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PROCESS FOR LIQUEFYING NATURAL GAS

Filed Dec. 3, 1964

2 Sheets-Sheet 1

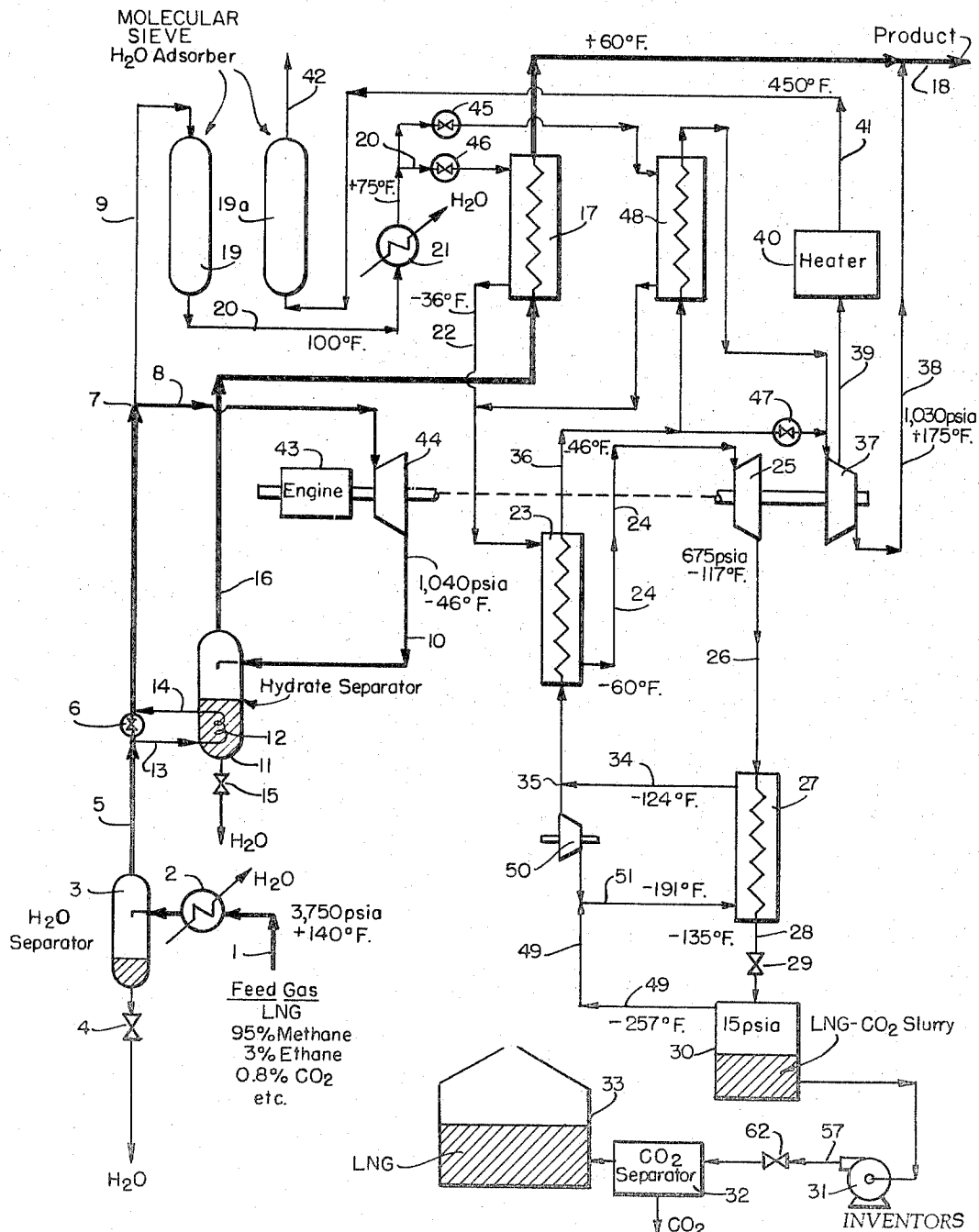


FIG. 1.

