United States Patent [19]

Allam et al.

[11] **3,813,889**

[45] **June 4, 1974**

[54] **SEPARATION OF GAS MIXTURES**

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[73] Assignee: **Air Products and Chemicals Inc.,** New Malden, Surrey, England; by said Allam and Bligh

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[21] Appl. No.: **126,727**

[30] **Foreign Application Priority Data**

Mar. 26, 1970 Great Britain 14896/70

[52] **U.S. Cl.** **62/22,** 62/17, 62/40, 62/28

[51] **Int. Cl.** **F25j 1/00,** F25j 1/02

[58] **Field of Search** 62/172, 22, 23, 24, 27, 62/28, 40

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Assistant Examiner—Arthur F. Purcell
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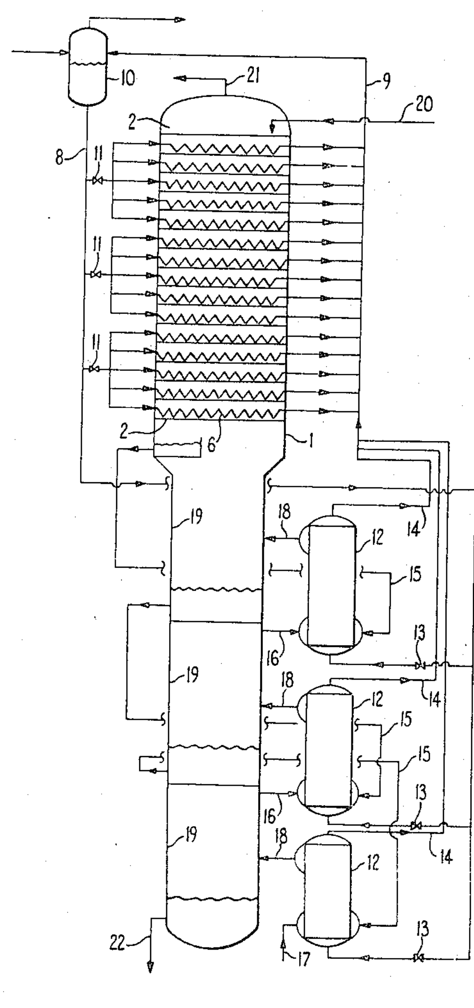
[57] **ABSTRACT**

A process and plant for obtaining substantially pure hydrogen or helium in which a mixture of hydrogen and/or helium and nitrogen and/or carbon monoxide, cooled to near its dew point at a pressure in the range 5 to 55 atmospheres, is fed into the bottom of a refrigerated wash-column while a liquid methane stream is fed in at the top. Hydrogen and/or helium is taken from the top of the column; a liquid stream containing methane and nitrogen and/or carbon monoxide is taken from the bottom.

