FIP7912 XR 2,720,265 CROSS REFERENCE

Oct. 11, 1955 J. H. TRACHT 2,720,265
ADJUSTING THE RETROGRADE CONDENSATION PRESSURE OF HYDROCARBON COMPOSITIONS
Filed March 31, 1954 3 Sheets-Sheet 1

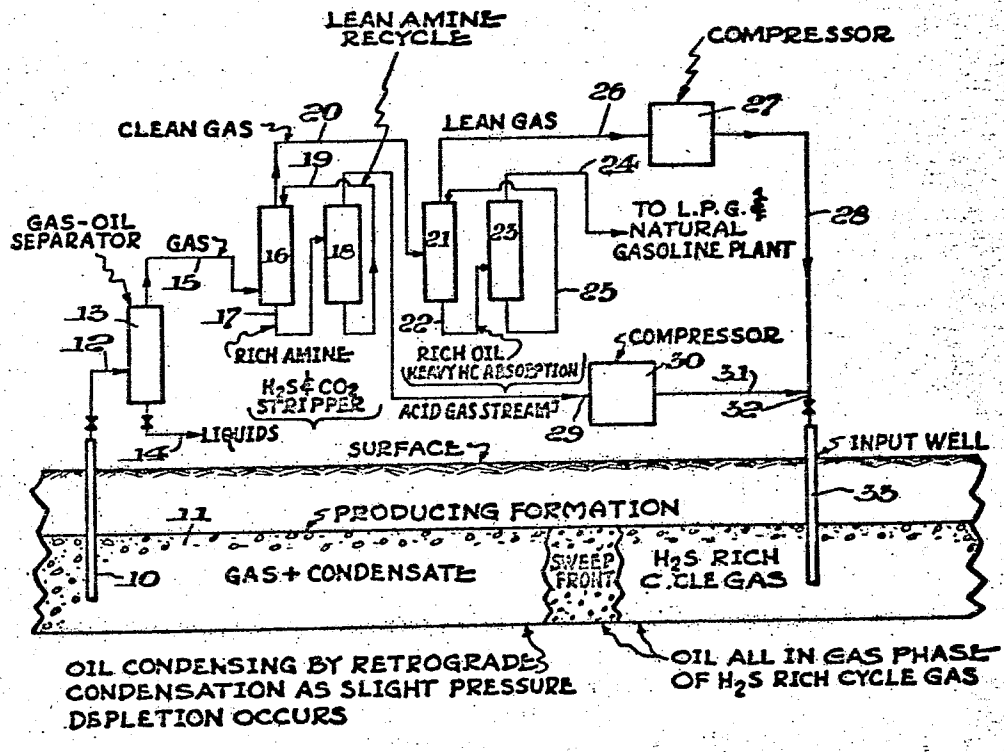


Fig. 1.

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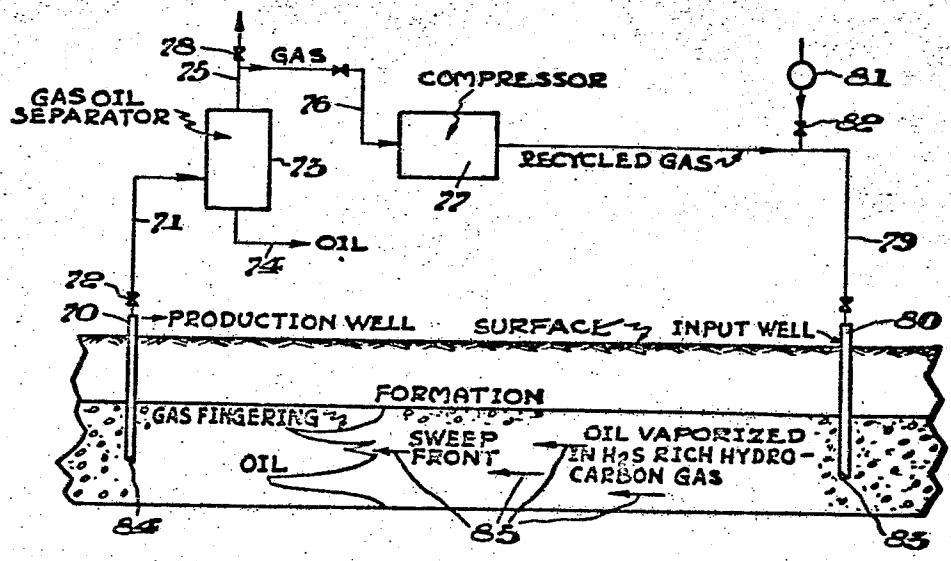


Fig. 3.

