NEW EUROPEAN PATENT SPECIFICATION

Method of simultaneously cooling and removing water from hydrocarbon gas mixtures and apparatus therefor.

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References cited:
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US-A-3 807 963

The file contains technical information submitted after the application was filed and not included in this specification

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Description

This invention relates to the simultaneous chilling and dehydration of water-containing gaseous hydrocarbon mixtures to which methanol has been added as a dehydrating agent.

When water-containing gaseous hydrocarbon mixtures are to be cooled to low temperatures and in particular to temperatures below those at which ice and/or hydrates of the hydrocarbons are formed, e.g. in order to facilitate the condensation of a part or all of the gas, it is essential either to dehydrate the mixture or to add a hydrate suppression agent/water absorbent such as methanol or a glycol. Otherwise the water in the gaseous mixture will freeze or form solid hydrates with the hydrocarbons during the cooling step.

A conventional method of using methanol for this purpose involves adding it in gaseous form to the mixture, cooling the resultant methanol-containing composition whereby to form a hydrocarbon-immiscible liquid aqueous phase containing methanol and water absorbed from the hydrocarbon mixture and separating the aqueous phase from the hydrocarbon phase. The temperature to which a gaseous hydrocarbon mixture can be cooled by conventional manner, however, is limited by the degree of condensation of the hydrocarbon mixture that can be tolerated. For example, for a binary mixture, in particular, the temperature to which it can be cooled must exceed the boiling point of the lighter hydrocarbon if separation of the mixture is desired.

The present invention provides a method which permits the cooling of binary gaseous hydrocarbon mixtures down to even the liquefaction temperature of the lighter component while still achieving separation of the two components, thereby lowering the permissible minimum temperature for the cooling step as compared with conventional processes and thus permitting (a) lower methanol losses in the gas phase, (b) improved hydrocarbon separation and (c) simultaneous dehydration of the mixture and stabilisation of the hydrocarbon liquid separated out by the cooling process. Similar benefits are possible with hydrocarbon mixtures containing three or more components.

The method of the present invention also permits a reduction in the amount of methanol required for a given final cooling temperature, thus permitting a higher water/methanol ratio in the aqueous layer which separates out which in turn reduces the solubility of the methanol in the hydrocarbon and therefore the loss of methanol in the hydrocarbon phase. Where the methanol is employed in the form of an aqueous solution of methanol, this in turn permits the use of more dilute solutions than would otherwise be possible.

A further advantage of the method is that it may be carried out in apparatus the efficient operation of which is relatively unaffected by movement or moderate inclination or tilting of the equipment and is therefore particularly suitable for use, e.g. on board ships, barges, moving platforms and tower loading buoys.

In accordance with this invention a water-containing gaseous hydrocarbon mixture is simultaneously dehydrated and cooled to a temperature below the ice- or hydrate-formation temperature of said water-containing hydrocarbon mixture by the incorporation of a controlled or known concentration of methanol vapour into said mixture and the subsequent cooling of the gaseous composition so obtained by indirect heat exchange with a coolant in a reflux heat exchanger through which the composition is passed upwards, a dehydrated hydrocarbon gas being recovered from the top of the exchanger and an aqueous condensate being recovered from the bottom. In the refluxing exchanger, the composition is cooled as it flows upwards and liquids condensed therefrom flow downwards in countercurrent fashion in contact with the rising stream being cooled.

Where partial condensation of the hydrocarbon mixture occurs as a result of the chilling, the condensate recovered from the base of the exchanger will comprise an aqueous phase and a condensed hydrocarbon phase which can readily be separated from the aqueous phase.

The condensed hydrocarbon in contact with the aqueous phase will be saturated with water and methanol in accordance with the ternary phase equilibria of the hydrocarbon/water/methanol system at that temperature. The liquid hydrocarbon may be separated and withdrawn as such or alternatively it may be separated and further chilled in order to further reduce its water/methanol content or it may be withdrawn and treated in accordance with our co-pending UK Application No. 30086787 to reduce its water and methanol content.

Alternatively the hydrocarbon and aqueous layers may be both chilled and separated at a lower temperature to further reduce the water and methanol content of the hydrocarbon water.

Gaseous hydrocarbon mixtures to which the process of the invention will generally be applied will predominate in C3 to C6 hydrocarbons and include, for example, natural gas streams containing some C2 and heavier hydrocarbons, gases associated with naturally occurring oil (associated gases), and gases from oil refining and gases derived from cracking, hydrocracking, hydrotreating or catalytic reforming of hydrocarbons. Because of the nature of these gaseous hydrocarbon mixtures, the process of the invention will normally be conducted at superatmospheric pressure, usually in the range 50 to 1000 psig, but pressure is not critical to the process.

The gaseous hydrocarbon mixtures may and generally will also include gases other than hydrocarbons. For example, naturally occurring mixtures will include inert gases such as N2 and He and/or acid gases such as CO2 and H2S, and manufactured gases may also contain H2 and CO.

As the gaseous composition passes upwards
through the exchanger and is cooled, the water therein will tend to condense in preference to the methanol, thus increasing the ratio of the methanol to water vapour in the gas and thus as the vapours pass up the heat exchanger the ratio of methanol to water vapour in the gas phase will increase. Likewise the ratio of methanol to water in the liquid phase will also increase as the temperature decreases. Thus, a hydrocarbon/water/methanol gas mixture of given composition may be chilled to a lower temperature than would be possible with the use of conventional heat exchanger arrangements. Alternatively less methanol is required in the wet hydrocarbon gas mixture for a given temperature drop and thus where the methanol is supplied to the wet hydrocarbon in the form of an aqueous solution of methanol, more dilute solutions may be employed thus simplifying methanol recovery in the case where the methanol-containing aqueous phase separated from the hydrocarbon by the chilling step is recycled.

A further advantage is that since the total inventory of methanol and water decreases up the heat exchanger it is possible to permit the temperature of the cold end of the exchanger to drop below that at which ice and or solid hydrates form while still achieving relatively continuous operation with only infrequent warming being required to melt the solids. Moreover, depending on the methanol/water ratio at the cold end of the exchanger, the maximum required temperature for the warming will generally not exceed about −90°C.

Where it is desired to cool the gaseous mixture below −90°C, it may be necessary to withdraw the gas from the heat exchanger before solids formation occurs and contact with a methanol/water mixture to reduce the methanol/water ratio in the gas to a level such that it is between about 68 and 78%, based on combined weight of methanol and water in the gas, before continuing the cooling.