7 Claims, 6 Drawing Figures



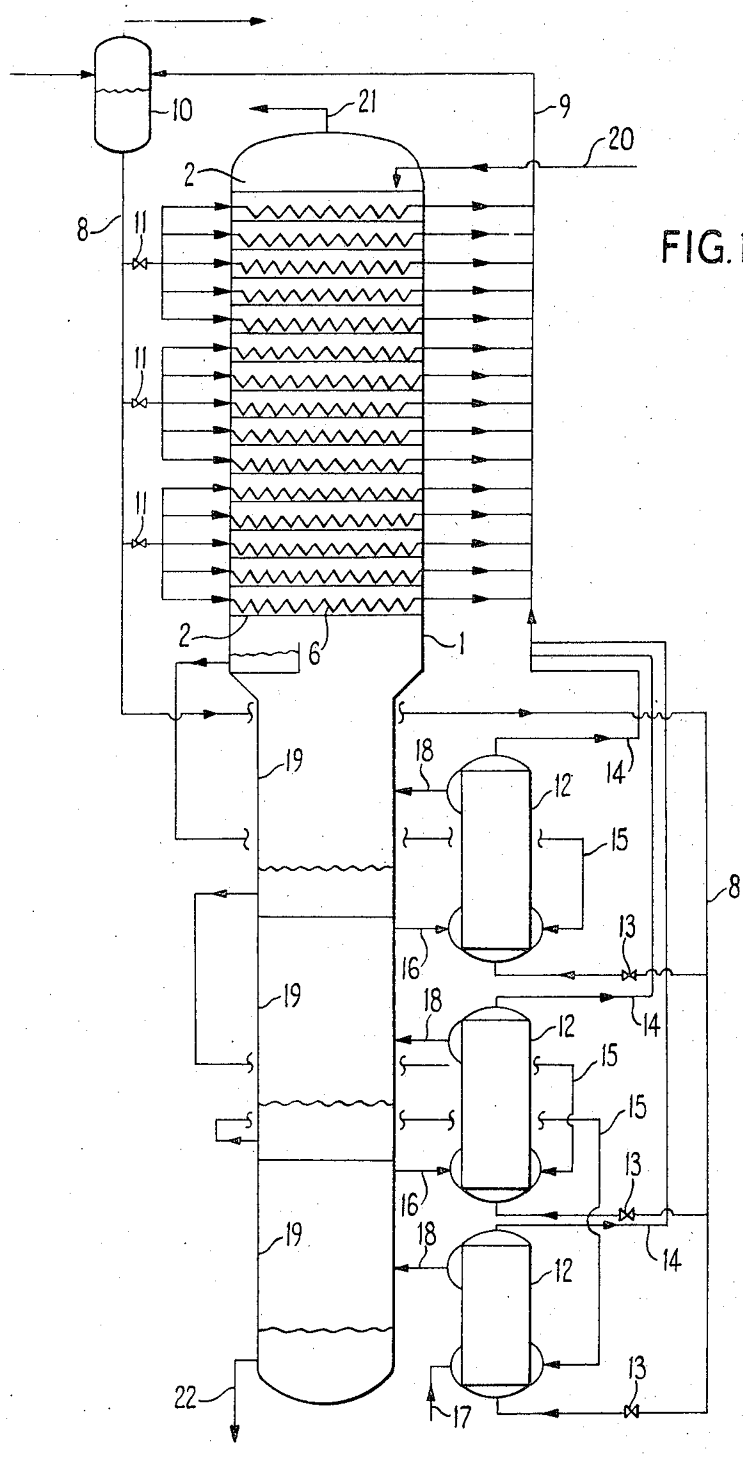

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FIG.1

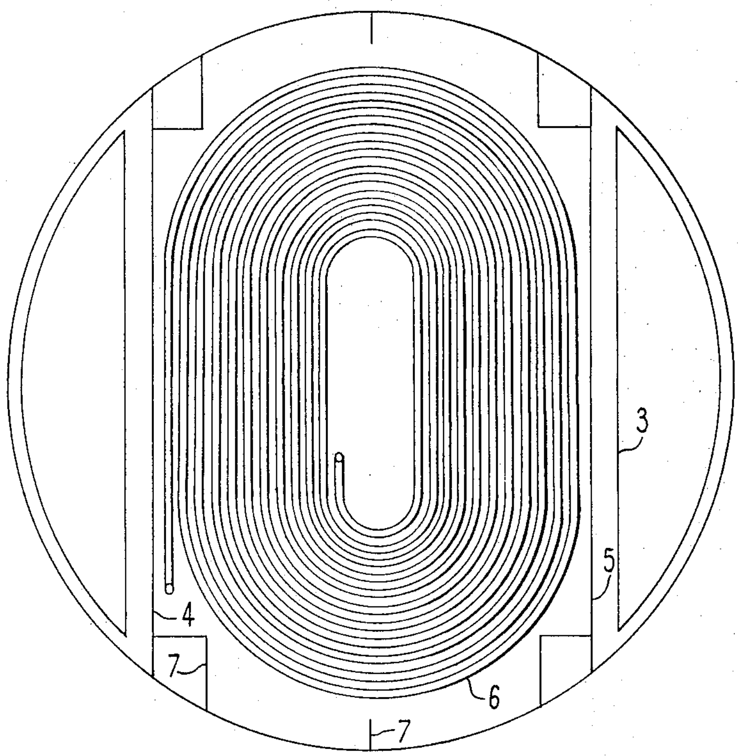

FIG.2

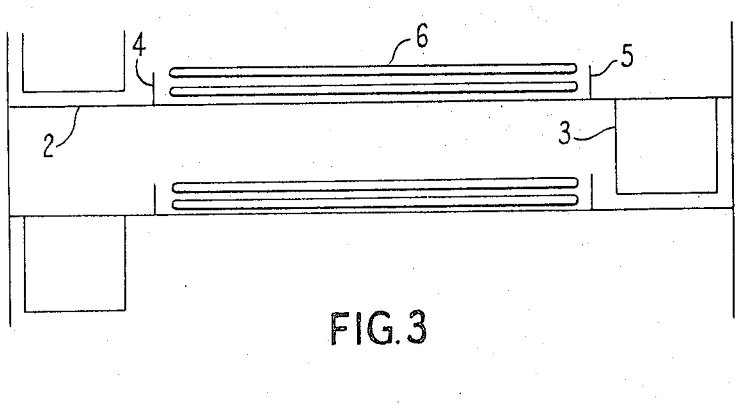

FIG.3

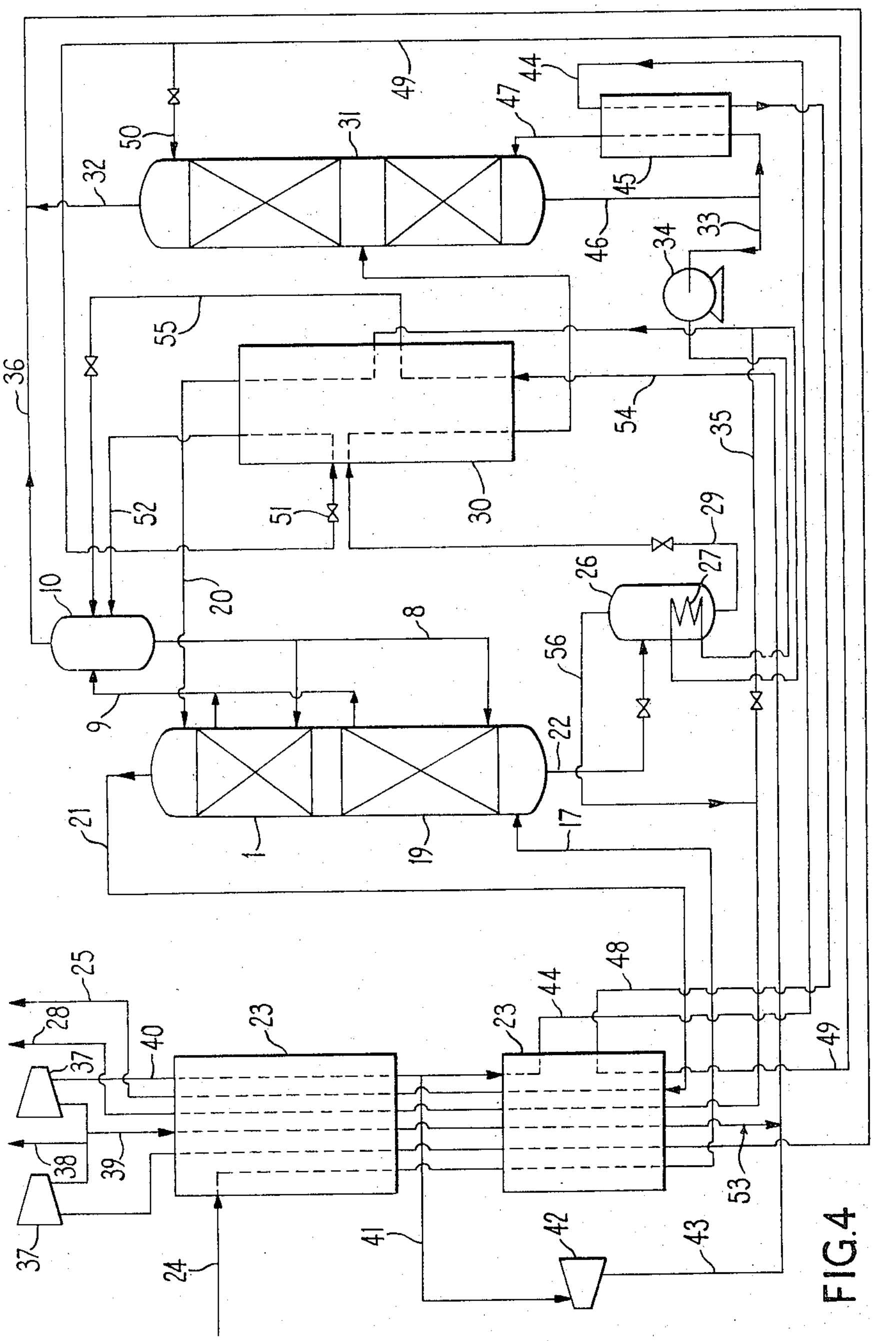

FIG.4

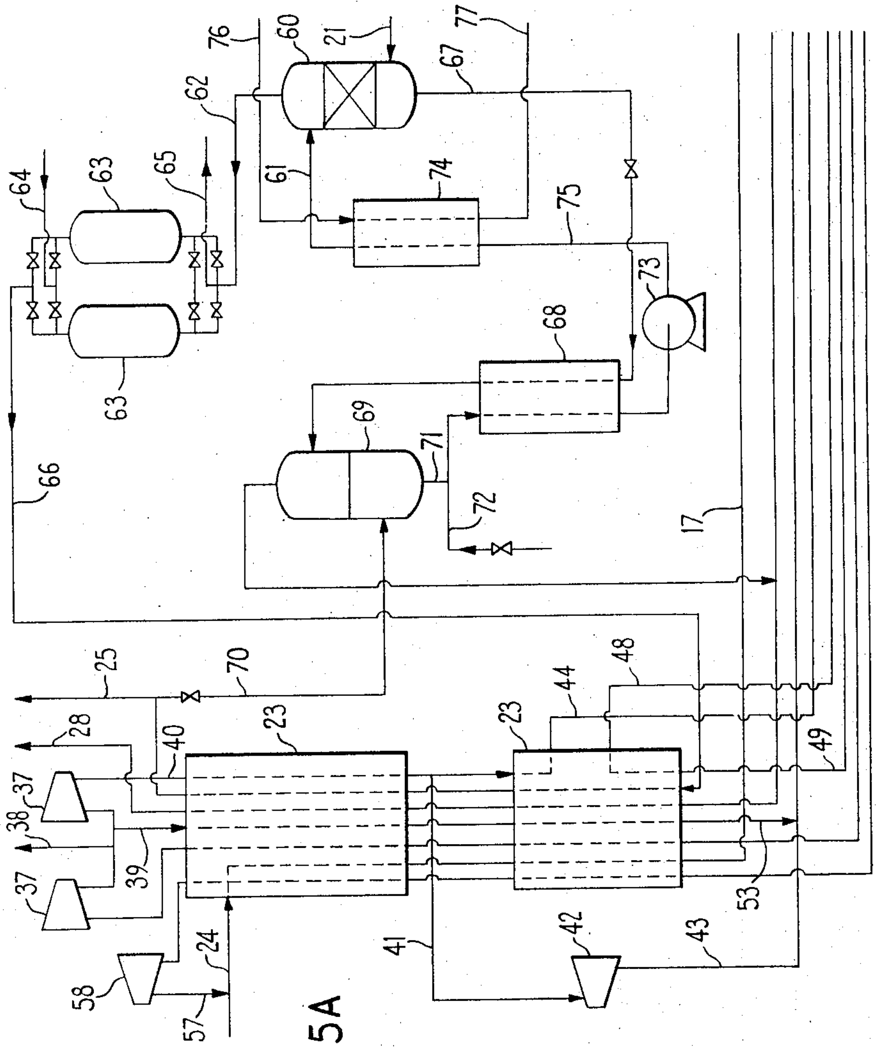
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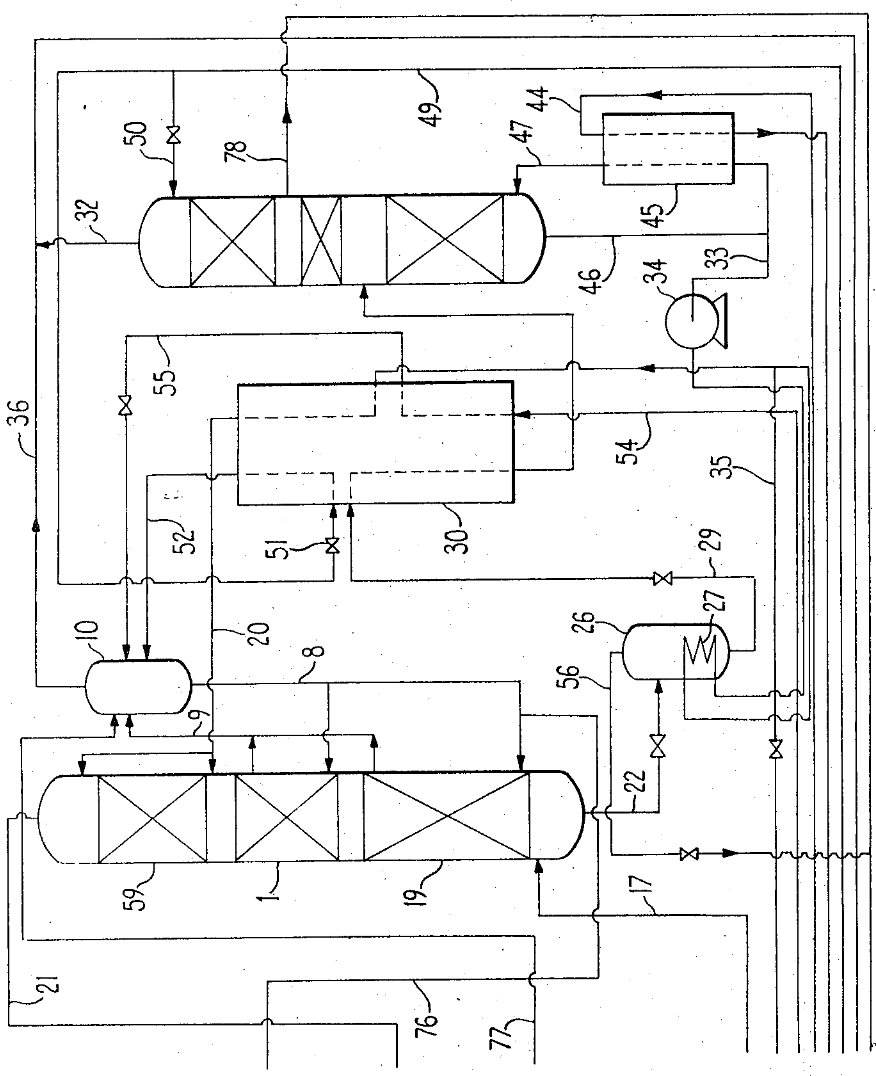
FIG. 5A

FIG.5B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SEPARATION OF GAS MIXTURES

This invention relates to the separation of gases, in particular, mixtures containing hydrogen and carbon monoxide.

A process is known in which a gas mixture containing hydrogen, and at least one of nitrogen and carbon monoxide is fed into the bottom of a column containing sieve trays, or other liquid vapour contacting devices, and liquid methane is fed into the top of the column. The liquid methane absorbs the greater part of the nitrogen and/or carbon monoxide, and a product of fairly pure hydrogen is obtained from the top of this column. If the feed gas is less than 90 molar percent hydrogen, a substantial amount of heat is given up when the nitrogen and/or carbon monoxide is transferred from the gas phase to the liquid phase: this heat is herein called the heat of absorption. Hence, in the prior art, a substantial flowrate of refrigerated liquid methane is required to absorb this heat of absorption, which makes a relatively high power demand on the process. A process is also known which absorbs the small quantity of methane present in the hydrogen gas leaving the methane absorption column by counter-current contact with liquid propane in a second column.

It is an object of the present invention to achieve a process which gives a substantially pure hydrogen or helium product and which is economical in power consumption.

A further object of this invention is to give a product of substantially pure carbon monoxide or substantially pure nitrogen.