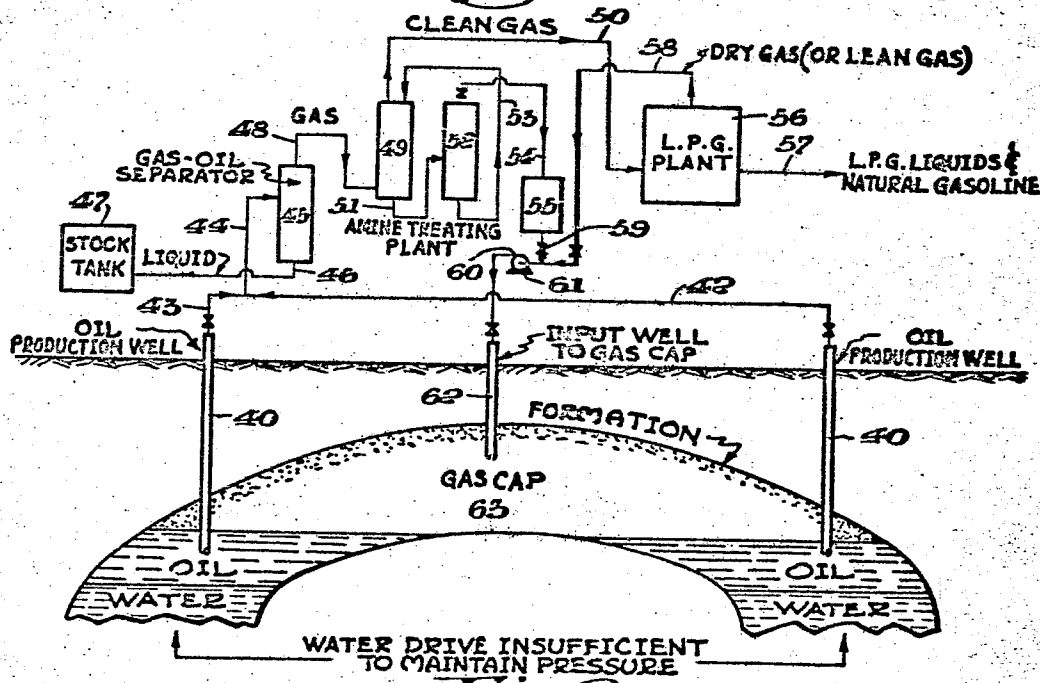


Fig. 2.

