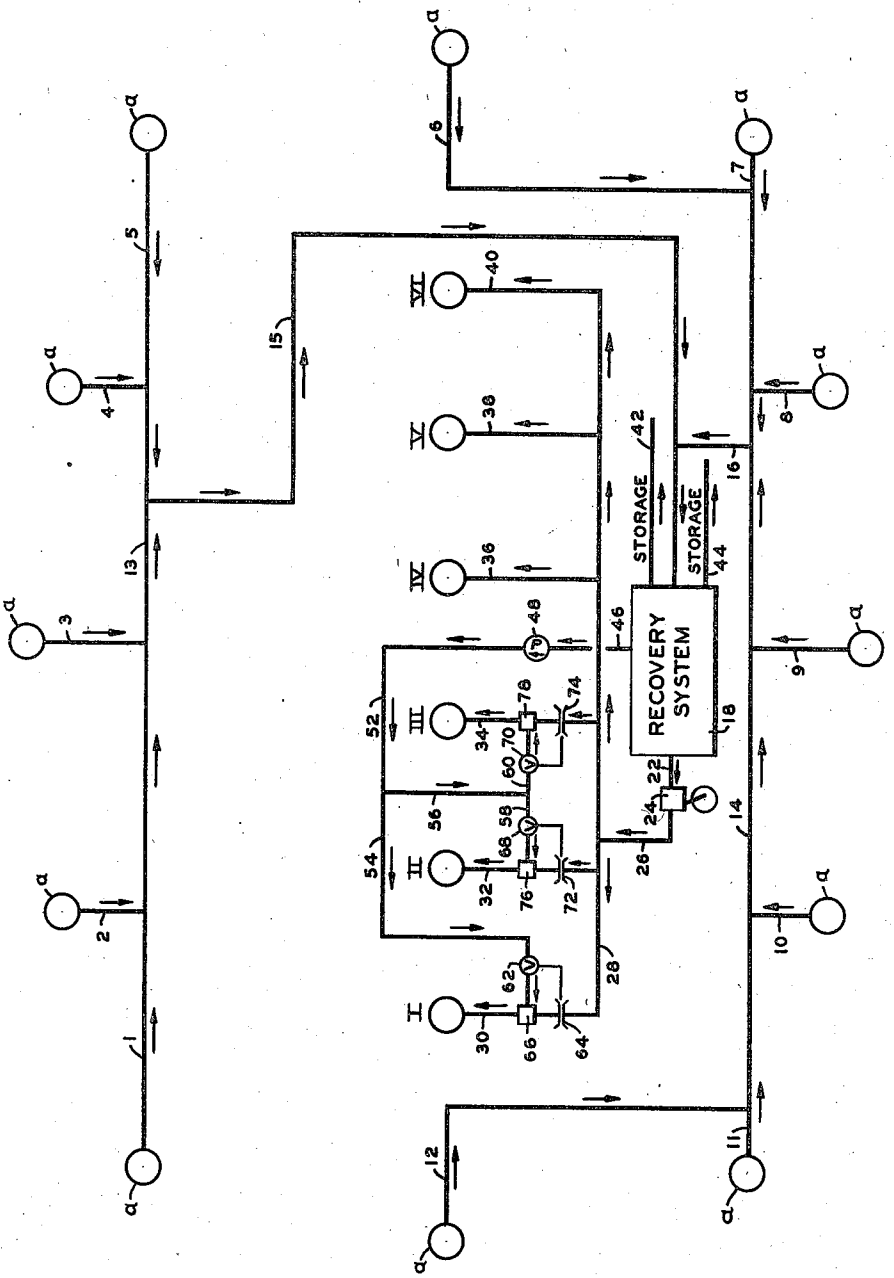
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METHOD OF STORING OILS

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METHOD OF STORING OILS

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This invention relates to a method for storing petroleum oils. More particularly, the invention relates to a method for the production of a distillate field whereby the desired fractions of the distillate fluid may be recovered and the fractions for which there is no ready market may be stored economically.