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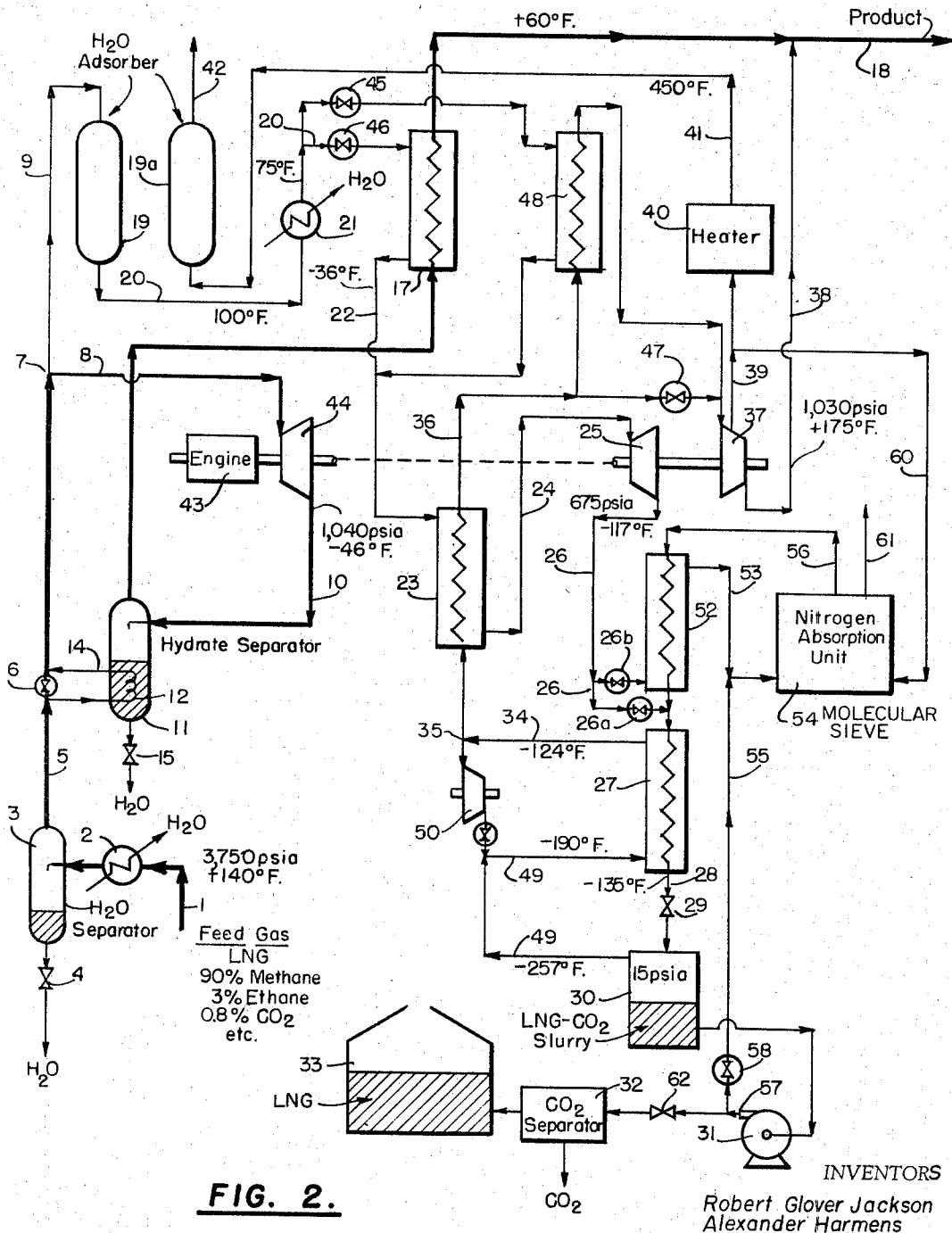
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## PROCESS FOR LIQUEFYING NATURAL GAS

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10 Claims. (Cl. 62—9)

This invention relates to a process for producing a supply of liquefied natural gas at a lower pressure than that at which the natural gas is available while delivering a second supply of natural gas into a distribution pipeline at an intermediate pressure.