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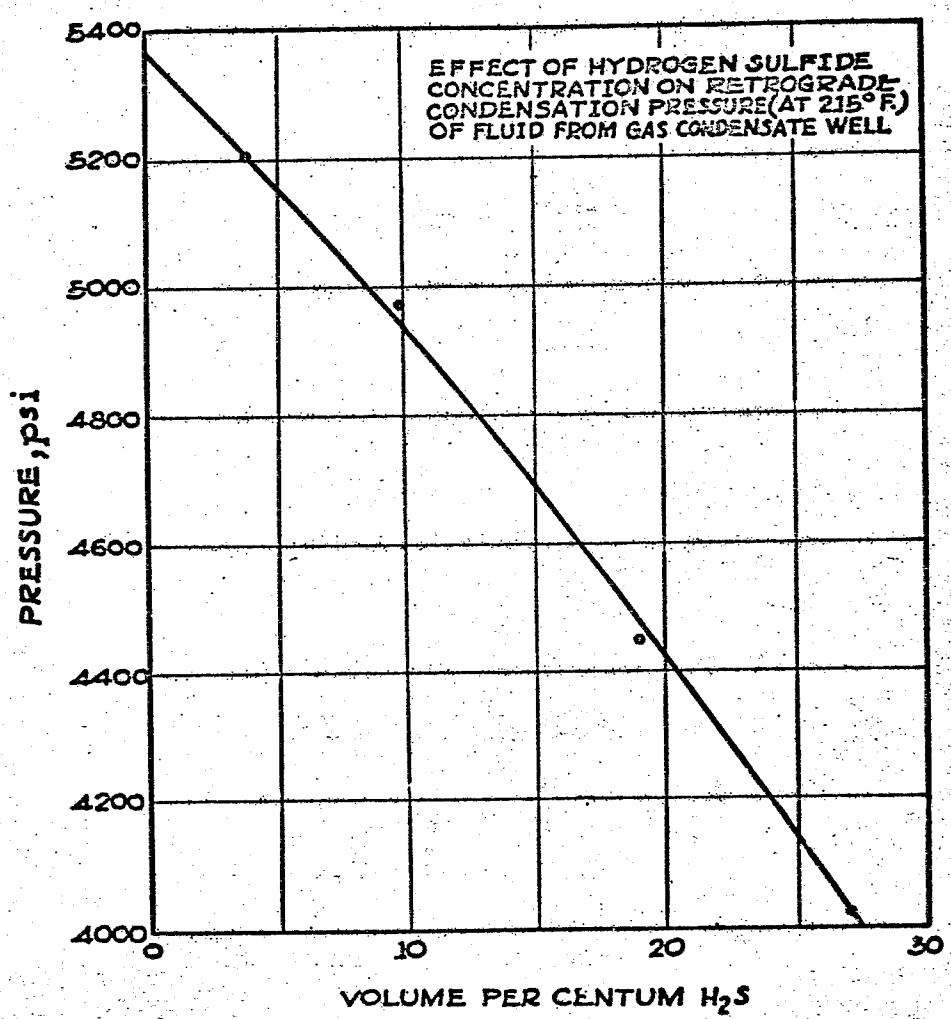
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Fig. 4.



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United States Patent Office 2,720,265 Patented Oct. 11, 1955

2,720,265

ADJUSTING THE RETROGRADE CONDENSATION PRESSURE OF HYDROCARBON COMPOSITIONS

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Application March 31, 1954, Serial No. 420,153

8 Claims. (Cl. 166—7)

This invention relates to the recovery of liquid distillate hydrocarbons at high pressures from high pressure oil and gas wells, and has particular reference to a method of treating the contents of high pressure hydrocarbon reservoirs so as to increase their total liquid yield.

In certain high pressure naturally occurring petroleum reservoirs normally gaseous and normally liquid hydrocarbons exist in a single phase usually termed a gas phase. The pressures in the formations of these wells are usually between about 1,200 and 10,000 pounds per square inch and the temperatures are usually between about 130° and 300° F.

Under normal conditions of temperature and pressure, the ratio of gas to liquid in a heterogeneous gas-liquid mixture increases with increase in temperature and decrease in pressure, and conversely decreases with temperature decrease and pressure increase. However, at temperatures above the critical point, which lies on the phase envelope of the mixture, and below the critical condensation isotherm an apparent reversal of the expected change in phase is encountered, and a decrease in pressure will effect a condensation of liquid from the gas. The phenomenon of forming a liquid condensate upon reducing rather than increasing pressure is known as retrograde condensation or more precisely isothermal retrograde condensation with decrease in pressure (Volumetric and Phase Behavior of Hydrocarbons, Sage & Lacey; Appendix, p. 293) and the range within which liquid condenses from solution is known as the retrograde condensation range. The retrograde condensation temperature range of the lighter hydrocarbons is relatively high and occurs at temperatures between the critical temperature of the hydrocarbon mixture and the cricondentherm of that mixture.

While it has been the practice to exploit the retrograde condensation of liquid hydrocarbons in the recovery of distillate hydrocarbons from well fluids by reducing the pressure on the produced well fluids and separating the condensate, the phenomenon also results in substantial loss in the reservoir of distillate hydrocarbons which condense as reservoir pressures decrease.