According to the present invention, there is provided a process in which a gas mixture including at least one of hydrogen and helium, and at least one of nitrogen and carbon monoxide, being at a pressure in the range 5 atmospheres to 55 atmospheres, is cooled near to its dew point and is fed into the bottom of a wash-column, into which liquid methane is fed at the top; the wash-column contains provision for bringing a refrigeration stream into indirect contact with the aforesaid gas mixture and the liquid methane; a gas stream is taken from the top of the wash-column consisting of hydrogen and/or helium substantially free from nitrogen and carbon monoxide, and a liquid stream is taken from the bottom of the wash-column containing methane and at least one of nitrogen and carbon monoxide.

The liquid taken from the bottom of the wash-column, containing methane together with nitrogen and/or carbon monoxide and a small quantity of dissolved hydrogen, can be reduced in pressure in one or more stages, and the hydrogen rich flash gas removed as a waste stream, which can be recycled to the feed if required. The liquid can then be distilled to obtain a stream of substantially pure liquid methane, and a stream of carbon monoxide and/or nitrogen substantially free of methane and hydrogen. The stream of substantially pure liquid methane is pumped to a pressure sufficient to enable it to be fed into the top of the wash-column.

The process requires a make-up of methane to replace losses in the gaseous product streams. This can be methane in the feed gas stream, or methane from some outside source.

The invention further provides wash-column apparatus receiving at the bottom a gas mixture containing at least one of hydrogen and helium and at least one of nitrogen and carbon monoxide, said gas mixture being at a pressure in the range 5 atmospheres to 55 atmospheres, and receiving at the top a feed of liquid methane, the column having means for refrigeration of the vapour and liquid flows therein comprising one or more vapour/liquid contactors and a plurality of cooling coils.

Apparatus for carrying out the process according to the invention will now be described by way of example with reference to the accompanying drawings, in which:

FIG. 1 is a diagrammatic elevation of the wash-column,

FIG. 2 shows a single plate of the column in plan,

FIG. 3 shows two consecutive plates in elevation,

FIG. 4 is a flow sheet of a complete plant incorporating the wash-column, and

FIGS. 5A and 5B form a flow sheet of an alternative plant.

The preferred design of the wash column is shown in FIGS. 1, 2 and 3. It is a counter-current vapour/liquid contacting device having means for providing heat exchange between the vapour/liquid mixture present and a boiling refrigerant. The device can be considered as two sections.

The top section of the wash-column 1 contains a number of horizontal perforated plates 2 fitted with side downcomers 3, inlet weirs 4 and outlet weirs 5. Liquid flowing down the wash column passes across the plates in a side-to-side manner as in a conventional distillation column. In addition, a number of tubes 6, each coiled in a flat spirally-wound coil are placed one above the other on the perforated area of the tray. The number of coiled tubes is such that the tube surfaces will be immersed in the biphase mixture which exists above the sieve tray perforations. The spacing between the coils in a vertical direction, and between the bottom coil and the tray is sufficient to allow liquid to flow across the tray, while the distance horizontally between the tubes within a coil is sufficient to allow the vapour to pass vertically upwards through the coils. In order to prevent vapour bypassing the coils, the perforations on the tray are confined to an area vertically below the coils and bounded by the outside and inside coil perimeters. In order to prevent liquid bypassing the coils, inwardly-directed barriers 7 are placed at the edge of the column between the inlet and outlet weirs 4 and 5. Other arrangements of perforated area and downcomers are possible, and depending on the shape of the perforated area, flat coils of other than an oval shape may be required. The inlet and outlet of each coil passes through the wall of the column and is connected to a vertical inlet header 8 and a vertical outlet header 9. Liquid refrigerant passes down pipe 8 from a reservoir 10 and the vapour, together with any excess liquid, returns to the reservoir 10 through pipe 9. The reservoir 10 acts as a vapour/liquid separator for the fluid returning along pipe 9. The feed from the refrigerant header 8 to the coils on the trays is passed through valves 11 which isolate the coils on different groups of trays. These valves are used to adjust the refrigerant flowrate to each of the tray groups so that the correct temperature profile can be maintained across the column to give the optimum mass transfer between the gas and liquid phases.

The bottom section of the wash-column comprises a number of co-current vapour liquid contactors 12 in which there is provision for heat exchange with the refrigerant stream. They are constructed in this example on the well-known aluminum plate-fin matrix principle. Liquid refrigerant enters the contactors through pipe 8 via valves 13, which allow the refrigerant flow to be adjusted to maintain the correct temperature profile across the column. The refrigerant vapour, together with any excess liquid, leaves the contactors along pipes 14, which join into the common return header 9. For each contactor, liquid from the stage above flows in along pipe 15 while vapour from the stage beneath flows in along pipe 16. The feed to the column enters the bottom contactor via pipe 17. The vapour and liquid feeds which have entered the contactor are mixed together evenly within the contactor and flow upwards through a common set of passages, which are adjacent to the refrigerant passage. The length of the passages and the fluid velocities are such as to ensure that the liquid vapour mixture has substantially reached equilibrium, and that the required amount of heat transfer has taken place when the vapour liquid stream leaves the contactor. The liquid-vapour mixture leaving each contactor along pipe 18 enters a vapour liquid separator 19. The separators are arranged in a vertical column which is a continuation of the shell of the upper section of the wash-column, the contactors 12 being external to this. The use of separate vapour-liquid contactor heat exchangers 12 is necessary when the amount of heat transfer required per equilibrium stage in the column exceeds that which can be accomplished on one or two of the sieve trays using the flat coils. The relative position of contactors and separators or sieve trays within the wash-column depends on the characteristics of the mixture which is to be separated.