Where natural gas is available from wells at very high pressures, for example between 2,000 and 4,000 p.s.i.a., and is to be delivered via distribution pipeline at a lower pressure, it is possible to utilize the pressure drop to liquefy a part of the natural gas and so make liquefied natural gas available for storage and/or transport, for example by means of tankers, barges or land vehicles specially designed to carry low-temperature liquids.

Thus, U.S. Patent No. 1,747,761 describes a process in which one stream of high pressure natural gas from the wells is expanded in an expansion machine to cool the gas which is then heat exchanged with a second stream of high pressure gas from the wells and then delivered to the distribution pipeline, and the cooled second stream is itself expanded in an expansion machine to liquefy part of it, the remainder going to storage or to a distribution pipeline. Further, German Patent No. 951,751 describes a similar process with the added refinement that the gas separated at the liquefaction stage (hereinafter called "flash gas") is used to cool further the already cooled second stream prior to its expansion.

We have now discovered that, if in a process of the type described in German Patent No. 951,751 the expansion of the second stream takes place in two stages, the first expansion being isentropic, i.e. with external work, and the second being isenthalpic, i.e. without external work, and the flash gas from the isenthalpic expansion is used to cool the second stream between the two expansion stages and, subsequently, prior to the first expansion stage, then a greater proportion of the natural gas fed into the system is liquefied (for given pressure at the well head and in the distribution pipeline) than was possible by these prior processes.

Accordingly, the present invention provides a process for producing a supply of liquefied natural gas at a lower pressure than that at which the natural gas is available while delivering a second supply of natural gas into a distribution pipeline at an intermediate pressure which comprises the following steps:

(I)

- (a) isentropically expanding a first stream of the natural gas from the high pressure at which it is available to the intermediate pressure and so cooling it,
- (b) passing the expanded and cooled first stream in indirect heat exchange with a second stream of the high pressure natural gas and then into the distribution pipeline,
- (c) further cooling the second stream,
- (d) isentropically expanding the second stream from step (c) to cool it further,
- (e) further cooling the second stream from step (d),
- (f) isenthalpically expanding the second stream from step (e) to produce liquefied natural gas and flash gas, and
- (g) passing the flash gas firstly to step (e) and then to step (c) to effect the cooling in those steps and

2

finally compressing it to the intermediate pressure and passing it into the distribution pipeline.

Work produced in the isentropic expansions, which may take place in any suitable type of expansion machine, may be used to provide some of the compression energy required in step (g). Generally some additional compression energy will have to be provided but the amount will depend upon a number of factors, such as the pressure at which the natural gas is available, the required intermediate pressure and the proportion of natural gas which is required in liquid form.

In this specification the expression "isentropic expansion" is used to mean expansion with external work although, of course, it is appreciated that theoretically expansion with external work is only isentropic if the expansion machine used is 100% efficient.

We have also found that the improved process described above can be readily combined with known processes for removing contaminants from the natural gas. Thus for example, the isentropic expansion and resulting cooling in step (a) will normally cause methane hydrates to form in the natural gas and these may be separated, decomposed and the water removed from the system before step (b) with the result that the first stream of natural gas goes into the distribution pipeline substantially dryer than it was originally.

Since the second stream of natural gas is intended for partial liquefaction, it is necessary to remove all of the water before the temperature becomes so low that hydrates or ice would form. This can be achieved by passing the second stream through a dehydrating bed before it is cooled by the expanded first stream. Dehydration may be achieved by activated alumina, silica gel, activated carbon, or other suitable molecular sieves.

