fluid issuing from valve 33 may, however, be at a pressure equal to or slightly above that indicated by point C in Fig. 2; it will, in this case, be a saturated liquid. This fluid, regardless of its state, is flowed through a heat exchanger 35, wherein it absorbs heat, resulting in vaporization of part of it, and thence into the fractionating column 32, which is preferably provided with bubble trays or packing of any suitable type and with a long rectifying section above the level of the feed. Dry gas, substantially freed of the de-

sired heavier constituents, is withdrawn at the top of the column. Reflux for the column is provided in any manner well known per se, as, for example, by compressing a portion of the top product in the gas compressor 36, preferably substantially adiabatically, thereby raising its temperature to above that of the fluid discharged from valve 33, and then condensing it by flow through the heat exchanger 35 and feeding it to the top of the column through reflux line 37 and valves 45 and 38. Valve 44 is closed, valve 45 is fully open and valve 38 is used to reduce the pressure. The pressure within the column 32 being less than that of the condensate in the reflux line 37, partial vaporization of the condensate and cooling will occur in the upper part of the column by return of condensate through valve 38. The rate of the reflux is regulated by the speed of the compressor 36 and by valve 38, which also acts as a throttle for expansion of reflux condensate to the pressure of the column. The heavier constituents are withdrawn in liquid form from the bottom of the column through a line 39 and valve 40. This is at the state represented by point E in Fig. 2. By further expansion of this product the refrigeration effect described above can be achieved.

The heat exchanger 35 may effect complete or only partial condensation of the overhead vapors. In the latter case the exchanger may be further cooled by refrigerant from the refrigerator plant 24. A preferred arrangement is to provide a separate after-cooler 41, supplied with cold refrigerant by pipe 42 and discharging spent refrigerant through pipe 43, and to pass the stream of compressed overhead product through valve 44, the valve 45 being then wholly or partially closed.

Refrigeration may be further realized by expansion of part of the overhead vapor to a lower pressure in an expansion valve or engine and discharging the expanded vapor from the process at a lower pressure (see Fig. 6). For example, if the pressure within the column 32 is of the order of 350 lbs. per sq. in., a part of the overhead vapor may be expanded to or partly to atmospheric pressure with a large cooling effect. This may be used in lieu of or together with the added refrigeration in the after cooler 41. Thus, there may be provided a vapor take-off line 47, having a flow control valve 48, a heat exchanger 49, a vapor-liquid separator 50, and an expansion engine 51 connected to the vapor discharge from the separator. Vapors flowing through line 47 are cooled and partly condensed in the heat exchanger 49 and the condensate separated therefrom is returned to the column as added reflux through conduit 52. The vapor is expanded in the engine 51, resulting in partial condensation and considerable cooling; the resulting cold mixture of vapor and liquid is flowed through the heat exchanger 49 and discharged from the process at low pressure via discharge conduit 53. Shaft work from the engine 51 may optionally be utilized in the process to operate compressors or pumps.

While one specific method of operating the separating zone was described, it should be clearly understood that the invention is not limited thereto. Thus, the expansion in the engine 31 and valve 33 may be such that the feed stream to the column 32 remains liquid after passage through the heat exchanger 35 so that substantially only a saturated liquid is fed into the column; vaporization is then effected in the fractionating column by introducing heat at a re-

boiler, or by further pressure reduction, as by locating the pressure relief valve 33 near the point at which the wet gas, in the state of a saturated liquid, is introduced into the column. The column 32 may be operated as a rectifying column without a reboiler. It is, however, also possible to achieve partial or complete stabilization of the liquid bottoms by providing a reboiler 56 by which heat is introduced into the column from any source e. g., the incoming wet gas, such as a portion of one or more of the three streams flowing through the heat exchanger 20—22; this heat drives off the fixed gas from the liquid. A more desirable source of heat is the recompressed dry gas taken overhead from the column. A stream of this overhead vapor may be passed through a valve 57 and pipe 58 and compressed in a gas compressor 59, thereby increasing its pressure to above the pressure within the column and concomitantly raising its temperature to above the temperature prevailing at the bottom of the column. This compressed gas is passed through a pipe 60 and flowed through the reboiler 56, wherein condensation of the compressed gas is effected in whole or in part. The condensed gas is discharged through a pipe 61 and valve 62 and commingled with the compressed gas of like composition discharged from the compressor 36. Partial or total vaporization, accompanied by autorefrigeration, occurs during flow through the valve 62. The valve 57 and the operation of compressor 59 are adjusted to divert only the portion of the dry gas through the reboiler required to effect stabilization in the column.