The liquid methane enters the top of the column along pipe 20. The gaseous product leaves the top of the column along pipe 21 while the liquid bottom product leaves the column along pipe 22.

Two plants incorporating such a wash-column will now be described, FIG. 4 being a flow sheet of the first.

Referring to FIG. 4, the feed gas, from which carbon dioxide and water have been removed, having a composition given in Table 1, enters the multipass plate-fin heat exchanger 23 along pipe 24 at a pressure of 161 psia and a temperature of 48°F, and is cooled to −270°F. It passes from the heat exchanger to the wash-column along pipe 17. The wash liquid consisting of 99 percent methane enters the column at −292°F along pipe 20. This wash liquid absorbs most of the carbon monoxide and nitrogen in the feed gas and the resulting hydrogen product having a composition given in Table 1 leaves the top of the column through pipe 21; passes through the multipass heat exchanger 23 and leaves the plant at 154 psia and 58°F along pipe 25. The heat of absorption in the wash column is removed by a boiling carbon monoxide stream which flows to the column along pipe 8 and returns as a vapour-liquid mixture along pipe 9 to the reservoir 10. The liquid leaving the bottom of the wash-column along pipe 22 is flashed to 70 psia and passes into a separator 26. The separator contains a heating coil 27 through which liquid methane is circulated to vaporize a small portion of the liquid and reduce the amount of hydrogen which remains dissolved in the liquid. The vapour leaving separator 26 along pipe 56 passes through the multipass heat exchanger 23 and leaves the plant as waste gas along pipe 28. The liquid leaves separator 26 through pipe 29, is reduced in pressure to 42 psia and enters heat exchanger 30 where it is heated to −272°F and partially vaporised before entering a distillation column 31.

TABLE 1

	FEED mole fraction	HYDROGEN PRODUCT mole	CARBON MONOXIDE PRODUCT mole fraction
Hydrogen	0.5852	0.9605	0.0049
Nitrogen	0.0415	0.0109	0.0891
Carbon Monoxide	0.3543	0.0051	0.9058
Methane	0.0190	0.0235	0.0002

This column separates the fluid into a substantially pure carbon monoxide stream, having the composition given in Table 1, which leaves the top of the column through pipe 32, and a liquid methane stream which leaves the bottom of the column through pipe 33, is raised in pressure to 165 psia in pump 34, passes through the heating coil 27 and enters the wash-column through line 20 after having been cooled in heat exchanger 30 to −292°F. A small quantity of liquid methane is passed along pipe 35, reduced in pressure to 70 psia, heated in the multipass heat exchanger 23 to 58°F, and leaves the plant in the waste gas through pipe 28.

The plant refrigeration, together with the wash-column refrigeration, and the reflux and reboil to column 31, is provided by a circulating carbon monoxide stream. Low pressure carbon monoxide gas leaving column 31 through line 32 and separator 10 through line 36 passes through the multipass heat exchanger 23 where it is heated to 58°F before entering the first stage of the compressor 37. The carbon monoxide stream is compressed in the first stage from 36 psia to 131 psia. The product carbon monoxide stream leaves the plant along pipe 38 while a stream of gaseous carbon monoxide enters the multipass heat exchanger along pipe 39. The remaining carbon monoxide gas enters the second stage of the compressor 37 and is compressed to 394 psia and enters the multipass heat exchanger 23 along pipe 40. A high pressure gaseous carbon monoxide stream leaves the multipass heat exchanger 23 at a temperature of −195°F through pipe 41 and enters the turbo-expander 42 where it is expanded to 129 psia and a temperature of −255°F and leaves through pipe 43. The remaining high pressure carbon monoxide stream leaves the multipass heat exchanger along pipe 44 at −216°F and condenses in the reboiler-condenser 45, providing the heat duty to boil the liquid methane stream which is taken from the base of the column 31 through pipe 46 and returned as vapour through pipe 47. The liquid carbon monoxide stream leaving reboiler-condenser 45 along pipe 48 enters the multipass heat exchanger 23 at a temperature of −232°F and is cooled down to −270°F leaving through pipe 49. Part of stream 49 is expanded down to 41 psia and introduced into the top of column 31 as reflux through pipe 50; the remainder of the high pressure liquid carbon monoxide stream is let down to 42 psia at valve 51 and is passed through the cold end of heat exchanger 30 where it cools the liquid methane wash liquid and it is then fed into the liquid carbon monoxide reservoir 10 through pipe 52. The gaseous carbon monoxide stream at 131 psia entering the warm end of the multipass heat exchanger 23 along pipe 39 is cooled to −270°F and leaves the cold end through pipe 53 where it joins the turbo-expander exhaust stream 43. The combined streams pass through pipe 54 to the heat exchanger 30 where they are condensed. The liquid carbon monoxide stream at 128 psia leaving heat exchanger 30 through pipe 55 is reduced in pressure to 41 psia and fed into the liquid carbon monoxide reservoir 10.