Any carbon dioxide or hydrogen sulphide in the natural gas can be removed prior to the carrying out of the process of the present invention by any of the well-known absorption processes in, for example, alkali metal carbonate solutions, alkali metal hydroxide solutions or alkanolamine solutions. If, however, these contaminants are present only in small proportions they need not be removed prior to the process, but any solid carbon dioxide or hydrogen sulphide forming in the liquefied natural gas product can be separated, e.g. filtered or centrifuged, off.

It will be appreciated that although in our brief description of the invention above we refer to a first stream and a second stream of the natural gas, it is clearly possible for the natural gas to come from the wells in a single pipeline and to be divided into the two streams at an appropriate point. The relative proportions of natural gas passing through the two streams will depend on the proportion of liquefied product required and on the difference between the pressure at which the natural gas is available and the intermediate pressure. The necessary relative proportions to meet any particular circumstances are a matter of calculation.

The specific nature of our invention, as well as other objects and advantages thereof, will clearly appear from a description of a preferred embodiment as shown in the accompanying drawings, in which:

FIG. I is a flow sheet illustrating the invention;

FIG. II is a flow sheet illustrating a modified form of the invention.

The raw natural gas in the examples described with reference to FIG. I contained 95.2% methane, 3% ethane, 1% propane, butane and higher hydrocarbons, and 0.8% carbon dioxide on a dry basis. The raw natural gas was saturated with water at 140° F. The raw natural gas in the example described with reference to FIG. II contained 90.2% methane, 3% ethane, 1% propane, butane and higher hydrocarbons, 5% nitrogen and 0.8%

carbon dioxide on a dry basis and also was saturated with water at 140° F.

Referring to FIG. 1 of the accompanying drawings, the raw natural gas enters the installation from the wells via pipe 1 at 3,750 p.s.i.a. and 140° F. It is cooled to 90° F. in water cooler 2 and then passed to the water separator 3. Since the raw gas is originally saturated with water, some of this water will condense upon cooling in cooler 2 and will separate in vessel 3 and can be removed by way of pressure reduction valve 4.

The natural gas leaves separator 3 through pipe 5 and, after passing through control valve 6, the purpose of which will be described below, is divided at 7 into two streams, the first stream flowing through pipe 8 and the second stream through pipe 9.

The first stream which comprises 55.8% of the gas stream before division, is led through expansion engine 44 in which the pressure of the gas is reduced to 1,040 p.s.i.a. and its temperature to -46° F. A small proportion (0.007 mol percent) of solid methane hydrate is formed in this expansion step and is carried along with the gas through pipe 10 to the hydrate separator 11. This hydrate separator contains a warming coil 12 heated by a small stream of gas flowing through pipe 13 and drawn off the main stream in pipe 5. The quantity of warm gas passing through pipe 13 is controlled by control valve 6. The relatively warm gas in coil 12 after melting the methane hydrates in vessel 11 is returned to the main gas stream via pipe 14. The water formed on decomposition of the hydrate is removed from the system via pressure reduction valve 15. It will be appreciated that the particular arrangement shown in the accompanying drawings for melting the methane hydrate in vessel 11 can be modified in many suitable ways. Any other relatively warm gas or liquid stream could be used in heating coil 12. The gas leaves vessel 11 via pipe 16 and then passes through heat exchanger 17 where it is heated to 60° F. by indirect heat exchange with the second stream of natural gas as will be described in more detail below. The gas at 60° F. is then fed into the distribution pipeline 18.

The second natural gas stream in pipe 9 which comprises 44.2% of the natural gas stream before division is passed through a bed of 2 or 3 Angstrom molecular sieve in adsorber 19. This molecular sieve retains all the water in the gas stream. The dry gas leaves the adsorber through pipe 20 at 100° F., is cooled to 75° F. in water cooler 21 and is then (in FIG. 1) cooled to -36° F. in heat exchanger 17 giving up its heat to the expanded gas of the first stream. Valve 45 is assumed to be closed.

The dried, cooled second stream leaves heat exchanger 17 through pipe 22 and passes through heat exchanger 23 in which it gives up heat to returning flash gas, as will be described in more detail below, and from which it emerges at -60° F. in pipe 24.

The gas at -60° F. from pipe 24 is passed through expansion machine 25 in which its pressure is reduced to 675 p.s.i.a. and its temperature to -117° F. The gas emerging from the expansion machine 25 passes through pipe 26 to heat exchanger 27 in which it is cooled again against flash gas and from which it emerges in pipe 28 at a temperature of -135° F. It is then isenthalpically expanded through throttle valve 29 to a pressure of 15 p.s.i.a. into flash vessel 30. As a result of this expansion 44.8% of the gas stream passing through valve 29 condenses and the carbon dioxide in the stream solidifies to form a slurry in the condensate. 55.2% of the stream leaves the flash vessel 30 as cold flash gas at -257° F. which is virtually pure methane.

The slurry of solid carbon dioxide in the liquefied natural gas collecting in flash vessel 30 is pumped by pump 31 through a separator 32 in which the solid carbon dioxide is separated, e.g. in a cyclone separator. The purified, liquefied natural gas leaving separator 32,

which contains only 0.05% of carbon dioxide, goes to the storage vessel 33.

The flash gas leaves the flash vessel 30 by pipe 49 and is fed into heat exchanger 27 to cool the second stream, as described above. If the flash gas was used in heat exchanger 27 at a temperature of -257° F. it would cause freezing of carbon dioxide on the heat exchange tubes. To avoid this, it is mixed with an approximately equal volume of warmer gas from blower 50 prior to entering the heat exchanger. The mixture of gases fed to the heat exchanger in pipe 51 is at -191° F., which temperature will not cause freezing of carbon dioxide on the heat exchanger tubes. The flash gases leave the heat exchanger by pipe 34 at -124° F. and are divided into two streams at point 35, approximately half flowing to blower 50 and the other half flowing to heat exchanger 23 in which it is further heated to -46° F. in cooling the second stream as described above.

The flash gas stream leaves heat exchanger 23 by pipe 36 and passes to compressor 37. Although the compressor is shown in the accompanying drawings as a single stage compressor in the interest of simplicity, in practice it will have a plurality of stages, say 5 with 4 intercoolers. The gas emerges from the fifth stage at 1,030 p.s.i.a. and 175° F. and is fed through pipe 38 to distribution pipeline 18.

Conveniently, as indicated in the accompanying drawings, gas may be taken off between suitable stages of compressor 37 for the purpose of reconditioning the molecular sieve in adsorber 19a. It will be appreciated that adsorber 19 and adsorber 19a are alternately switched into the system for gas purification purposes and out of the system for reconditioning. A suitable arrangement for the reconditioning step is to withdraw about 3% of the gas after the first stage of compression when the gas is at 74 p.s.i.a. and 187° F. This gas is taken off through pipe 39 and is heated to 450° F. by means of waste heat in heater 40. The hot gas then passes through pipe 41 into spent adsorber 19a for reconditioning the same.

The adsorber effluent leaving through pipe 42 may be used as fuel gas.

The reconditioning of the adsorbers may be carried out as follows. When adsorber 19 is spent it is taken out of the gas purification system and replaced in that system by reconditioned adsorber 19a. The pressure in adsorber 19 which, when in operation, is 3,750 p.s.i.a. is let down to atmospheric pressure which releases part of the adsorbed water to the atmosphere. The contaminants left behind on the molecular sieve are desorbed by the stream of hot natural gas from pipe 41 described above. After reconditioning, adsorber 19 has to be cooled down to ambient temperature before reinsertion into the gas purification system. This is achieved by passing a stream of cooled purified natural gas through the adsorber. For this purpose one may use either a side stream of repressurized pure methane leaving the compressor 37 which has been cooled against water or evaporating carbon dioxide produced in carbon dioxide separator 32, or evaporated, but still cold, carbon dioxide gas derived from carbon dioxide separator 32 can be passed through the adsorber and vented to the atmosphere. If the former alternative is used, the gas used to cool the adsorber can, of course, be fed into the distribution pipeline 18.