According to still another method of operation the wet gas is expanded in the engine 31 and/or the valve 33 to effect substantially complete vaporization and partially condensed within the column 32 by providing a refrigerated reflux, e. g., by using the cooler 41 (Fig. 4). In this case the heat exchanger 35 may be cooled by a refrigerant from the plant 24 or by expansion of a product instead of the incoming wet gas, which may by-pass the exchanger 35.

A portion of the dry gas may optionally be discharged from the process at a low pressure equal to that prevailing in the column at 63 through the valve 64, at the state indicated by point K in Fig. 2, or at a still lower pressure by further expansion in an engine 51 described above, to attain an energy balance. The dry gas not so discharged at low pressure is liquefied by compressor 36, exchanger 35 and, optionally, cooler 41, and is withdrawn through valve 65 at the state indicated by point D in Fig. 2, or at a pressure slightly in excess of that of point D. It is then repressured or "compressed" in the liquid state in the liquid pump 66. This pump may contain any suitable number of stages, two being illustrated. When the volume of liquefied dry gas compressed is small enough the work supplied by the expansion engine 31 is sufficient to drive the pump 66; if necessary, other power may be required for driving the pump to attain the ultimate pressure necessary for return of the gas to the well. The repressured and liquefied dry gas has the state indicated by point H in Fig. 2. It is flowed through valve 67 to the heat exchanger 21 and is returned through pipe 68 to the repressuring well 69 at a state indicated by point J in Fig. 2.

While the pump 66 has been shown as driven by the expansion engine 31, it is also possible to use the energy derived from the latter to operate any other machine or unit in the refinery,

and drive pump 66 from an outside source of power, the energy balance being the same.

The fluid in the line 37 is a liquefied dry gas and the portion thereof fed to the pump 66 is further compressed in the liquid state throughout the several compression stages. Under these conditions only a small amount of work is needed to attain the required pressure and there is but a small rise in temperature. The compressed liquid is, therefore, at a low temperature and can effect substantial cooling of the incoming wet gas. The heat exchange between the wet gas and the dry gas may be effected in a single heat exchanger. However, due to the relatively great contraction in the volume of the incoming wet gas and expansion of the outgoing dry gas it is preferable to use a plurality of stages, having the tubes of proper dimensions to accommodate the volumes involved.

All or part of the liquid product withdrawn at the bottom of the column 32 through line 39 can be flowed through valves 70 and 71, heat exchanger 20, and may be withdrawn from the process at low pressure as a gas or as a gas and liquid mixture through the valve 72, at a state indicated on Fig. 2 by a point to the right of point E, such as point L. When it is desired to apply pressure to this liquid it is preferably compressed before it is warmed in the heat exchanger 20, to permit it to be handled as a liquid. For this purpose the valve 70 may be closed and the liquid flowed through the valve 73 and through a liquid pump 74 to bring the liquid to a state indicated by point F in Fig. 2. After flow through the heat exchanger 20 it is in the state indicated by point G.

The liquid product may be further fractionated or stabilized in the fractionating column 75 by flowing the liquid, either at low pressure (at state L) or after flow through the compressor 74 (at state G), through a line 76 and valve 77. Vapors from the top of the column taken off through vapor line 78, condensed in the heat exchanger 79, and withdrawn through valve 80. The heat exchanger 79 is conveniently cooled by the liquid bottom product from the column 32 prior to passage through the heat exchanger 20. For this purpose the valve 81 is opened and the valve 71 is either closed or throttled to divert cold liquid through line 82 to the exchanger and thence through return line 83. A portion of the condensate is returned to the column 75 as reflux through the valve 84. The stabilized bottom product is withdrawn through valve 85. It should be understood that suitable pumps or compressors may be applied to boost the pressure of the products withdrawn at 80 and 85, this being necessary when the compressor 74 is not used and the column 75 is operated at sub-atmospheric pressure. When the compressor 74 is used a portion of the liquid product may optionally be discharged from the process at low pressure through the valve 40, or at an increased pressure through the valve 72.

As was explained above, substantially isenthalpic expansion may be used in this process, because the work developed in the engine 31 and that required for repressuring in the pump 66 are small. In this case, referring to Figs. 3 and 5, the valve 29 is closed and the valve 30 is opened and the cooled wet gas, in the liquefied state, is flowed through a pressure release valve 86, regulated by the pressure control line 31 in accordance with the pressure within the fractionating column. The liquid is expanded in

the valve 86, either to produce a saturated liquid or to produce partial vaporization. In the former alternative vaporization is effected by heat absorbed in the heat exchanger 35 and from the reboiler 56. The operation of the column is the same as described previously. The pump 66 is, however, driven entirely by extraneous power, as indicated by engines 66a in Fig. 5, the engine 31 being out of operation.