Where the hydrocarbon mixture is partially condensed in the chilling step, there is preferential condensation of heavier components at the lower, warmer end of the exchanger and also the warm gases at the lower end tend to strip or remove light components from the descending condensed hydrocarbons which then return upwards with the gas to be cooled. In this way, the condensed hydrocarbon material contains a much lower percentage of lighter fractions than would be obtained by normal cooling and removal of condensate, and thus stabilisation of the condensed hydrocarbon is improved.

If the cooling is effected by passing the composition through the tubes of a shell and tube exchanger, the distribution of liquid throughout the tubes is unaffected by movement or inclination of the tubes and because condensation is taking place on the tube surface the maldistribution of the liquid within each tube is reduced. Thus, using this arrangement enables the process of the invention to be operated satisfactorily e.g. on a ship, floating barge, moving platform or tower loading buoy.

This effect is increased with decrease in tube internal diameter and it is preferred that this dimension be from 1/4 to 3/4 inch. Plate and fin exchangers of the kind which can be regarded as the equivalent of shell and tube exchangers in which the gas-processing passageways are vertical or inclined may also be employed.

The cooling for the heat exchanger may be provided by a refrigerant stream which may be gaseous or a boiling liquid. Where it is a boiling liquid, it is preferred that there is a second heat transfer fluid between the refrigerant and the downwardly flowing liquid condensed out of the gas under treatment. This is particularly desirable if the methanol/water ratio in the mixture being fed to the heat exchanger is such that the freezing point of the initially condensed aqueous phase is below that of the boiling refrigerant.

In one preferred embodiment, the chilled gas recovered from the top of the heat exchanger is passed back down the heat exchanger in indirect countercurrent heat exchange relationship with the gas being chilled and in passageways lying between the gas being chilled and the passageways carrying the boiling liquid refrigerant. If it is desired to recover the gas from the cold end of the exchanger, the gas may then be passed back up through the heat exchanger in further passageways, and then recovered from the top, or cold end, of the exchanger.

Further rectification of the condensate obtained by the process of the invention can be achieved by passing the gas to be treated in indirect heat exchange relationship with the condensate recovered from the lower or hot end of the heat exchanger before passing the gas into said heat exchanger. This improvement is applicable whether or not partial condensation of the hydrocarbon mixture is effected in the heat exchanger.

Methanol condensed from the chilled gas in the heat exchanger may be recovered and re-incorporated into gas to be treated in the heat exchanger by contacting at least some of the aqueous phase in the condensate recovered from the lower or hot end of the heat exchanger with gas to be fed to the heat exchanger and at a temperature at which at least some of the methanol will be vapourised from the aqueous phase and entrained in the gas.

The invention also provides apparatus for simultaneously cooling and dehydrating a water-containing gaseous hydrocarbon stream, the apparatus including a mixer for mixing methanol with said stream and having inlets for a methanol-containing stream and said hydrocarbon stream and an outlet for the gaseous composition formed by mixing said streams; a heat exchanger having at least a first passageway adapted for generally upward passage therethrough of said composition from an inlet at the bottom to an outlet at the top and generally countercurrent downward passage therein to the inlet of condensate formed in said passageway from said composition and at least a second passageway adapted for passage
therethrough of a coolant in indirect heat exchange relationship with said composition in said first passageway to cool said composition as it passes upwards from said inlet to said outlet; means for supplying said composition from said mixer outlet to said heat exchanger passageway inlet; a gas/liquid separator having at least one outlet for liquid collected therein; and conduit means connecting the gas space in said separator with the inlet of said first passageway and adapted to pass gas from said space generally upwardly to said passageway inlet and permit condensate formed in said passageway to fall back from said inlet to said separator.

The invention further provides apparatus for simultaneously cooling and dehydrating a gaseous composition comprising a water-containing hydrocarbon gas mixture and methanol vapour and obtaining a chilled condensate from said gas mixture, e.g. for eventual storage in a cargo space of a tanker, said apparatus comprising a heat exchanger having at least a first passageway adapted for generally upward passage therefor of said composition from an inlet at the bottom to an outlet at the top and generally countercurrent downward passage therein to the inlet of condensate formed in said passageway from said composition and at least a second passageway adapted for passage therefor of a coolant in indirect heat exchange relationship in said composition in said first passageway to cool said composition as it passes upwards from said inlet to said outlet, means for supplying said composition to said inlet; a gas/liquid separator; conduit means connecting the gas space in said separator with the inlet of said first passageway and adapted to pass gas from said space generally upwardly to said passageway inlet and permit condensate formed in said passageway to fall back from said inlet to said separator, said separator also having first and second outlets for a hydrocarbon phase and an aqueous phase, respectively, of said condensate; and means for contacting an aqueous stream from said aqueous phase outlet with said water-containing hydrocarbon gas mixture whereby to transfer methanol values from said aqueous stream to said hydrocarbon stream.

Where a boiling liquid is employed as coolant, the heat exchanger preferably includes means for returning gas recovered from the outlet of said first passageway downwardly through the heat exchanger in indirect heat exchange relationship with the composition passing up said first passageway and between said first passageway and said second passageway.

In a preferred embodiment, the apparatus includes means for effecting indirect heat exchange between said composition and condensate falling back from said first passageway inlet to said separator through said first conduit means before said composition enters said first passageway inlet.

When used on a tanker, with means for transferring hydrocarbon liquid from the separator to a cargo space in the tanker, the apparatus may further include mixing means for intimately mixing hydrocarbon liquid recovered from said separator with an aqueous methanol solution, cooling the resultant mixture and separating it into a hydrocarbon phase and aqueous phase and passing the last-mentioned hydrocarbon phase to said cargo space, and optionally also means for reducing the pressure of said last mentioned hydrocarbon phase whereby a portion thereof is vaporised to form a second gaseous composition comprising a water-containing gas mixture and methanol vapour and including a second apparatus of the reflux heat exchanger kind as defined above for cooling and partially condensing said second composition and returning the condensate to a cargo space.

The apparatus of the invention may also be provided on an off-shore installation such as a moving platform or barge or tower loading buoy, in which case it may include means for transferring hydrocarbon liquid from the gas/liquid separator to a means for dispensing the liquid into a cargo space of a tanker ship.

The invention will now be described in more detail with reference to preferred embodiments thereof and with the aid of the accompanying drawings in which:

Figure 1 is a diagrammatic flow sheet of one arrangement in accordance with the invention for treating a gas comprising a water-containing gaseous hydrocarbon mixture and methanol;

Figure 2 is a modification of the arrangement shown in Figure 1 in which the heat exchanger is adapted for use with a boiling liquid refrigerant;

Figure 3 is a modification of the arrangement shown in Figure 2;

Figure 4 shows a modification of the arrangement under the heat exchanger of Figures 1, 2 or 3, which modification is particularly suitable where simultaneous partial condensate of the gaseous hydrocarbon mixture is required; and

Figure 5 shows an arrangement which permits recovery of at least some of the methanol condensed from the gas and recycle of the reclaimed methanol for admixture with fresh gas.

In all Figures, the heat exchanger is shown with the passageways vertical. However they may also be inclined to the vertical, although preferably by an angle of not more than 45°.

Referring to Figure 1, reference numeral 2 is a mixing or dispersing device, 4 is a gas/liquid separator and 6 is a heat exchanger. A gaseous hydrocarbon mixture containing water and which is to be cooled or chilled is passed via pipeline 10 to the mixing or dispersing device 2. The mixing or dispersing device may be a spray chamber, a packed column, a bubbling device or some similar device in which a controlled amount of methanol either as such or as an aqueous solution thereof may be added through pipeline 12 to the incoming gas stream. Alternatively the gas in pipeline 10 may come from a prior process or separator in which methanol has been incorporated into the gas such that additional
methanol need not be added in the mixing device or dispersing device 2 which is merely employed to effect intimate mixing or dispersing of the methanol in the gas. It may be discarded if intimate mixing has already taken place. Such an alternative scheme would be where the gas comprises boil-off gases from a tank containing refrigerated gas liquids to which methanol has been added to permit the gas liquids to be cooled to the storage temperature without the formation of ice or hydrate by any water present in them.

Gas from the mixing or dispersing device 2 and containing a controlled amount of methanol vapour passes via pipeline 14 to the gas/liquid separator 4.

The gas may contain hydrocarbons which are to be condensed and stabilised as well as water vapour which is to be removed down to a temperature at or below the hydrate or ice formation temperature of the incoming hydrocarbon gas mixture.

The gas passes from the gas/liquid separator 4 upwards via the pipeline, or gas passage, 16 which may be in effect a multiplicity of such passages such as the extended tubes of a vertical shell and tube heat exchanger. As will be shown, the gas passing upward through 16 flows counter-current to downward flowing condensate from the heat exchanger 6. Gas from 16 passes into the tubes or passageways of the heat exchanger 6, one of which is illustrated and identified by reference numeral 18. The passageways 18 will generally be the tubes of a shell and tube heat exchanger or passageways in a plate and fin exchanger or some similar heat exchanger device offering vertical heat exchange surfaces such that gas may pass upwards in close contact with liquid condensate passing down the walls of the heat exchange surfaces. The device illustrated in Figure 1 is a section of a plate and fin exchanger. As the gas passes up through 16, it is cooled and its temperature progressively decreased. Condensate carrying condensed hydrocarbons, water and methanol flows down the tube counter-current to the upflowing gas. This has the effect of stabilising the down-flowing liquid, to remove light hydrocarbons in preference to heavier hydrocarbons from the downflowing liquid and to remove water vapour in preference to methanol vapour from the upflowing gas. Therefore the gas at the top has a higher methanol/water ratio than at the inlet and can withstand a lower temperature without ice or hydrate formation than would be possible in a conventional heat exchanger. Condensate passes down the walls of pipe or passageway 18 and thence via pipe or passageway 16 to the gas liquid separator 4 where it is drawn off via pipeline or duct 26.

Cold gas leaves the top of passageway 18 depleted in condensate and is passed via transfer pipe or duct 20 to the heat exchanger pipe or passageway 22 where it flows downward by counter-current to the gas flow in the pipe or passageway 18 and extracts heat from the gases in 18. It is then recovered via pipe or duct 24.

In the embodiment shown in Figure 1, the necessary refrigeration for the heat exchanger 6 is provided by a cooled stream which in this case is a refrigerated gas entering via pipeline or duct 28 and thence to duct or passageway 30 in which it flows downwardly counter-currently to the gas flow in duct or passageway 18, extracting heat from the gases in 18. It is then withdrawn from the heat exchanger via pipe or duct 32. The refrigerated gas may be provided from an external refrigeration loop using for example a compressor and expansion turbine or may be derived by externally cooling the gas from duct 24 in a refrigerator heat exchanger or if the gas recovered in duct 24 is at a suitably elevated pressure it may be derived by expanding gas from duct 24 in an expansion turbine to a suitable pressure and passing the gas to duct 26. Other schemes will occur to those skilled in the art as suitable to provide the refrigerated gas.

If a boiling liquid refrigerant is employed as the cooling medium, it is preferred not to use it directly as outlined in the above description. It is not desirable to use a boiling liquid refrigerant directly against the wall of the passageway or duct 18 carrying the upward flowing gas to be cooled. This is because the heat exchange coefficients for boiling refrigerants are very high and therefore the heat exchange surface in contact with this liquid refrigerant would tend to have a more uniformly cold temperature than would be the case where a cold gas is used as the refrigerant. It is preferred that there be a reasonably uniform temperature drop in the heat exchange surface in contact with down-flowing condensate and up-flowing gas in the passageway 18 so that the minimum amount of methanol is required in order to prevent freezing or hydrate formation on the tube wall.

A further embodiment of the invention will now be described by way of example with reference to the accompanying Figure 2 in which, as in Figure 1, reference numeral 4 is a gas liquid separator and 6 is a heat exchanger of the plate and fin type. In this embodiment, however, the exchanger has two parallel heat exchange clusters. This arrangement permits the use of a boiling liquid refrigerant in the heat exchanger without causing excessive cooling and a uniform temperature of the walls next to the gas to be treated.

The gas to be treated enters via pipeline or duct 14 and passes to the gas liquid separator 4 and then, as in Figure 1, via duct or ducts 16 into the passageways 18 in the heat exchanger block. The gas passes upward in the passageways 18 which can be formed by vertical plain or slotted corrugated plates between the flat spacer plates in the heat exchanger or alternatively by special plates such as overflow packing or alternative designs of plate which ensure that the condensate formed from the rising gas flows downward wetting the walls of 18 in counter-current flow with the rising gas. Cooled gas from the tops of the passageway 19 is passed to the transfer duct or header, 20 and
thence is passed back downwards through the heat exchanger in the passageways 22 leaving the exchanger through outlet duct or header 24.

Boiling liquid refrigerant to provide the refrigeration load enters the heat exchange block via duct or header 28 and passes to passageways 30 which are adjacent to passageways 22 but not adjacent to passageways 18. Whilst the refrigerant ducts may extend the whole length of the block and the refrigerant, with careful liquid distribution, might be allowed to flow downward in true counter-current flow, the arrangement shown is the normal upward flow in which total evaporation is not essential and where the liquid in header 32 may be recovered and returned with fresh refrigerant to duct or header 28. In this arrangement the refrigerant is isolated from direct proximity to the gas being chilled and treated in passageway 18 by the gas passageways 22 and in this way the temperature profile through the walls of the passageways 18 is kept such that the walls become progressively cooler up the heat exchanger and do not undergo the sudden cooling which would occur if the boiling liquid refrigerant were in direct contact with the walls of the passageways 18.

It should be noted that whereas Figures 1 and 2 show the gas to be treated being cooled to the required treatment temperature and thereafter being reheated by heat exchange with the incoming gas prior to being discharged, the same treatment system may also be used without the step of reheating the gas in passageway 22. Such an arrangement may be desirable, for example, in the case of treatment of natural gas prior to passing it onwards to a liquefaction stage to produce LNG. In this case the treated gas leaving passageways 18 at the top of the exchanger may pass onward and not back via duct or passageways 22. Where a boiling liquid refrigerant is used and where it is desirable not to over chill the heat transfer surfaces of passageways 18, the scheme shown in Figure 3 may be used. In this arrangement, chilled and treated gas leaving passageways 18 passes via duct or header 20 into passageways 22 and thence counter-current to the gas flow in 18 leaving via duct or header 25 and into passageway 23 which passes on the other side of 18 upward and co-current with the gas flow 18 with the gas leaving the top of the exchanger via duct or header 24. The gas is thus recovered from the cold end of the exchanger.

Where the gas to be treated comprises a multi-component mixture of compounds some of which are to be condensed and removed by chilling; e.g. a gas liquids fraction in a natural gas stream, the liquids leaving the heat exchanger as shown in Figures 1 and 2 are stabilised but nevertheless are in equilibrium with the incoming gas and may thus still contain some undesirable light fractions. These may be removed by separate flashing or distillation steps or alternatively they may be rectified employing the arrangement shown in Figure 4.

In Figure 4, as in Figures 1 and 2, reference numeral 4 is a gas liquid separator. Similarly, passageway or duct 16 is a multiplicity of passageways or ducts leading to the heat exchanger 6 of Figure 1, 2 or 3 and may be continuations of the passageways 18 shown in Figures 1 and 2.

As in Figures 1, 2 and 3, gas flows upward in 16 and condensed liquid flows down the walls of the passageways. An opening or openings 44 are located near the top of 16 near where it passes upwards and becomes passageway 18 of the heat exchanger. The openings 44 are arranged such as to allow ingress of gas into the passageway 16 without escape of liquid from passageway 16 into 42 which is a heat exchange area or passageway adjoining the passageway 16. If a unit is a shell and tube heat exchanger, 42 may be a shell zone separated from passageways 22 and 30 (see Figure 1) by a tube plate. If the unit is a plate and fin unit as shown in Figures 1, 2 and 3, 42 may be gas passages at the bottom of the exchanger adjacent to 16 with 16 being a continuation of 18 and with passageway 42 being isolated from the passageways 22, 23 and 30 shown in Figures 1, 2 and 3.

Hot incoming gas to be treated enters the system in duct or passageways 14 and is directed into the base of passageway 42 or by-passed to the top of passageway 42 by means of valves 34 and 36 and ducts or passageways 38 and 40 respectively. Hot gas entering via valve 34 and passageway or duct 38 into 42 heats the liquid flowing down the walls of passageway 16 and boils off undesirable light fractions in the liquid. Passageway 16 thus acts as a distillation column with the removed light gases passing upwards to join the incoming gas which enters passageway 16 via the openings 44 before passing to the duct or passageways 18 (as shown in Figures 1, 2 and 3) for cooling in heat exchanger 6 (see Figures 1, 2 and 3). The degree of removal of light fraction in 16 may be controlled by the direction or by-passing of hot incoming gas via valves 34 and 36 to the base or top of 42.

Where the chilling causes partial condensation of the hydrocarbon mixture, the condensate removed will be in two phases; a hydrocarbon phase and an aqueous phase. Because this invention allows the reduced usage of methanol for a given duty, the water content of the methanol-water condensate recovered from the gas will be higher than with conventional treatment and as a result the solubility and loss of methanol in the hydrocarbon phase is reduced. The aqueous and hydrocarbon phase may be separated and at least part of the methanol in the aqueous phase may be recovered and recirculated for injection into the incoming gas. An arrangement for such a technique is shown in Figure 5.

In Figure 5, 2 is a mixing device as described for Figure 1, 4 is a three phase gas/hydrocarbon liquid/aqueous phase separator, 100 is a contacting device such as a spray tower, packed tower,
bubble cap tower, or similar device, and 130 is a heating device such as a heating coil, element, exchanger or similar device.

In this arrangement, condensate falling back down passageway 16 as described with reference to Figures 1, 2, 3 and 4 passes to the separator 4 in which it separates into a lower aqueous phase and upper hydrocarbon phase. The upper hydrocarbon phase is drawn off via line 116 and valve 118 and may be disposed of as such or further stabilised or treated by conventional means.

The lower aqueous phase containing the bulk of the recovered methanol is drawn off via line 106 and valve 108 and may subsequently be distilled by conventional means to recover the methanol or may, as shown in Figure 5, pass to a contacting device in which the incoming gas to be treated in heat exchanger 6 (Figures 1, 2 and 3) enters at the bottom via pipeline or duct 14 and contacts the aqueous liquid and preferentially strips methanol from said liquid before leaving via pipeline 132 and passing to the mixing device 2 where make-up methanol is added as required via pipeline 114 to the gas liquid separator 4 and then via duct or passageway 16 for treatment as described with reference to Figures 1, 2, 3 or 4.

Further rectification of the liquid hydrocarbon phase recovered through pipeline 116 may be achieved by countercurrently contacting it, either in contacting device 100 or in a separate contacting device not shown, with the feed gas mixture entering in line 14.

While the invention has been described and illustrated with reference to a single refluxing heat exchanger and a single draw-off point for condensate formed in the heat exchanger, several such heat exchange steps may be provided in series to produce a plurality of condensates when partial condensation of the gaseous hydrocarbon mixture is effected. Other processing operations may be interspersed between the heat exchange steps. For example, the process is particularly well suited to pretreating a natural gas or associated gas prior to a low temperature methanol or methanol/water wash to remove acid gases.

One particularly important application of the process is for the recovery at superatmospheric pressure of a liquid fraction consisting predominantly of hydrocarbons selected from C4—C6 hydrocarbons and mixtures thereof from a wet associated gas or natural gas stream, with simultaneous dehydration of the gas stream.

The liquid fraction thereby obtained is particularly suitable for conversion to olefin gases by steam cracking. However, it will generally still contain some water and thus where the steam cracking facility is geographically remote from the location where the fraction is formed and it is necessary to transport the fraction at a sub-zero temperature in a tanker, it may be necessary to remove more water from the fraction. This may conveniently be achieved by intimately mixing the liquid fraction with an aqueous solution of methanol and then cooling the mixture whereby water in the fraction is absorbed preferentially in the aqueous methanolic solution and a hydrocarbon phase and aqueous methanol phase are formed, and the hydrocarbon phase is separated from the aqueous phase, the aqueous solution being substantially insoluble in the fraction and having a freezing point below the temperature to which the mixture is cooled. Preferably, at least part of the aqueous phase is recycled to be mixed with fresh liquid fraction, the methanol concentration of the recycling liquor being continuously or intermittently restored towards that of the aqueous solution initially employed and the inventory of said liquor continuously or intermittently restored towards its initial level. This process with recycle of the aqueous phase forms the subject of our copending UK Application No. 30085/78.

The chilled fraction thereby obtained will generally still be at a superatmospheric pressure and a portion of it will vapourise when it is let down to about atmospheric pressure for storage and or transport. The gas thereby produced, and which will still contain water vapour up to saturation point at the prevailing temperature and pressure, and some methanol, is normally thereafter re-compressed and separated into a light fraction which is vented, stored or used as fuel, and a heavier fraction which is desired to recover and return to mix with the remainder of the chilled fraction. The compression step, however, increases the water vapour pressure and it is therefore desirable to remove more water from this gas. Conveniently, this may be achieved simultaneously with the separation step by using the process of the present invention.

All the above steps of recovering and subsequently treating the liquid fraction can be operated using apparatus which is compact and which is relatively unaffected by movement or lifting and which can thus be installed on moving platforms, ships, barges or tower loading buoys. There is thus provided a valuable overall method of obtaining from a natural or associated gas from an offshore source, a hydrocarbon material which is particularly suitable for conversion to valuable olefin gases by steam cracking at a location which is geographically remote from the point of supply of the material and to which the material is transferred at least in part by transport at sub-zero temperature in a tanker ship.

The invention will now be illustrated by way of the following Example.

Example

The exchanger consisted of a bundle of 5 parallel tubes formed from 3/8 inch o.d. tubing, arranged with a central tube surrounded by and soldered to the other 4. The central tube was formed to change its cross-sectional shape from circular to parallel sided with semicircular ends, the radius of the ends being 3/32 inch and the overall length and width of the tube being 3/8 inch and 3/16 inch respectively (internal dimensions). Two of the outer tubes were formed to have flat sides to fit alongside the parallel flat sides of the
central tube, and the remaining two were formed to adopt a kidney shape in cross-section to fit round the semicircular ends of the central tube. Each outer tube was 6 ft long; the inner tube was 6 ft 8 inches long with 8 inches extending downwardly from the bottom of the bundle into a receiver which had an inlet for the gas to be treated and a drain leading to a second vehicle where recovered liquid separated into aqueous and hydrocarbon phases.

The gas to be treated passed upwards through the central tube and cooling was provided by passing refrigerated gaseous Freon 502 downwards through the outer tubes. Thermocouples measuring the outside wall temperature of the central tube and gas sampling points were provided at top, mid-point and bottom of the bundle.

The feed supplied to the central tube was the product of contacting a gaseous methane, ethane, propane and butane mixture with an aqueous methanol solution. The feed had a composition A and was supplied at a temperature B, and a pressure C. Product gas was recovered from the top of the tube at a flow rate D.

The bottom, mid-point and top temperatures of the tube (outside wall temperatures as measured by the thermocouples) were E, F and G.

Samples of the gas in the central tube were taken at the bottom and the top of the tube and were found by gas chromatographic analysis to have compositions H and J respectively.

After K of gas had been recovered from the top of the tube, the condensate recovered from the bottom of the central tube of the column was found to comprise L of aqueous phase of composition M and N of hydrocarbon phase of composition P.

In a comparative experiment where the feed gas is cooled by conventional means with concurrent flow of gas and condensate formed from the gas by the cooling, hydrate and ice formation occur at or above R. If ice and hydrate formation is suppressed by adding more methanol, S of hydrocarbon condensate having a composition T is obtained after treating the same amount of feed as above.

The values for A to T are given below.

<table>
<thead>
<tr>
<th></th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>CH₃OH</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>feed gas composition</td>
<td>0.55</td>
<td>39.88</td>
<td>56.15</td>
<td>2.34</td>
<td>0.06</td>
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<td>H</td>
<td>Gas composition at bottom of tube</td>
<td>0.55</td>
<td>52.98</td>
<td>44.55</td>
<td>1.57</td>
<td>0.10</td>
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<tr>
<td>J</td>
<td>Gas composition at top of tube</td>
<td>2.51</td>
<td>95.76</td>
<td>1.63</td>
<td>&lt;0.1</td>
<td>0.10</td>
</tr>
<tr>
<td>M</td>
<td>Composition of recovered liquid aqueous phase</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>3.6</td>
</tr>
<tr>
<td>P</td>
<td>Composition of recovered liquid hydrocarbon phase</td>
<td>&lt;0.1</td>
<td>24.65</td>
<td>72.32</td>
<td>3.03</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>T</td>
<td>Composition of condensate obtained by conventional treatment</td>
<td>0.56</td>
<td>40.32</td>
<td>56.75</td>
<td>2.37</td>
<td>—</td>
</tr>
<tr>
<td>B</td>
<td>Feed Gas Temperature</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>31.5°C</td>
</tr>
<tr>
<td>C</td>
<td>Feed Gas Pressure</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>14.8 atm</td>
</tr>
<tr>
<td>D</td>
<td>Product Gas Flow Rate</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>79.3 litres/hr</td>
</tr>
<tr>
<td>E</td>
<td>Tube Bottom Temperature</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>13.5°C</td>
</tr>
<tr>
<td>F</td>
<td>Tube Mid-Point Temperature</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—10°C</td>
</tr>
<tr>
<td>G</td>
<td>Tube Top Temperature</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—19.5°C</td>
</tr>
<tr>
<td>K</td>
<td>Quantity of Gas recovered from Tube Top</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>304 normal litres</td>
</tr>
<tr>
<td>L</td>
<td>Quantity of Liquid Aqueous Phase recovered</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>12 ml</td>
</tr>
<tr>
<td>N</td>
<td>Quantity of Liquid Hydrocarbon Phase recovered</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4080 ml</td>
</tr>
<tr>
<td>R</td>
<td>Hydrate/ice formation temperature for conventional cooling</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—5.4°C</td>
</tr>
<tr>
<td>S</td>
<td>Amount of gas condensed using conventional cooling</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>100%</td>
</tr>
</tbody>
</table>

It will thus be seen that under the conditions employed substantially all the C₃ in the feed gas is recovered in the condensate and no freezing occurs. However if conventional cooling had been used, freezing would have occurred less than half way along the heat exchanger and if this had been
suppressed by adding more methanol all the gas would have condensed and no separation would have occurred.

Claims

1. A method in which a water-containing gaseous hydrocarbon mixture is simultaneously dehydrated and chilled to a temperature below the ice or hydrate-formation temperature of said mixture by the incorporation of a controlled or known concentration of methanol vapour into said mixture and the subsequent cooling of the gaseous composition so obtained by indirect heat exchange with a coolant characterised in that the indirect heat exchange step is effected in a reflux exchanger through which said composition is passed upwards, a dehydrated hydrocarbon gas being recovered from the top of the exchanger and an aqueous condensate being recovered from the bottom.

2. A method as claimed in claim 1 in which prior to entering the heat exchanger the composition is passed in indirect heat exchange relationship with condensed liquids recovered from the lower end of the heat exchanger, to further rectify said liquids.

3. A method as claimed in claim 1 or claim 2 in which at least some of the aqueous phase recovered from the lower end of the heat exchanger is contacted with fresh gaseous hydrocarbon mixture containing water prior to the latter entering the heat exchanger, said contacting being effected at a temperature at which at least some of the methanol in said aqueous phase is vaporised from said phase and entrained in said fresh gaseous hydrocarbon mixture, water and a controlled or known concentration of methanol vapour.

4. A method as claimed in any one of the preceding claims in which the gaseous hydrocarbon mixture is partially condensed by said chilling, the condensate recovered from the bottom of the heat exchanger is separated into an aqueous phase and a liquid hydrocarbon phase, and the liquid hydrocarbon phase is recovered.

5. A method as claimed in claim 4 in which the liquid hydrocarbon phase is countercurrently contacted with the gaseous composition prior to the latter entering the heat exchanger.

6. A method as claimed in any one of claims 1 to 5 in which the gaseous composition is at a superatmospheric pressure.

7. A method as claimed in any one of claims 1 to 6 in which the gaseous hydrocarbon mixture comprises a natural gas or associated gas and the chilling is effected at superatmospheric pressure to separate and recover from said gas a condensed liquid fraction consisting predominantly of hydrocarbons selected from C₂ to C₆ hydrocarbons and mixtures thereof.

8. A method as claimed in claim 7 in which said liquid fraction is intimately mixed at superatmospheric pressure with an aqueous solution of methanol and then cooled whereby water in the fraction is absorbed preferentially into the aqueous methanolic solution and a hydrocarbon phase and aqueous methanol phase are formed, and the hydrocarbon phase is separated from said aqueous phase, the aqueous solution being substantially insoluble in the liquid fraction and having a freezing point below the temperature to which the mixture is cooled.

9. A method as claimed in claim 7 or claim 8 in which the pressure of the hydrocarbon phase separated from the aqueous phase is reduced and the vapours thereby generated are recompressed and thereafter simultaneously dehydrated and chilled by the method claimed in claim 4 to separate them into a gaseous light fraction and a condensed heavier fraction which is returned to be mixed with the hydrocarbon phase at said reduced pressure.

10. Apparatus for simultaneously cooling and dehydrating a water-containing gaseous hydrocarbon stream, according to one of the processes of claims 1—9 the apparatus including a mixer for mixing methanol with said stream and having inlets for a methanol-containing stream and said hydrocarbon stream and an outlet for the gaseous composition formed by mixing said stream; a heat exchanger having at least a first passageway adapted for generally upward passage there-through of said composition from an inlet at the bottom to an outlet at the top and countercurrent downward passage therein to the inlet of condensate formed in said passageway from said composition and at least a second passageway adapted for passage there-through of a coolant in indirect heat exchange relationship with said composition in said first passageway to cool said composition as it passes upwards from said inlet to said outlet; means for supplying said composition from said mixer outlet to said heat exchanger passageway inlet; a gas/liquid separator having at least one outlet for liquid collected therein; and conduit means connecting the gas space in said separator with the inlet of said first passageway and adapted to pass gas from said space generally upwardly to said passageway inlet and permit condensate formed in said passageway to fall back from said inlet to said separator.

11. Apparatus for simultaneously cooling and dehydrating a gaseous composition comprising a water-containing hydrocarbon gas mixture and methanol vapour according to the process of claim 3, said apparatus comprising a heat exchanger having at least a first passageway adapted for generally upward passage there-through of said composition from an inlet at the bottom to an outlet at the top and generally countercurrent downward passage therein to the inlet of condensate formed in said passageway from said composition and at least a second passageway adapted for passage there-through of a coolant in indirect heat exchange relationship with said composition in said first passageway to cool said composition as it passes upwards from said inlet to said outlet, means for supplying said
composition to said inlet; a gas/liquid separator; conduit means connecting the gas space in said separator with the inlet of said first passageway and adapted to pass gas from said space generally upwardly to said passageway inlet and permit condensate formed in said passageway to fall back from said inlet to said separator, said separator also having first and second outlets for a hydrocarbon phase and an aqueous phase, respectively, of said condensate; and means for contacting an aqueous stream from said aqueous phase outlet with said water-containing hydrocarbon gas mixture whereby to transfer methanol values from said aqueous stream to said hydrocarbon stream and supply the resultant methanol containing composition to said first passageway inlet of said heat exchanger.

12. Apparatus as claimed in claim 10 or claim 11 in which the heat exchanger includes means for returning gas recovered from the outlet of said first passageway downwardly through the heat exchanger, in indirect heat exchange relationship with the composition passing up said first passageway and between said first passageway and said second passageway.

13. Apparatus as claimed in claim 10, claim 11 or claim 12, including means for effecting indirect heat exchange between said composition and condensate falling back from said first passageway inlet to said separator through said first conduit means before said composition enters said first passageway inlet.

Revendications

1. Procédé dans lequel un mélange d’hydrocarbures gazeux contenant de l’eau, est simultanément déshydraté et refroidi à une température inférieure à la température de formation de glace ou d’hydrates de ce mélange, par incorporation d’une concentration connue ou contrôlée de vapeur de méthanol dans ce mélange et refroidissement subégalement de la composition gazeuse ainsi obtenue, par échange de chaleur indirect avec un réfrigérant, lequel procédé est caractérisé en ce que l’étape d’échange de chaleur indirect est réalisée dans un échangeur à reflux traversé par la composition en un courant ascendant, un gaz hydrocarburodé déshydraté étant récupéré en haut de l’échangeur et un condensat aqueux étant récupéré à la base de ce dernier.

2. Procédé selon la revendication 1, caractérisé en ce qu’avant d’entrer dans l’échangeur de chaleur, la composition subit un échange de chaleur indirect avec des liquides condensés récupérées à la partie inférieure de l’échangeur de chaleur afin d’améliorer la rectification de ces liquides.

3. Procédé selon la revendication 1 ou la revendication 2, caractérisé en ce qu’au moins une petite partie de la phase aqueuse récupérée à la partie inférieure de l’échangeur de chaleur est mise en contact avec un mélange d’hydrocarbures gazeux frais contenant de l’eau, avant que ce dernier ne pénètre dans l’échangeur de chaleur, cette mise en contact étant réalisée à une température à laquelle au moins une petite partie du méthanol présent dans la phase aqueuse est vaporisée hors de cette phase aqueuse et entraînée dans ledit mélange d’hydrocarbures gazeux frais pour former une composition gazeuse contenant ce mélange d’hydrocarbures gazeux, de l’eau et une concentration contrôlée ou connue de vapeurs de méthanol.

4. Procédé selon l’une quelconque des revendications 1 à 3, caractérisé en ce que le mélange d’hydrocarbures gazeux est partiellement condensé par ce refroidissement, en ce que le condensat récupéré à la base de l’échangeur de chaleur est séparé en une phase aqueuse et une phase hydrocarbonée liquide et en ce que la phase hydrocarbonée liquide est récupérée.

5. Procédé selon la revendication 4, caractérisé en ce que la phase hydrocarbonée liquide est mise en contact à contrecourant avec la composition gazeuse avant que celle-ci n’entre dans l’échangeur de chaleur.

6. Procédé selon l’une quelconque des revendications 1 à 5, caractérisé en ce que la composition gazeuse se trouve sous une pression supérieure à la pression atmosphérique.

7. Procédé selon l’une quelconque des revendications 1 à 6, caractérisé en ce que le mélange d’hydrocarbures gazeux comprend un gaz naturel ou un gaz associé et en ce que le refroidissement est réalisé sous une pression supérieure à la pression atmosphérique pour séparer et récupérer à partir de ce gaz, une fraction liquide condensée essentiellement constituée par des hydrocarbures choisis parmi les hydrocarbures en C₂ à C₄ et leurs mélanges.

8. Procédé selon la revendication 7, caractérisé en ce que cette fraction liquide est intimement mélangée sous une pression supérieure à la pression atmosphérique, à une solution aqueuse de méthanol et est ensuite refroidie de telle sorte que l’eau présente dans la fraction est absorbée préréférentiellement dans la solution méthanolique aqueuse et qu’il se forme une phase hydrocarbure et une phase méthanolique aqueuse et en ce que la phase hydrocarbonée est séparée de la phase aqueuse, la solution aqueuse étant pratiquement insoluble dans la fraction liquide et présentant un point de congélation inférieur à la température à laquelle le mélange est refroidi.

9. Procédé selon la revendication 7 ou la revendication 8, caractérisé en ce que la pression de la phase hydrocarbonée séparée de la phase aqueuse est réduite et les vapeurs ainsi engendrées sont recomprimées et ensuite simultanément déshydratées et refroidies par le procédé selon la revendication 4, afin de les séparer en une fraction légère gazeuse et une fraction plus lourde condensée qui est renvoyée pour être mélangée avec la phase hydrocarbonée, à cette pression réduite.

10. Appareillage pour refroidir et déshydrater simultanément un courant d’hydrocarbures gazeux contenant de l’eau selon l’une quelconque des revendications 1 à 9, caractérisé en ce qu’il
comprend un mélangeur pour mélanger du méthanol avec ce courant, qui est muni d’entrées pour un courant contenant du méthanol et le courant d’hydrocarbures et d’une sortie pour la composition gazeuse formée par mélange de ces courants; un échangeur de chaleur ayant au moins un premier passage conçu pour une circulation généralement ascendante de la composition à partir de l’entrée située à la base vers une sortie située au sommet et pour une circulation généralement descendante à contrecourant vers l’entrée, du condensat formé dans ce passage à partir de cette composition, et au moins un second passage conçu pour la circulation d’un réfrigérant en relation d’échange de chaleur indirect avec la composition dans le premier passage afin de refroidir celle-ci alors qu’elle monte de l’entrée vers la sortie; des moyens pour amener la composition de la sortie du mélangeur à l’entrée du passage de l’échangeur de chaleur; un séparateur gazliquide ayant au moins une sortie pour le liquide collecté dans celui-ci; et des conduits reliant l’espace du gaz du séparateur à l’entrée du premier passage et conçus pour laisser passer le gaz dans cet espace suivant un courant généralement ascendant vers cette entrée du passage et permettre au condensat formé dans ce passage de retomber de l’entrée dans le séparateur.

11. Appareillage pour refroidir et déshydrater simultanément une composition gazeuse comprenant un mélange d’hydrocarbures gazeux contenant de l’eau et de la vapeur de méthanol par le procédé selon la revendication 3, caractérisé en ce qu’il comprend un échangeur de chaleur ayant au moins un premier passage conçu pour une circulation généralement ascendante de la composition depuis une entrée située à la base jusqu’à une sortie placée au sommet et pour la circulation généralement descendante à contrecourant vers l’entrée, du condensat formé dans ce passage à partir de la composition, et au moins un second passage conçu pour la circulation d’un réfrigérant en relation d’échange de chaleur indirect avec la composition dans le premier passage de façon à refroidir celle-ci alors qu’elle monte de l’entrée vers la sortie, des moyens pour envoyer la composition à cette entrée; un séparateur gazliquide; des conduits reliant l’espace du gaz de ce séparateur à l’entrée du premier passage et conçus pour faire monter le gaz de cet espace en un courant généralement ascendant vers l’entrée dudit passage et permettre au condensat formé dans ce passage de retomber de l’entrée dans le séparateur, ce séparateur comportant également des première et seconde sorties pour une phase hydrocarbonnée et une phase aqueuse, respectivement, du condensat; et des moyens pour mettre un courant aqueux provenant de cette sortie de la phase aqueuse, en contact avec le mélange d’hydrocarbures gazeux contenant de l’eau, de façon à transférer du méthanol de ce courant aqueux au courant hydrocarbonné et amener la composition contenant du méthanol résultante à l’entrée du premier passage de l’échangeur de chaleur.

12. Appareillage selon la revendication 10 ou la revendication 11, caractérisé en ce que l’échangeur de chaleur comprend des moyens pour renvoyer le gaz récupéré à la sortie du premier passage en un courant descendant à travers l’échangeur de chaleur, en relation d’échange de chaleur indirect avec la composition qui monte dans le premier passage, lequel moyen est situé entre le premier et le second passages.

13. Appareillage selon la revendication 10, la revendication 11 ou la revendication 12, caractérisé en ce qu’il comprend des moyens pour effectuer un échange de chaleur indirect entre la composition susdite et le condensat qui retombe de l’entrée du premier passage dans le séparateur, à travers ces premiers conduits avant que la composition ne pénètre dans l’entrée du premier passage.

Patentansprüche


2. Verfahren nach Anspruch 1, worin die Mischung vor dem Eintreten in den Wärmestau- tsaucher einem indirekten Wärmestausch mit kondensierten Flüssigkeiten unterzogen wird, die von dem unteren Ende des Wärmestauschers gewonnen worden sind, um diese Flüssigkeiten weiter zu rekultivieren.

3. Verfahren nach Anspruch 1 oder 2, worin mindestens ein Teil der aus dem unteren Ende des Wärmestausachers gewonnenen wässrigen Phase mit frischer, wasserhaltiger, gasförmiger Kohlenwasserstoffmischung in Kontakt gebracht wird, bevor diese in den Wärmestausch eintritt, wobei das Inkontaktbringen bei einer Temperatur erfolgt, bei der mindestens ein Teil des Methanols in der wässrigen Phase aus der Phase verdampft und mit der frischen, gasförmigen Kohlenwasserstoffmischung mitgerissen wird unter Bildung einer Gasmischung, die die gasförmige Kohlenwasserstoffmischung, Wasser und eine gesteuerte oder bekannte Konzentration von Methanol dampf enthält.

4. Verfahren nach einem der vorhergehenden Ansprüche, worin die gasförmige Kohlenwasserstoffmischung teilweise durch Kohlen kondensiert wird, das aus dem unteren Abschnitt des Wärmestauschers gewonnene Kondensat in
eine wässrige Phase und eine flüssige Kohlenwasserstoffphase getrennt wird und die flüssige Kohlenwasserstoffphase gewonnen wird.

5. Verfahren nach Anspruch 4, worin die flüssige Kohlenwasserstoffphase im Gegenstrom mit der gasförmigen Mischung in Kontakt gebracht wird, bevor diese in den Wärmeaustauscher eintritt.

6. Verfahren nach einem der Ansprüche 1 bis 5, worin die gasförmige Mischung bei über- atmosphärischem Druck gehalten wird.

7. Verfahren nach einem der Ansprüche 1 bis 6, worin die gasförmige Kohlenwasserstoffmischung ein Naturgas oder ein ähnliches Gas umfaßt und das Kühlen bei über- atmosphärischem Druck bewirkt wird, um aus dem Gas eine kondensierte flüssige Fraktion abzutrennen und zu gewinnen, die überwiegend aus Kohlenwasserstoffen besteht, die aus \( C_4 \)–\( C_8 \)-Kohlenwasserstoffen und Mischungen davon ausgewählt sind.

8. Verfahren nach Anspruch 7, worin die flüssige Fraktion bei überatmosphärischem Druck innig mit einer wässrigen Lösung von Methanol vermischt und dann gekühlt wird, wodurch das in der Fraktion vorhandene Wasser bevorzugt in der wässrigen methanolischen Lösung absorbiert wird und eine Kohlenwasserstoffphase und eine wässrige Methanolphase gebildet werden, welche Kohlenwasserstoffphase von der wässrigen Phase abgetrennt wird, wobei die wässrige Lösung in der flüssigen Fraktion im wesentlichen unlöslich ist und einen Gefrierpunkt unterhalb der Temperatur aufweist, auf die die Mischung abgekühlt wird.

9. Verfahren nach Anspruch 7 oder 8, worin der Druck der von der wässrigen Phase abgetrennten Kohlenwasserstoffphase vermindert wird und die in dieser Weise gebildeten Dämpfe erneut verdichtet und anschließend gemeinsam nach der Verfahrensweise von Anspruch 4 entwässert und abgekühlt werden, um sie in eine gasförmige leichte Fraktion und eine kondensierte schwere Fraktion zu trennen, welche im Kreislauf zurückgeführt und mit der Kohlenwasserstoffphase bei dem verminderten Druck vermischt wird.