The expansion machines 44 and 25 do not produce enough power under the conditions of the above example to drive the compressor 37. The additional power required is provided by a suitable engine 43. However, it will be appreciated that if the pressure required in the distribution pipeline 18 were less than the 1,030 p.s.i.a. referred to above then it may well be possible to operate the above described process without the use of external power.

Operating the above described process on a scale of

5

515 x 10<sup>6</sup> st. cu. ft./day will produce 410 x 10<sup>6</sup> st. cu. ft./day pipeline gas for distribution at 1,030 p.s.i.a., 100 x 10<sup>6</sup> st. cu. ft./day of natural gas in liquefied form at atmospheric pressure, and 5 x 10<sup>6</sup> st. cu. ft./day of low pressure fuel gas. It will also produce 106 tons/day of carbon dioxide. With these through-puts expander 44 generates 9,100 horsepower and expander 25 generates 4,500 horsepower in each case assuming that the expander has an efficiency of 80%. Compressor 37 (75% efficiency) consumes 31,500 horsepower so that 17,900 horsepower have to be fed into the system by engine 43.

In addition to the essential heat exchange steps set out in the above description, other further heat exchange steps may be employed. For example, the flash gas after effecting the cooling in step (c) of process (I) above may be heat exchanged against part of the second stream in parallel with the heat exchange of the remainder of the second stream with the expanded first stream in step (b). By controlling the relative proportion of the said part of the second stream it is possible to vary the proportion of the incoming natural gas which will finish up in the liquid form.

Thus in FIG. I heat exchanger 48 is interposed in the flash gas stream just upstream of the compressor. The relative flows through heat exchangers 17 and 48 are controlled by valves 45, 46 and 47. When valve 47 is fully closed, valves 45 and 46 will be adjusted so that 44% of the second stream passes through heat exchanger 48 and 56% of the second stream passes through heat exchanger 17. With the plant so operated, an input of 395 x 10<sup>6</sup> st. cu. ft./day of natural gas will produce 290 x 10<sup>6</sup> st. cu. ft./day partially purified pipeline gas for distribution at 1,030 p.s.i.a., 100 x 10<sup>6</sup> st. cu. ft./day of natural gas in liquefied form at atmospheric pressure and 5 x 10<sup>6</sup> st. cu. ft./day of low pressure fuel gas. Expander 44 will generate 5,000 horsepower and compressor 37 consume 34,500 horsepower. Thus the power to be fed into the system by engine 43 will increase to 25,000 horsepower. Any intermediate condition can, of course, be attained by suitable adjustments of valves 45, 46 and 47.

Referring to FIG. II, the plant is adapted to apply the process of the present invention to a liquefied natural gas when it is desired to remove nitrogen from the gas. The treatment of the natural gas before division into two streams is the same as in FIG. I. The treatment of the first stream taken off through pipe 8 is also the same as in FIG. I. The treatment of the second stream taken off through pipe 9 is the same as in FIG. I up to pipe 26 carrying the gas emerging from expander 25, except that in the present case the beds 19 and 19a are designed so as to remove most of the carbon dioxide as well as the water. In FIG. I pipe 26 leads directly to heat exchanger 27. In order to adapt the plant for removal of nitrogen an additional heat exchanger and low temperature nitrogen adsorption unit are inserted before heat exchanger 27 is reached. For this purpose valve 26a (used to provide the previously described operation) is closed and valve 26b (previously closed) is opened.

Thus the cold expanded natural gas in pipe 26 passes first to heat exchanger 52 and then through pipe 53 to the nitrogen adsorption unit 54. Before it enters the nitrogen adsorption unit, the natural gas is mixed with a controlled amount of liquefied natural gas from pipe 55 to lower its temperature sufficiently for efficient operation of the adsorption unit.

The nitrogen adsorption unit 54 which, in the interest of simplicity, is not shown in detail is of the type described in British patent specification 12,480/63. It comprises at least two alternating adsorption columns containing a molecular sieve (3 Angstroms) which are alternately adsorbing nitrogen and being regenerated and a small column containing a heat accumulating bed in accordance with British patent specification 12,480/63 and which is operated in the manner described in that speci-

6

cation to ensure that the gas emerging from the adsorption unit is at a substantially constant temperature.

The purified natural gas leaves adsorption unit 54 via pipe 56, then passes through heat exchanger 52 in which it is cooled by the gas leaving expander 25 and then passes through heat exchanger 27 in which it is further cooled by flash gas. It leaves heat exchanger 27 by pipe 28 and is then isenthalpically expanded through throttle valve 29 into flash vessel 30 when a considerable proportion of the gas liquefies.

The liquefied natural gas in flash vessel 30 is pumped by pump 31 to storage vessel 33 through pipe 57 and control valve 62. Pipe 55 branches off from pipe 57 and some of the liquefied natural gas is directed to pipe 53 as has already been described. The proportion of liquefied natural gas flowing through pipe 55 is controlled by control valve 58.

The flash gas leaves vessel 30 by pipe 49 and hence is passed through heat exchangers 27 and 23 and is thereafter treated as in FIG. I. Warm gas for regeneration of the adsorption beds in the nitrogen adsorption unit 54 is supplied by pipe 60 branching off from pipe 39 and leaves the adsorption unit together with the desorbed nitrogen by pipe 61. If the natural gas contains helium as well as nitrogen, helium can be separated from the effluent from pipe 61.

It will be apparent that by operating the appropriate control valves, the system of FIG. II can be used exactly as in FIG. I, if the amount of nitrogen in the feed gas is sufficiently low so that the nitrogen adsorption unit need not be operated.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made in construction and arrangement within the scope of our invention as defined in the appended claims.

We claim:

1. A process for producing from natural gas at high pressure a supply of liquefied natural gas at a lower pressure than the high pressure at which the natural gas is available while delivering a second supply of natural gas into a distribution pipeline at an intermediate pressure which comprises

- (a) isentropically expanding a first stream of the natural gas from the high pressure at which it is available to the intermediate pressure and so cooling it,
- (b) passing the expanded and cooled first stream in indirect heat exchange with a second stream of the high pressure natural gas and then into the distribution pipeline,
- (c) further cooling the second stream,
- (d) isentropically expanding the second stream from step (c) to cool it further,
- (e) further cooling the second stream from step (d),
- (f) isenthalpically expanding the second stream from step (e) to produce liquefied natural gas and flash gas, and
- (g) passing the flash gas firstly to step (e) and then to step (c) to effect the cooling in those steps and finally compressing it to the intermediate pressure and passing it into the distribution pipeline.

2. A process as claimed in claim 1 in which methane hydrates formed in step (a) are separated and decomposed and the resulting water removed from the system before step (b).

3. A process as claimed in claim 1 in which the second stream is passed through a dehydrating bed before it is cooled by the expanded first stream.

4. A process as claimed in claim 3 wherein the dehydrating bed comprises a molecular sieve.

5. A process as claimed in claim 4 in which warm purified natural gas produced in the compression operation referred to in step (g) is used to recondition the dehydration bed.

7

6. A process as claimed in claim 1 in which the flash gas from step (f) is mixed with warm flash gas before being passed to step (e).

7. A process as claimed in claim 1 in which the flash gas, after effecting the cooling in step (c), is heat exchanged against part of the second stream in parallel with the heat exchange of the remainder of the second stream with the expanded first stream in step (b).

8. A process as claimed in claim 7 in which the relative proportion of said part of the second stream is controlled to vary the proportion of the incoming natural gas which will finish up in the liquid form.

9. A process as claimed in claim 1 in which nitrogen is removed from the natural gas by adsorption therefrom between the isentropic and the isenthalpic expansions.

10. A process as claimed in claim 9 in which some liquefied natural gas is added to the isentropically ex-

8

panded gas to cool the same prior to removal of nitrogen therefrom.

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