Wet gas from any other source may be treated in the same manner and introduced into the process at any desired point in advance of the heat exchangers as, for example, through a high pressure feed valve 81.

This application is a continuation-in-part of my copending application Serial No. 719,231, filed December 30, 1946, now abandoned.

I claim as my invention:

1. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of hydrocarbons having less than three carbon atoms, together with lesser amounts of said liquefiable hydrocarbons, and producing a dry gas in a compressed state, comprising the steps of subjecting said wet gas to fractional distillation at a pressure causing the formation of vapor phase containing dry gas and a liquid phase containing said liquefiable hydrocarbons and at a temperature below the critical temperature of the dry gas, separating said vapor phase from the liquid phase liquefying the separated vapor phase, and compressing it in the liquid state.

2. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of hydrocarbons having less than three carbon atoms, together with lesser amounts of said liquefiable hydrocarbons, and producing two dry gas portions, one at a low pressure and the other at a high pressure, comprising the steps of subjecting said wet gas to fractional distillation in a distillation zone at a superatmospheric pressure causing the formation of vapor phase containing dry gas and a liquid phase containing said liquefiable hydrocarbons and at a temperature below the critical temperature of the dry gas, separating said vapor phase from the liquid phase, cooling and partly condensing at least a portion of said vapors, separating uncondensed cooled gas from condensate, returning a part of the condensate as reflux to the distillation zone, compressing another portion of said condensate in the liquid state to a pressure above said superatmospheric pressure to produce dry gas in a compressed state, expanding the said uncondensed cooled gas to a lower pressure and thereby further cooling it, flowing the resulting further cooled material in heat exchange with at least a portion of said vapors from the distillation for partly condensing said vapor and thereafter discharging the vapors as low pressure gas.

3. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of hydrocarbons having less than three carbon atoms, together with lesser amounts of said liquefiable hydrocarbons, and leaving a dry gas unrecovered, comprising the steps of cooling the wet gas at a pressure above the bubble point pressure of the wet gas in the separating zone, described hereinafter, to a temperature from which expansion to the temperature and pressure of the separating zone by a substantially reversible process is possible, thereafter expanding it to effect at least partial vaporization and forming a vapor containing dry gas and a liquid contain-

ing the liquefiable hydrocarbons, separating said vapor from the liquid in a separating zone at a temperature below the critical temperature of the dry gas, liquefying at least a portion of the separated vapor and compressing it in the liquid state at a temperature below its critical temperature.

4. The method according to claim 3 in which the expansion is substantially isenthalpic.

5. The method according to claim 3 in which the expansion is substantially isentropic.

6. The method according to claim 3 in which the expansion is effected in an expansion engine to derive kinetic energy from the expansion, at least a portion of the dry vapor is liquefied and compressed in the liquid state, and the said derived kinetic energy is used for the compression of the liquefied dry gas.

7. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of methane, together with lesser amounts of said liquefiable hydrocarbons and leaving a dry gas unrecovered, comprising the steps of cooling the wet gas by indirect cooling including heat exchange with compressed, outgoing dry gas at a pressure above the bubble point pressure of the wet gas at the temperature of the separating zone, described hereinafter, to a temperature from which isentropic expansion to the temperature and pressure of the separating zone is possible, thereafter expanding it in the liquid state substantially to the bubble point pressure for the temperature in the separating zone, at least partially vaporizing the resulting liquid and forming a vapor containing dry gas and a new liquid containing the liquefiable hydrocarbons, separating the vapor from the new liquid in a separating zone at a temperature below the critical temperature of the dry gas, liquefying at least a portion of the separated vapor, recompressing the liquefied vapor in the liquid state and flowing it in heat exchange relation to cool additional wet gas.

8. The method of recovering liquefied hydrocarbons from a well fluid tapping a distillate reservoir and leaving a dry gas unrecovered, said well fluid being produced at a pressure above the critical pressure of the dry gas, comprising the steps of liquefying said well fluid by cooling at a pressure above the critical pressure of the dry gas to a temperature from which isentropic expansion to the conditions of the separating zone, described hereinafter, is possible, thereafter expanding the well fluid in the liquid state substantially to the bubble point pressure for the temperature in the separating zone, forming from the resulting liquid a vapor containing dry gas and a new liquid containing the liquefiable hydrocarbons, separating the vapor from the new liquid in a separating zone at a temperature below the critical temperature of the dry gas, liquefying and thereafter recompressing at least a portion of the dry gas in the liquid state to at least well pressure, and returning compressed dry gas into a well.

9. The method of recovering liquefiable hydrocarbons from a well fluid of a well tapping a distillate reservoir and leaving a dry gas unrecovered, said well fluid being produced at a pressure above the critical pressure of the dry gas, comprising the steps of liquefying said well fluid by cooling it substantially isobarically to a temperature from which isentropic expansion to the conditions of the separating zone, described hereinafter, is possible, thereafter expanding the liq-

uefied well fluid to cause the formation of a vapor containing dry gas and a liquid containing the liquefiable hydrocarbons, separating the vapor from the liquid in a separating zone at a temperature below the critical temperature of the dry gas, liquefying and thereafter recompressing at least a portion of the dry gas in the liquid state to at least well pressure, isobarically heating the compressed dry gas by heat exchange with additional well fluid undergoing isobaric cooling, and returning compressed and heated dry gas to a well.

10. The method of recovering liquefiable hydrocarbons from a well fluid and leaving a dry gas unrecovered, said well fluid being produced at a pressure above the critical pressure of the dry gas and above the critical temperature of the well fluid, said well fluid consisting predominantly of methane, together with lesser amounts of said liquefiable hydrocarbons, comprising the steps of liquefying said well fluid by cooling it substantially isobarically to a temperature below the critical temperature of the dry gas, thereafter expanding the well fluid to a pressure at which a vapor phase is formed, subjecting the expanded fluid to fractionation in a separating zone to produce a liquid containing the liquefiable hydrocarbons and a vapor containing dry gas is formed, liquefying and thereafter compressing at least a portion of the dry gas in the liquid state to at least well pressure, isobarically heating the compressed dry gas by heat exchange with additional well fluid undergoing isobaric cooling, and introducing compressed and heated dry gas into a well.

11. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of methane, together with lesser amounts of said liquefiable hydrocarbons and leaving dry gas in a compressed state comprising the steps of cooling the wet gas at a pressure above the bubble point pressure of the wet gas to a temperature below the critical temperature of the dry gas, thereafter expanding it in the liquid state to form a vapor containing dry gas and a liquid containing the liquefiable hydrocarbons, separating vapor containing dry gas from liquid, liquefying the separated vapor, and compressing the resulting liquefied material in the liquid state.

12. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of methane, together with lesser amounts of said liquefiable hydrocarbons and leaving a dry gas in a compressed state comprising the steps of coolings the wet gas by indirect cooling including heat exchange with compressed, outgoing dry gas at a pressure above the bubble point of the wet gas to a temperature below the critical temperature of the dry gas, thereafter expanding it in the liquid state to form a vapor containing dry gas and a liquid containing the liquefiable hydrocarbons, separating vapor containing dry gas from liquid, liquefying the separated vapor, compressing the resulting liquefied material in the liquid state, and flowing the compressed material in heat exchange relation to cool additional wet gas.

13. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting

predominantly of hydrocarbons having less than three carbon atoms, together with lesser amounts of said liquefiable hydrocarbons, and leaving a dry gas unrecovered, comprising the steps of liquefying said wet gas and decompressing the liquefied wet gas in the liquid state substantially to its bubble point and to a temperature below the critical temperature of the dry gas, completely vaporizing the resulting liquid by lowering the pressure thereof to a pressure below that of the said bubble point and thereafter cooling the resulting vapors to thereby cause partial condensation thereof with the formation of vapor containing dry gas and a new liquid containing the liquefiable hydrocarbons, and separating said vapor from the new liquid.

14. The method of recovering liquefiable hydrocarbons from wet hydrocarbon gas consisting predominantly of hydrocarbons having less than three carbon atoms, together with lesser amounts of said liquefiable hydrocarbons and producing a dry gas in a compressed state, comprising the steps of cooling the wet gas at a pressure above the bubble point pressure of the wet gas in the separating zone, described hereinafter, to a temperature from which expansion to the temperature and pressure of the separating zone by a substantially reversible process is possible, decompressing the liquefied wet gas in the liquid state substantially to its bubble point and to a temperature below the critical temperature of the dry gas, at least partially vaporizing the thus decompressed liquid and causing the formation of vapor containing dry gas and a new liquid containing the liquefiable hydrocarbons, separating said vapor from the liquid in a separating zone at a temperature below the critical temperature of the dry gas, liquefying at least a portion of the separated vapor and compressing it in the liquid state at a temperature below its critical temperature.

15. The method according to claim 14 wherein the said resulting liquid is vaporized by adding heat thereto.

16. The method according to claim 14 wherein the said resulting liquid is vaporized by lowering the pressure thereof to a pressure below that of the said bubble point.

17. The method according to claim 14 in which the vapor and the new liquid are separated by fractional distillation.

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