There are a number of variations possible in the design of this plant. The waste gas stream 56 and the waste methane stream 35 can be taken through separate passages in the multipass heat exchanger 23, and the waste gas can then be recycled to the feed stream 24 after being compressed from 65 psia to 161 psia. This will result in an increase in the recovery of carbon monoxide. The liquid stream leaving separator 26 through line 29 can be passed into a separator after being reduced in pressure to 42 psia and a hydrogen rich waste gas stream can be removed. This will result in the hydrogen concentration of the product carbon monoxide stream being reduced from 0.0049 mole fraction to 0.0005 mole fraction. The expander flow can be taken from the 131 psia intermediate pressure carbon monoxide stream, and the expander exhaust can discharge at 41 psia into the low pressure carbon monoxide stream.

The second plant to be described, with reference to FIGS. 5A and 5B, is designed to produce hydrogen containing less than 10 ppm of total impurities.

The feed gas from which carbon dioxide and water have been removed, having the composition given in Table 2, is mixed with a recycle gas stream flowing through pipe 57 from compressor 58, and the mixture enters the multipass plate-fin heat exchanger 23 along pipe 24 at a pressure of 161 psia and a temperature of 50°F. It is cooled to −270°F and passes from the multipass plate-fin heat exchanger to the wash column along pipe 17. The wash column is divided into three sections. The bottom two sections 1 and 19 which are cooled by boiling carbon monoxide refrigerant, are shown in FIGS. 1 to 3 and described above. The liquid carbon monoxide flows to the column along pipe 8 and returns as a vapour-liquid mixture to the reservoir 10 along pipe 9.

hydrogen leaving the propane scrub column pipe 62 has a composition given in Table 2. It then flows through one of the beds of a dual bed carbon adsorber 63 where the remaining nitrogen and methane are removed. The adsorber vessels are switched over at regular intervals and heated up to 250°F by means of a dry reactivation gas which enters along pipe 64 and leaves along pipe 65. The hydrogen product gas having a composition given in Table 2 leaves the adsorbers along pipe 66, passes through the multipass plate-fin heat exchanger 23, and leaves the plant at 154 psia and 58°F along pipe 25. The propane containing methane leaves the bottom of the propane wash column 60 along pipe 67 and is then reduced in pressure to 100 psia and heated to −178°F in heat exchanger 68 before being introduced into the propane stripping vessel 69. The propane is stripped of methane in a single stage vapour-liquid contact with hydrogen gas which is taken from stream 25 and reduced in pressure to 100 psia, and introduced directly into vessel 69 along pipe 70. Approximately equal molar flowrates of hydrogen stripping gas and propane are used while the hydrogen stripping gas flow is approximately 5 molar percent of the flowrate of stream 21. The temperature in the stripping vessel 69 is −140°F. The purified propane leaving the bottom of vessel 69 along pipe 71 is mixed with a small amount of propane makeup from pipe 72 to compensate for propane losses from the system. The propane is cooled in heat exchanger 68 to −286°F. and raised in pressure to 160 psia in pump 73. The liquid propane flows from the pump to heat exchanger 74 along pipe 75. It is cooled to −292°F. by carbon monoxide which enters heat exchanger 74 along pipe 76 and returns to the liquid carbon monoxide reservoir 10 along pipe 77.

The liquid mixture leaving the bottom of the wash column along pipe 22 is flashed to 70 psia and passes into a separator 26. The separator contains a heating coil 27 through which liquid methane is circulated to vaporise a small portion of the liquid mixture and reduce the amount of hydrogen which remains dissolved in the liquid mixture. The vapor leaving separator 26

TABLE 2

[All figures are mole fractions]

	Feed	Hydrogen from section 1	Hydrogen from section 59	Hydrogen from vessel 60	Hydrogen product from vessel 63	Carbon monoxide product
Hydrogen	0.715	0.9556	0.981915	0.998105	0.999990	0.00524
Nitrogen	0.004	0.0062	0.00089	0.00089	0.000005	0.01320
Carbon monoxide	0.245	0.0105	0.000005	0.000005	0.000002	0.98138
Methane	0.036	0.0277	0.01719	0.00100	0.000003	0.00018

The third section 59 consists of distillation trays having no provision for heat transfer to a refrigerant. The compositions of the gas leaving section 1 and section 59 are given in Table 2. The wash liquid, consisting of pure methane containing 5 ppm carbon monoxide enters the column at −292°F along pipe 20. The wash liquid removes the last traces of carbon monoxide in the feed gas in section 59 of the wash column and absorbs the bulk of the nitrogen and carbon monoxide in the feed gas in sections 1 and 19. The hydrogen gas leaves the top of the column through pipe 21 and flows into an absorption column 60 fitted with vapour-liquid contacting devices such as sieve trays. The hydrogen is scrubbed by a liquid propane stream which enters the column at a temperature of −292°F along pipe 61. The