The problem with which the present invention is concerned has occupied the producers of petroleum oils for many years. During all periods it has been the case that a more ready market was available for certain fractions of the crude than for other fractions, and when conversion of the unmarketable fractions has not been feasible, the problem of storing these oils has arisen. Although storage on the surface has been followed as a general practice, this requires the acquisition and use of expensive tanks and other equipment. It has also been proposed to store the oil in a depleted oil reservoir, and this has been practiced in certain instances. This procedure, however, has the disadvantage that the rate of introduction of oil into the sand is relatively slow and only a part of the oil so introduced can be recovered in later production.

Under present conditions the problem of finding storage space for the unmarketable fractions is acute because, while the demand for high octane gasoline and lubricants is heavy, the demand for ordinary gasoline fractions has been materially reduced. Thus the C_4 and C_5 hydrocarbons, particularly isobutane, butane and isopentane, are in demand for use in the manufacture of 100 octane gasoline, the gas oil and kerosene fractions are employed in various conversion processes for the production of high octane gasoline, and the heavier fractions may be employed as lubricants and for other purposes, but the gasoline fractions (e. g., fractions composed of hydrocarbons containing more than five carbon atoms and having an end boiling point of about 400° F.) cannot be sold or utilized in the quantities in which they are being made available by the rate of production required to produce the desired lighter and heavier hydrocarbons. This is particularly true in the case of distillate fields, which should be produced at this time because distillate fluids contain a high percentage of the desired C_4 and C_5 hydrocarbons.

It is an object of the present invention to provide a novel and efficient method for storing normally liquid petroleum hydrocarbons, which method is characterized in that it may be carried out economically and the hydrocarbons are maintained under such conditions that they may later be recovered. Another object of the invention is to provide a method for the production of distillate fields whereby such fields may be operated to recover and dispose of hydrocarbons having a ready market, and hydrocarbons for which no market exists may be stored in a simple and efficient manner.

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

In accordance with the present invention, liquid petroleum fractions are stored by a method comprising mixing the normally liquid fraction with light, normally gaseous hydrocarbons, and then injecting the mixture into an underground formation where conditions of temperature and pressure are maintained at which the mixture is a single phase material. By following this procedure, the normally liquid hydrocarbons together with the light gases will enter the formation as a gas, and therefore may be introduced relatively easily. Also, since the normally liquid hydrocarbons will be stored as a vapor phase material at a relatively high pressure, the stored hydrocarbons may be recovered easily by permitting the gases to flow from producing wells, and separating these hydrocarbons from the light gases by separation methods well-known in the art.

As is becoming well-known, mixtures of compounds under high pressure and temperature conditions exhibit unusual behavior. It is generally recognized, for example, that the hydrocarbons in a distillate formation are present therein in the form of a single dense phase resembling a gas, and that upon a reduction in pressure on this single phase material condensation of liquefiable hydrocarbons occurs, resulting in the production of a two-phase product. This phenomenon has been termed "retrograde condensation," and the reverse effect noted upon increasing the pressure at a high temperature on a mixture of gaseous and liquid hydrocarbons has been termed "retrograde vaporization." For a discussion of these phenomena see the article by D. L. Katz and F. Kurata, entitled "Retrograde Condensation" which appears in Industrial and Engineering Chemistry, volume 32, No. 6, pages 817–827, and the article by J. E. Sherborne, entitled "Fundamental Phase Behavior of Hydrocarbons," American Institute of Mining and Metallurgical Engineers, Technical Publication No. 1152.

It seems to be established that a mixture of paraffin hydrocarbons may be subjected to con-

ditions of temperature and pressure such that the mixture is a single phase material subject to retrograde condensation upon a reduction in pressure. Also, mixtures of light hydrocarbons such as methane, ethane and propane with heavier hydrocarbons may be converted to single phase materials at lower temperatures than would be the case at intermediate pressures, by placing them under high pressures.

The present method is particularly applicable where a very high pressure gas field is available for storage purposes. In such cases, the method is carried out so as to take advantage of the phenomenon of retrograde vaporization. The underground formation should have a natural pressure of above 1500 pounds per square inch, usually from 3000 to 5000 pounds per square inch or above. Fields of this type generally have bottom hole temperatures of above 150° F., for example, temperatures from about 150° F. to 225° F. When storing normally liquid fractions in fields of this type the normally liquid hydrocarbons are combined with light gases in such proportions as to produce at formation conditions of temperature and pressure a homogeneous, single phase material subject to retrograde condensation—the mixture undergoes retrograde vaporization. In other words, the composition of the introduced mixture is such that at bottom hole conditions of temperature and pressure, these conditions are above the temperature and pressure at the critical point (the point at which the liquid and gas phases have the same composition) of the two-phase boundary for the mixture on the temperature-pressure plane. The temperature is also below the temperature at the cricondentherm (the maximum temperature at which two phases can exist).

The invention is preferably employed in the production of a distillate or condensate field. Such fields, as is well-known, are produced by a process comprising, generally, passing the distillate fluid from a number of producing wells, recovering from the fluid the desired liquefiable hydrocarbons, usually at a pressure below wellhead pressure, compressing residual gases, which may comprise, for example, methane, ethane and propane, and returning the compressed gases to the formation through a number of injection wells.

The recovery methods in use at the present time include simple retrograde condensation methods wherein the condensation of hydrocarbons is accomplished substantially entirely by reducing the pressure on the fluid, similar methods wherein the condensation due to the reduction in pressure is aided by artificial cooling and by various heat exchange procedures, and absorption methods wherein the distillate fluid is contacted with an absorption oil to absorb the liquefiable hydrocarbons; e. g., the hydrocarbons containing four and more carbon atoms. In any case, it has been the practice to dispose of the recovered fractions to the best advantage. In efficient operation, these fractions may include the C_4 and C_5 hydrocarbons, the gasoline fraction having an end boiling point of 400° F., and heavier material having an initial boiling point of about 400° F. At the present time, as indicated above, the gasoline fraction cannot be marketed economically and suitable storage facilities are difficult to obtain.

In accordance with the present invention, a distillate field is produced in the familiar manner using any desired recovery method, with absorption generally preferred. The recovered liquefiable hydrocarbons are separated into fractions such as those mentioned above. The C_4 and C_5 hydrocarbons are marketed for such purposes as use in the manufacture of high octane gasoline or the manufacture of liquid butane, and the fraction having an initial boiling point of 400° F. is utilized in conversion reactions for the production of high octane gasoline. The gasoline fraction is pumped up to a pressure substantially the same as the pressure at which the residual gases are returned to a formation. In this connection it is pointed out that the residual gases are not always returned to the formation from which the fluid was removed but sometimes are returned to another distillate formation. In any event, the gasoline fraction at the injection pressure is intimately mixed with the residual gases in a proportion adjusted in accordance with the principles discussed above. The mixture of residual gases and gasoline, therefore, will be in a single phase in the formation and will have properties similar to the properties of a naturally-occurring distillate fluid. Thus, after a time the formation around the injection well or wells will be converted to a formation resembling a natural distillate formation, and when recovery of the stored gasoline fraction is desirable this may be accomplished by normal methods utilized in the production of distillate fields. For example, the recovery plant employed in the initial production of the field may be used in the recovery of this gasoline fraction.

In addition to the advantages pointed out above in connection with the storage of petroleum fractions in gas rather than in liquid form, the production of a distillate field in the manner described has the advantage that it involves the return to the formation of a greater amount of hydrocarbons than is the case when only residual gases are used for pressure maintenance. One reason for the gradual drop in pressure in a distillate field is due to the fact that fewer mols of hydrocarbons are returned to the formation than are removed therefrom. The present method provides a means for increasing the number of mols of hydrocarbons employed for pressure maintenance, during the period of storage.

The drilling of wells in a distillate field is planned so as to place the producing and injection wells at the most desirable points in the formation. In some fields the production wells may be located in the flanks of the structure and the injection wells in the central portion; in other fields, these positions may be reversed. With either lay-out in accordance with the invention, the storage of the undesired liquid fractions is preferably accomplished only in one portion of the formation. By so carrying out the method, when later recovery is desired, removal of single phase material only from one portion of the field is necessary. To practice this method most efficiently it may be desirable in some fields to select different wells as injection wells than would normally be selected.

In order that the invention may be understood more fully reference should be had to the accompanying drawing in which the single figure is a diagrammatic illustration of the operation of the method as applied to a distillate field. The drawing is in the nature of a flow sheet, and valves and other equipment unnecessary to a description of the method have been omitted.

Referring to the drawing, the wells designated by the letter *a* are producing wells which may

produce a distillate fluid at a well-head pressure of above 1500 pounds per square inch, say a pressure of about 2300 pounds per square inch. The fluid is collected by means of gathering lines 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, and 16, and is conducted to a recovery system represented generally at 18. This recovery system may comprise any familiar method for the recovery of liquefiable hydrocarbons from distillate fluids as discussed above. This system also will include fractionation equipment making possible the fractionation of the recovered hydrocarbons into desired fractions. The residual gases consisting largely of methane, ethane and propane, are removed from the system through line 22 and are compressed in compressor 24 to some pressure above the pressure at the heads of the production wells. At this elevated pressure, these gases are passed through lines 26 and 28 into lines 30, 32, 34, 36, 38 and 40 leading to injection wells I, II, III, IV, V, and VI.

The C_4 and C_5 hydrocarbons may be removed from the recovery system through line 42 and passed to storage, or these hydrocarbons may be separated and recovered and stored separately. The heavier material, for example, the material having an initial boiling point of about 400° F. may be removed to storage and eventually disposed of through line 44. The gasoline fraction having an end boiling point of about 400° F. is removed from the system through line 46, and is pumped up to the injection pressure by means of pump 48. At this pressure, it passes through line 52 and lines 54, 56, 58 and 60. The portion of the gasoline flowing in line 54 is mixed with the residual gases in line 30 in carefully regulated proportions. The flow of gasoline in line 54 is controlled by means of valve 62 which in turn is controlled by flow meter 64 disposed in line 30. Thus, the amount of gasoline introduced is adjusted in accordance with the rate of flow of the residual gases. The actual mixing takes place in a mixing device represented at 66 whereby a substantially homogeneous mixture may be produced. This mixing device may be of a conventional injector design. Similarly, gasoline flowing in lines 58 and 60 is controlled and mixing is accomplished by means of valves 68 and 70, flow meters 72 and 74, and mixing devices 76 and 78.

It will be noted that the gasoline is introduced only into injection wells I, II, and III and, therefore, when recovery of the gasoline is desirable this can be accomplished by putting these wells on production or producing through nearby wells without producing the remainder of the field.

When operating in the manner illustrated in the drawing, the proportions of gasoline introduced into the residual gases are adjusted so as to produce in the formation a single phase material subject to retrograde condensation. These proportions, of course, will vary depending upon the composition of the residual gases, the composition of the gasoline, and the formation conditions of temperature and pressure. The necessary proportions can be determined by mixing samples of the residual gases with samples of the gasoline, and determining the phase relations of the resulting mixtures, as described in the Katz and Kurata article previously mentioned. Thus, the two-phase boundaries on the temperature-pressure plane, including the critical points and cricondentherms can be determined for the system of components represented by the mixtures. A mixture is selected as to which the formation conditions of temperature and pressure are above the temperature and pressure at the critical point, and as to which the cricondentherm is at a higher temperature than the formation temperature.

The above description has stressed the preferred manner of carrying out the method of the invention involving storing the liquid fractions in a mixture such that at formation conditions the mixture is a single phase material subject to retrograde condensation. This is preferred for reasons given above and also because a larger amount of liquid can be stored at the high pressures. In its broader aspects, however, the invention is not restricted to this method of operating. The invention includes, for example, a method wherein the fractions are stored in a gas field at a moderate pressure, say, 300 to 500 pounds per square inch, and the mixture underground, while in a single phase, is in the nature of an ordinary natural gas substantially saturated with the hydrocarbons to be stored. These hydrocarbons may be recovered later by passing the gas through an ordinary natural gasoline plant. Incidentally, when a gas formation is referred to in the claims it will be understood that a distillate formation or an ordinary gas formation are intended unless otherwise indicated.

Although the specific description has been principally concerned with an operation wherein the liquid hydrocarbons are returned to a formation in the same field from which they were produced, it is obvious from what has been said heretofore that the invention is not restricted to this type of operation and that it includes processes wherein the liquid hydrocarbons to be stored are obtained from various sources, such as refineries.

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.

We claim:

1. The method of storing hydrocarbons which are in the liquid phase at atmospheric temperature and pressure under conditions at which said hydrocarbons may later be recovered efficiently, which comprises mixing said hydrocarbons with hydrocarbons which are in the gas phase at atmospheric temperature and pressure in proportions selected such that the resulting mixture will exist as a single, homogeneous phase material subject to retrograde condensation under the temperature and pressure existing in a selected high pressure subsurface formation, and introducing said mixture into said high pressure subsurface formation, whereby said mixture is maintained as a single, homogeneous phase material subject to retrograde condensation and in condition to permit the later efficient recovery of said hydrocarbons which are in the liquid phase at atmospheric temperature and pressure.

2. A method in accordance with claim 1 wherein the pressure prevailing in the subsurface formation is at least 1500 pounds per square inch.

3. In the production of a distillate field wherein the distillate fluid is flowed from a production well, liquefiable hydrocarbons are recovered from said fluid, residual gases consisting essentially of hydrocarbons containing not more than three carbon atoms and which are in the gas phase at atmospheric temperature and pressure are introduced into a distillate formation, and the liquefiable hydrocarbons are separated into fractions,

the method which comprises mixing a liquid fraction consisting essentially of hydrocarbons which are in the liquid phase at atmospheric temperature and pressure with residual gases in proportions selected such that the resulting mixture will exist as a single, homogeneous phase material subject to retrograde condensation under the temperature and pressure existing in a distillate formation in which the pressure is above 1500 pounds per square inch, introducing the resulting mixture into said distillate formation, whereby said mixture is maintained as a single, homogeneous phase material subject to retrograde condensation and in condition to permit the later efficient recovery of the hydrocarbons of said liquid fraction.

4. The method of producing a distillate field which comprises flowing distillate fluid from a plurality of wells tapping a distillate formation, recovering liquefiable hydrocarbons comprising hydrocarbons containing four and more carbon atoms from said fluid, leaving residual gases consisting essentially of hydrocarbons containing not more than three carbon atoms and which are in the gas phase at atmospheric temperature and pressure, separating said liquefiable hydrocarbons into fractions including a gasoline fraction consisting of hydrocarbons which are in the liquid phase at atmospheric temperature and pressure, compressing said residual gases, flowing the compressed residual gases to a plurality of injection wells leading to a selected distillate formation which is at a pressure above 1500 pounds per square inch, during the flow of at least a part of said compressed residual gases mixing the gasoline fraction therewith in proportions selected such that the resulting mixture will exist as a single, homogeneous phase material subject to retrograde condensation at the temperature and pressure existing in said selected distillate formation, whereby said mixture is introduced into said selected distillate formation and is maintained therein as a single, homogeneous phase material subject to retrograde condensation and in condition to permit the later efficient recovery of the hydrocarbons of said gasoline fraction.

5. A method in accordance with claim 4 in which the gasoline fraction is mixed with only a part of the residual gases, and the mixture of the gasoline fraction and said part of the residual gases is introduced into one section of the distillate formation, whereby the gasoline fraction may later be recovered by producing only from said section.

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