Briefly stated, my invention comprehends the adjustment of the retrograde condensation pressure of petroleum hydrocarbon fluids at elevated pressures by establishing a predetermined hydrogen sulfide content of said fluids, increased hydrogen sulfide concentrations decreasing the retrograde condensation pressure and decreased concentrations increasing the said pressure.

More specifically, my invention comprises a treatment of fluids in the reservoir of gas condensate wells by injection of hydrogen sulfide, or of gas containing hydrogen sulfide, to raise the concentration of hydrogen sulfide in the reservoir an amount within the range of 1 to 30 percent by volume of the total well fluids being treated, whereby the retrograde condensation pressure of the hydrocarbon liquids constituting the well fluids is decreased. When depletion of the well results in a decrease in the formation pressure, the decrease in retrograde condensation pressure resulting from my treatment of the well fluids will cause the distillate fluids to remain in the single gas-like phase or be redissolved in the single phase. The dissolved distillate fluids will consequently be carried to the producing surface and be recoverable there.

It is a well known practice to return gas by an injection or input well to the formation beyond that amount of gas that it is permissible to recover relative to the recovery of oil. The increased recovery of oil provided by the method of this invention decreases the amount of gas that must be returned to the formation; on the other hand existing provision for returning the gas through the input wells will provide some if not all of the equipment necessary for the treatment of wells according to the method of this invention.

According to this invention the hydrogen sulfide concentration of the input gas is so adjusted that the hydrogen sulfide will have a concentration in that portion of the formation which it penetrates of between 1 and 30 percent by volume. As demonstrated more specifically in the following description of the method of invention, the optimum hydrogen sulfide concentration of the well fluids is maintained within the said limits by several methods of adjusting the hydrogen sulfide content of the recycled gases or by direct addition of hydrogen sulfide from an outside source. Separation in apparatus at the surface of hydrogen sulfide-rich acid gases from the produced fluids and the addition of predetermined quantities of the said gases to recycled gases can also be employed.

Depending upon the temperature and concentration of the liquid hydrocarbon mixture, the incipient retrograde condensation pressure can vary from about 700 pounds per square inch to the maximum pressures encountered in deep well operations. Specific operating conditions in any particular well will govern the amount of hydrogen sulfide which should be added to the formation or the optimum concentration of hydrogen sulfide that should be maintained in the input gas. The operation of a primary gas-oil separator at the well head in usual condensate-reservoir operation employs retrograde condensation for primary separation of distillate hydrocarbons. The optimum concentration of hydrogen sulfide to be maintained in the input gas can be determined with sufficient accuracy to procure the desired results by observing variations in the operating characteristics of the said gas-oil separator and adjusting these observations to conform to bottom-hole pressures.

In the accompanying drawings which are supplied for the purpose of illustrating and not of limiting the invention,

Fig. 1 is an elevational flow diagram of a plant for producing liquefiable hydrocarbons from a condensate reservoir and a schematic diagram of the underlying producing formation,

Fig. 2 is an elevational flow diagram of a system for the production of well fluids from a combination condensate and crude oil reservoir,

Fig. 3 is an elevational flow diagram showing recovery operation from a partially depleted crude oil reservoir, and

Fig. 4 is a curve showing the effect of the hydrogen sulfide concentration on the retrograde condensation pressure.

With particular reference to Fig. 1, producing gas-condensate well 10 is employed to recover gas and oil from a high pressure formation 11. The well produces fluids under high pressure which flow from the well 10 and through a valved line 12 into a gas-oil separator 13 which can represent a plurality of separators ordinarily disposed in series. The pressure in the gas oil separator 13 is maintained below the retrograde condensation pressure and the temperature is reduced to a temperature

below reservoir temperature. Separated liquefied hydrocarbons are flowed from the separator 13 through valved line 14 to storage or utilization means or the like (not shown). Gas from the separator 13 flows from line 15 to the scrubber 16 in which the gas flows countercurrently to a treating solution such as an aqueous solution of ethanolamine. The amine treating solution removes acid gases from the gas and the so-enriched amine solution flows from the scrubber 16 through a line 17 into a regenerator 18 in which heat is employed to strip the acid gases from the amine. Regenerated amine solution is recycled from the regenerator 18 through line 19, and gases from which acid gases have been removed flow through line 20 into an absorber 21 for recovery of the heavier hydrocarbons in the gaseous fraction. The gases enter absorber 21 and are scrubbed therein by an absorbent oil. The oil, enriched with absorbed hydrocarbons, flows through line 22 into a still 23 wherein the absorbed hydrocarbons are stripped and passed through line 24 to storage or utilization means (not shown). Regenerated scrubber oil is recycled from the still 23 through a line 25 to the absorber 21. Lean gas from the absorber 21 flows through line 26 to a compressor 27 which raises the pressure of the gas to above the pressure of the formation. Compressed gas flows from the compressor 27 through line 28 and is mixed therein with a measured amount of hydrogen sulfide introduced into the line 28 from the regenerator 18, line 29, compressor 30, and line 31.

The mixed recycled gas is introduced through valved line 32 into the input well 33 by which means the recycled gas is introduced into the producing formation 11. The hydrogen sulfide-rich recycle gas flows through the formation and toward the producing well because of the induced pressure differential. Hydrogen sulfide from any other source can be introduced by the compressor 30 in measured amount into the formation.

Highly concentrated or pure hydrogen sulfide can intermittently be introduced into the formation 11 and thus pass through the formation in relatively high concentrations even though diluted by the fluids in the formation. These surges of gas more concentrated in hydrogen sulfide are introduced to provide an even greater potential to redissolve condensed hydrocarbons in the gaseous phase. The solvent power of the hydrogen sulfide-enriched cycled gases will redissolve oil which has condensed in the formation by retrograde condensation as reservoir pressure declines.

A well producing crude oil under pressure maintained over the producing formation by a gas cap in the reservoir is shown in Fig. 2 in which producing wells 40 penetrate the oil formation. In the example illustrated by Fig. 2 oil is flowed from the producing wells 40 through valved lines 42 and 43 and line 44 into gas-oil separator 45 which can represent several separators usually arranged in series and which is operated at a pressure below the reservoir pressure. Liquefied hydrocarbons are withdrawn from the separator 45 through line 46 and are passed into a stock tank 47 or other means (not shown) for refining, utilization or storage of these liquid hydrocarbons. Gas is flowed from the gas-oil separator 45 through line 48 into an absorber 49 of an amine treating plant. Gas from which acid gases, particularly hydrogen sulfide and carbon dioxide, have been removed is flowed from the absorber 49 through a line 50. The amine treating liquor, which can for example be a solution of ethanolamine, and will contain hydrogen sulfide and other acid gases, is removed from the absorber 49 through line 51 and is flowed therefrom into a regenerator 52 in which heat such as steam is employed to drive the acid gases from the amine treating solution thereby regenerating the solution. The regenerated solution is returned to the absorber 49 through the line 53. Acid gases which are stripped from the amine treating solution in the regenerator 52 flow through valved line 54 into a storage means 55 which can represent also conventional means for separation, drying or compression of the constituent acid gases.

Light petroleum gas substantially free of acid gases flows from line 50 into a liquefied-petroleum-gas plant 56 which yields product liquids or natural gasoline which are withdrawn from line 57 to storage or utilization means not shown. Dry or lean gas flows from the LPG plant 56 through a valved line 58 and is mixed with a measured amount of hydrogen sulfide in acid gases flowing from storage means 55 through a valved line 59. The acid gas and the lean gas are mixed in line 60 and are pumped by a pump 61 disposed therein into input well 62 which penetrates the gas cap formation 63. Thus hydrogen sulfide is added to the gas cap at the same time that gas is injected to maintain producing pressure and when all of the recoverable oil is produced sufficient hydrogen sulfide will have been added to the gas cap to significantly lower the dewpoint of its contents making the production of the petroleum constituents of the gas cap more efficient. As the hydrogen sulfide-rich gas is injected into the top of the reservoir and the final blowdown after oil production is accomplished through the wells previously used for oil production, the hydrogen sulfide-rich gas expanding behind the gas being produced will automatically sweep up any liquid condensate left behind. According to the foregoing procedure, the lowering of gas pressure in the formation during oil production is reduced by the recycle of the lean gas and, to the extent that hydrogen sulfide that was separated from the well fluids is added to the formation, the retrograde condensation pressure of the gas in the formation will also be lowered. Where it is desired to reduce still further the gradual decrease of gas pressure in the formation, which occurs as crude oil is being produced, or to maintain a fixed pressure, lean gas from an outside source can be added to the cycled gas. In like manner hydrogen sulfide from an outside source can be added to the cycled gas, whether or not lean gas from an outside source is added, in order to increase the hydrogen sulfide concentration of the gas in the formation and thus, according to the present invention, lower the retrograde condensation pressure and ensure increased yields of liquid hydrocarbons during subsequent condensate-well operation. A further advantage is achieved by the method of my invention in the fact that an increase in the hydrogen sulfide concentration of the gas cap, resulting as it does in a lowering of the retrograde condensation pressure, would permit if desired the recycle of lower volumes of lean gas since greater reduction in pressure can be encountered in the formation without causing a loss of condensate liquids by retrograde condensation.

With reference now to Fig. 3 an example will be described of a partially depleted crude oil reservoir which is pressured upon substantial depletion of the oil production to a pressure in the retrograde condensation range and which is subsequently operated as a combination crude-oil and gas-condensate well. During crude oil production from the formation, well fluids flow from the well 70 through line 71 and pressure reduction valve 72, and are introduced into separator 73 at a pressure below reservoir pressure. Crude oil that has separated in the said separator is withdrawn through line 74 to conventional means (not shown) for storing the oil. Gas flows from the separator 73 through line 75 from which at least a portion of the separated gas is flowed through valved line 76 to a compressor 77. The remainder of the gas is flowed through valved line 78 to purification liquid-separating means (not shown). Gas which has been compressed in the compressor 77 to a pressure higher than the pressure in the formation is recycled through line 79 to an input well 80.

Upon substantial depletion of the crude oil production, the formation is then raised in pressure by injec-

tion of gas through the input well to a pressure in the retrograde condensation pressure range. This gas is enriched with hydrogen sulfide, which may also have been added with cycled gas during the oil production, so as to increase the hydrogen sulfide concentration of the formation, lower the retrograde condensation pressure, and thus dissolve distillate hydrocarbons into the major gas phase and permit their recovery as gas condensate with the well fluids. Hydrogen sulfide or gas containing hydrogen sulfide in a concentration higher than the concentration of hydrogen sulfide in the cycled gas is introduced from a source 81 through valved line 82 into the recycled-gas line 79 and, in admixture with the cycled gas, through the input well 80 into the formation. The added hydrogen sulfide can also be introduced into the gas line 76 ahead of the said compressor 77. The so introduced hydrogen sulfide-rich gas mixture flows from the bottom 83 of the input well 80 into the formation and flows under the force of the higher injection pressure through the formation towards the well bottom 84 of the production well 70 as indicated by arrows 85. The hydrogen sulfide-rich hydrogen gas mixture flowing from the input well to the production well in the formation and will admix with the gas and oil in the formation and will form with the gas and liquid a gas phase of the retrograde condensation type.

The higher concentration of hydrogen sulfide in the cycled gas will also cause hydrogen sulfide to dissolve in liquid hydrocarbons in the formation thus reducing the viscosity of the oil and rendering it more easily displaced by the cycled gases. It can be seen that oil no longer recoverable by primary depletion methods wi be vaporized and will pass with the well fluids to the surface in the production well 70.

In an example of operation according to the invention, a well fluid from a condensate type reservoir and containing 19 percent of hydrogen sulfide and 9 percent of carbon dioxide was produced. The formation temperature was 215° F. and the pressure was above its retrograde condensation pressure, which was found to be 4450 pounds per square inch. The gas was then passed through a system for the removal of hydrogen sulfide, after which it was observed that the retrograde condensation pressure of the gas, substantially free of hydrogen sulfide, had risen to 5370 pounds per square inch. The same well fluid, when its hydrogen sulfide content had been adjusted to 9.78 percent, exhibited a retrograde condensation pressure of 4975 pounds per square inch. In another example hydrogen sulfide was added to the well fluid to provide a hydrogen sulfide concentration of 27.04 percent in which case the retrograde condensation pressure was reduced to 4025 pounds per square inch.

As illustrated in Fig. 4, increasing the concentration of hydrogen sulfide in a gas-condensate fluid effects a linear reduction of the retrograde condensation pressure. Even small amounts of hydrogen sulfide, it can be seen, will reduce the retrograde condensation pressure in a typical condensate gas reservoir sufficiently to substantially prolong the operating period before such depletion phenomena as retrograde condensation occur. For example, addition of about five percent of hydrogen sulfide to such a well fluid will reduce the retrograde condensation pressure over 200 pounds per square inch.

The amount of reduction in the retrograde condensation pressure which an individual well fluid will show upon addition of a given amount of hydrogen sulfide will vary according to the original hydrogen sulfide content of the well fluids. However, alternation of the oil to gas ratio of the well fluids appears to have considerably less effect on the retrograde condensation pressure or on the influence which added hydrogen sulfide will have on the retrograde condensation pressure.

My invention comprehends the adjustment of the retrograde condensation pressure of petroleum fluids at high pressures in the order of the critical pressures of the fluids and consequently includes such adjustment whether or not the hydrogen sulfide content of the fluids is to be raised or lowered by the adjustment. Thus while my preferred embodiment of such a process of adjusting the said condensation pressure is the adjusting upwardly to a predetermined amount of hydrogen sulfide within the limits of about 1 to 30 percent by volume, my invention includes also adjustment downwardly of the hydrogen sulfide content for other purposes. For example the well fluids from a gas condensate well can be treated at pressures above the retrograde condensation pressure for removal of hydrogen sulfide from the fluids so that the retrograde condensation pressure will be considerably increased. Thereafter a substantial amount of liquid hydrocarbons can be recovered in a primary separator by retrograde condensation without lowering the pressure of the well fluids to the degree formerly necessary. Gas separated by this condensation step can be scrubbed with absorbent oil at these high pressures and the resulting gas can be returned to the formation with considerably less additional compression than would be required if it had been necessary to lower the pressure of the fluids below the original retrograde condensation pressure.

Having described my invention, I claim:

1. A method of producing increased yields of normally liquid hydrocarbons from a gas condensate well, which process comprises flowing well fluids containing hydrogen sulfide from a production well to a zone of pressure reduced to below the retrograde condensation pressure of the well fluids and thereby condensing liquid hydrocarbons from the fluids, withdrawing liquefied hydrocarbons from the condensing zone, passing gaseous fluids from the condensing zone to a purification zone, separating acid gases including hydrogen sulfide from the gaseous fluids in the purification zone, withdrawing hydrocarbon gases substantially free of acid gases from the separation zone and compressing at least a portion of said gases, adding to the said compressed gases sufficient quantity of hydrogen sulfide of the said acid gases to provide a hydrogen sulfide concentration of the compressed gases higher than that of the said well fluids and recycling the so-formed mixture of compressed gas and hydrogen sulfide to the said well formation.

2. A method of producing increased yields of normally liquid hydrocarbons from a gas condensate well, which process comprises flowing well fluids containing hydrogen sulfide from a production well to a zone of pressure reduced to below the retrograde condensation pressure of the well fluids and thereby condensing liquid hydrocarbons from the fluids, withdrawing liquefied hydrocarbons from the condensing zone, passing gaseous fluids from the condensing zone to a purification zone, separating acid gases including hydrogen sulfide from the gaseous fluids in the purification zone, withdrawing hydrocarbon gases substantially free of acid gases from the separation zone and compressing at least a portion of said gases, adding to the said compressed gases sufficient quantity of hydrogen sulfide of the said acid gases to provide a hydrogen sulfide concentration of the compressed gases at a selected concentration higher than that of the said well fluids and such that, when the compressed gases are added to fluids in the formation, a concentration of the formation fluids will range between 1 and 30 volume percent, and recycling the so-formed mixture of compressed gas and hydrogen sulfide to the said well formation.

3. An improved method of operating a gas condensate well to produce an increased yield of distillate hydrocarbons, which method comprises: withdrawing fluids having a hydrogen sulfide content from the said well; separating distillate hydrocarbons therefrom at a pressure less than the incipient retrograde condensation pressure of the well fluids; withdrawing so-separated gases and absorbing acid

gases therefrom in a liquid absorbent; stripping acid gases from the so-enriched absorbent; scrubbing gases from which acid gases have been removed with a hydrocarbon absorbent to recover liquid hydrocarbons therefrom; compressing gas from which the acid gases and liquid hydrocarbons have been removed to a pressure in excess of the said formation pressure; mixing with the so-compressed gas, acid gases containing hydrogen sulfide and additional hydrogen-sulfide-containing gases from an outside source; introducing the compressed gas mixture into the formation, the said hydrogen sulfide of the lean gases and that hydrogen sulfide obtained from an outside source being added to the formation in an amount that will increase the hydrogen-sulfide content of fluids in the said formation; and withdrawing fluids from the formation having an increased hydrogen-sulfide content.

4. A method of operating a depleted crude oil well to recover additional quantities of liquid hydrocarbons therefrom, which method comprises: introducing into a partially depleted formation underlying said oil well during production of crude oil, the fluids in the formation supplying the crude oil containing some hydrogen sulfide, a lean gas derived at least in part as a fraction of the produced crude oil and hydrogen sulfide in admixture with the lean gas; maintaining the hydrogen-sulfide content of the lean gas mixture at a concentration in excess of the hydrogen-sulfide concentration of fluids in the formation; continuing production of the crude oil until primary recovery is completed; subsequently operating said well as a gas condensate well, the pressure within the formation being maintained in excess of the retrograde condensation pressure of fluids in the formation by the said introduction of lean gas and hydrogen sulfide into the formation maintaining the hydrogen-sulfide concentration in the formation in excess of the hydrogen-sulfide concentration originally occurring therein and thereby reducing the retrograde condensation pressure of the fluids in the formation to a value below the pressure maintained in the formation during gas condensate well operation.

5. The method of claim 4 wherein lean gas and hydrogen sulfide from an outside source are also pumped into the well formation to reduce the rate of decrease in pressure in the well during crude oil production and subsequent distillate hydrocarbon production and to maintain the hydrogen-sulfide concentration in the formation at a value in excess of the concentration originally existing in the formation.

6. An improved method of operating oil and gas wells that produce petroleum fluids from a formation under a pressure in the order of the retrograde condensation range of the well fluids and of a magnitude that the fluids are in gaseous phase, which method comprises introducing into the said formation a gas containing hydrogen sulfide, after said introduction of gas containing hydrogen sulfide introducing another gas having a substantially lower concentration of hydrogen sulfide, the said concentrations of hydrogen sulfide in each case being so selected that upon ultimate diffusion of hydrogen sulfide in the formation the resulting average concentration of hydrogen sulfide in the fluids of the formation will be between 1 and about 30 volume percent, and thereby reducing the retrograde condensation pressure of the well fluids abruptly in increments so as to reabsorb liquid hydrocarbons, which have condensed out of gaseous phase during operation of the well, into the gaseous phase and retain hydrocarbons in the gaseous phase in the formation and permit their recovery in the well fluids.

7. An improved method of operating a gas condensate well that produces fluids from a formation under a pressure in the order of the retrograde condensation range of the well fluids, which method comprises introducing into the said formation a gas containing hydrogen sulfide in higher concentration than the concentration of hydrogen sulfide found to be present in the produced well fluids to increase the hydrogen sulfide concentration of the fluids in the said formation, and thereby proportionately reducing the retrograde condensation pressure of the well fluids so as to retain hydrocarbons in gaseous phase in the formation and permit their recovery in the well fluids.

8. An improved method of operating a gas condensate well that produces fluids from a formation under a pressure in the retrograde condensation range of the well-fluids mixture, which method comprises introducing into the formation a gas containing hydrogen sulfide in such concentration that when it mixes with well fluids in the formation a concentration of hydrogen sulfide of the well fluids will range between 1 and 30 percent by volume and thereby proportionately reducing the retrograde condensation pressure of the well fluids so as to retain hydrocarbons in gaseous phase in the formation and permit their recovery in the well fluids.

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