along pipe 56 is reduced in pressure to 41 psia and passes through the multipass plate-fin heat exchanger 23, and enters the recycle compressor 58. The liquid mixture leaves separator 26 through pipe 29. It is reduced in pressure to 42 psia and enters heat exchanger 30 where it is heated to −272°F. and partially vaporised before entering the distillation column 31. This column separates the fluid into a substantially pure carbon monoxide stream having a composition given in Table 2, which leaves the top of the column through pipe 32, a liquid methane stream which leaves the bottom of the column through pipe 33, and a waste gas stream, which leaves the column through pipe 78. The waste gas stream must be removed because of the high purity products which are withdrawn from each end of the column. The waste gas stream joins with the vapour from separator 26. The liquid methane stream from the bottom of the column is raised in pressure to 165 psia in pump 34, passes through the heating coil 27 and enters the wash column through line 20 after being cooled in heat exchanger 30 to −292°F. A small quantity of liquid methane is passed along pipe 35, reduced in pressure to 70 psia, heated in the multipass heat exchanger 23 to 58°F. and leaves the plant as a waste gas stream through pipe 28.

The carbon monoxide recycle refrigeration system is identical to that described in the first plant example.

What we claim is:

1. A process for removing impurities comprising at least one of the group of nitrogen and carbon monoxide from a gaseous feed stream having a principle component comprising at least one of the group of hydrogen and helium comprising the steps of:

a. introducing said gaseous feed stream into the lower portion of an absorption column and flowing said gaseous stream upwardly through said column,
b. introducing cold, liquid methane into the top of said absorption column and flowing said methane downwardly through said column to absorb said impurities from said feed stream,
c. introducing said stream of methane and absorbed impurities into a fractionation column and separating said impurities from said methane,
d. withdrawing said separated methane and recycling it to the top of said column,
e. withdrawing a stream of said impurities from said fractionation column, cooling and condensing at least a portion of said impurity stream by compression, heat exchange and pressure reduction,
f. supplying additional refrigeration to said absorption column by passing a plurality of streams of said condensed impurity in indirect heat exchange relationship with the fluids in both the upper and lower portions of said absorption column, said plurality of condensed impurity streams being passed in parallel flow through the upper portion of said absorption column,
g. separating said column fluids into a plurality of gaseous and liquid fractions in a plurality of liquid separators vertically arranged in the lower portion of said absorption column,
h. directly mixing separated liquid fractions from upper separators with separated gaseous fractions from respectively lower separators in a plurality of contactor-exchangers, and
i. supplying additional refrigeration to the fluids at the lower portion of said absorption column by passing streams of said condensed impurity through said contactor-exchangers in indirect heat exchange relationship with the mixed fractions therein.

2. The process as claimed in claim 1 wherein a substantial portion of the cooling and condensing of the impurity stream is performed by:

a. cooling said impurity stream in heat exchange with at least one colder product stream withdrawn from the process, and
b. condensing said impurity stream against a portion of the methane withdrawn from said fractionation column before said methane portion is returned to said fractionation column as reboil fluid.

3. The process as claimed in claim 1 wherein a portion of said cooled and condensed impurity stream is introduced into the top of said fractionation column as reflux.

4. An absorption column comprising:

a. wall means forming a shell for the column,
b. inlet means for introducing a gaseous feed stream connected to the lower portion of said column,
c. inlet means for introducing a wash liquid connected to upper portion of said column,
d. first and second outlet means for discharging a purified product stream and an impurity stream,
e. a plurality of trays in the upper portion of said column,
f. partition means in the lower portion of said column forming a series of phase separators for separating said feed and wash fluids after direct contact thereof,
g. a plurality of fluid contactors, each of said contactors being connected to two of said phase separators for contacting gaseous feed and wash liquid from a phase separator thereabove,
h. fluid passage means in said contactors in indirect heat exchange with the feed and wash fluids therein, and
i. a source of refrigerant connected to said fluid passage means in said contactors for passing refrigerant in indirect heat exchange with the feed and wash fluids for removing a substantial portion of the heat of absorption thereof.

5. The absorption column as claimed in claim 4 including a plurality of refrigeration coils positioned above at least some of said trays and immersed in the fluids on said trays for providing additional refrigeration to the top portion of said column.

6. The absorption column as claimed in claim 5 wherein said trays are perforated and said coils comprise horizontally extending, flat spirals of tubing positioned vertically above said perforations with spaces between concentric portions of said tubing for the passage of fluids vertically through said coils and perforations.

7. The absorption column as claimed in claim 5 including a source of refrigerant, a plurality of passage means connecting said plurality of refrigeration coils to said source of refrigerant, and a plurality of valve means in said passage means for controlling the flowrate of refrigerant to said coils for maintaining an optimum temperature profile along the upper portion of said column.

* * * * *

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,813,889 Dated June 4, 1974

Inventor(s) Rodney John Allam, Bernard Ramsey Bligh & Lee S. Gaumer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading:

The address of the Assignee now reading "New Malden, Surrey, England;" should read --Allentown, Pennsylvania--.

In the Specification:

Column 4, Table 1, under the "Hydrogen Product" column, add the word --fraction-- under the subheading "mole" as in adjacent columns.

Signed and sealed this 24th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents