July 18, 1967 R. C. PROCTOR ET AL 3,331,214

METHOD FOR LIQUEFYING AND STORING NATURAL GAS AND CONTROLLING THE B.t.u. CONTENT

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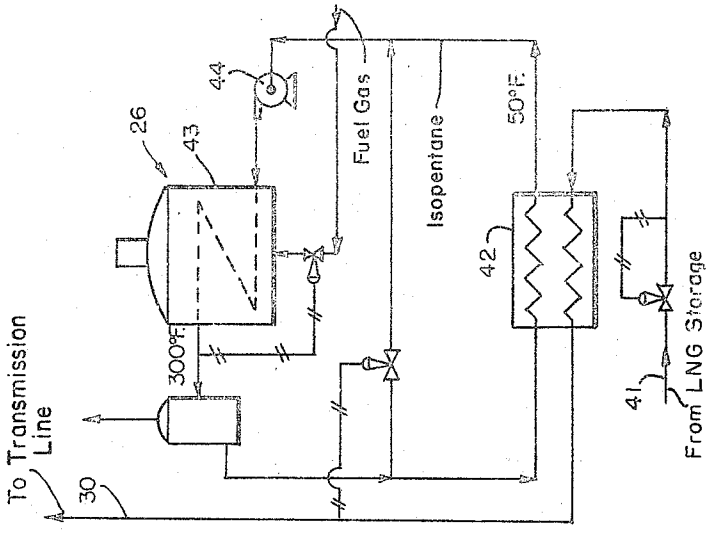


FIG. 3.

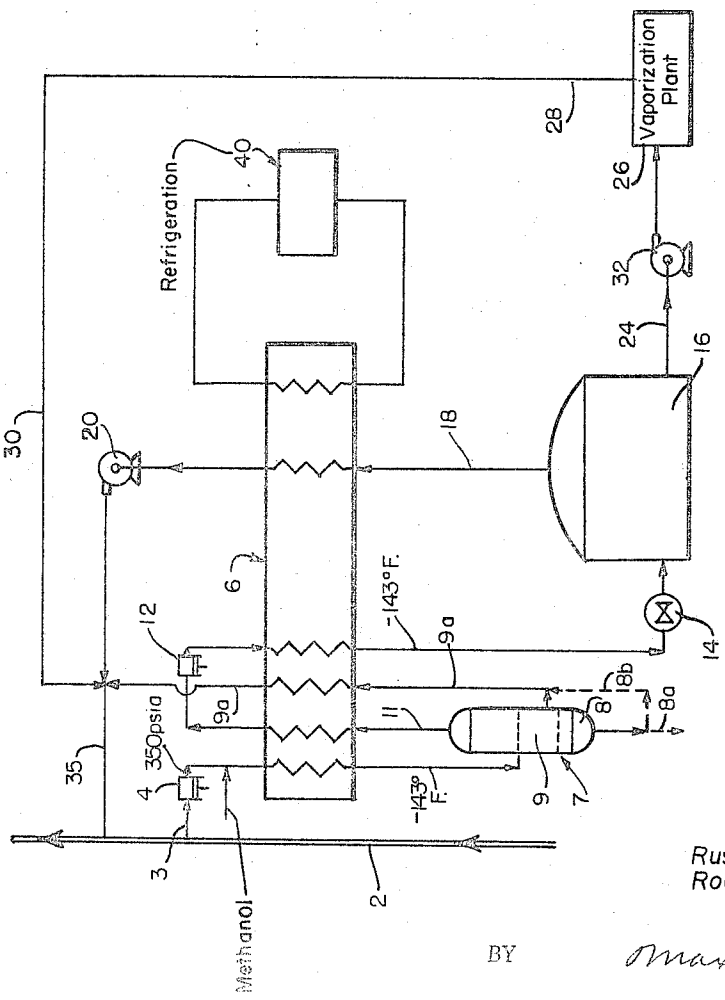


FIG. 1.

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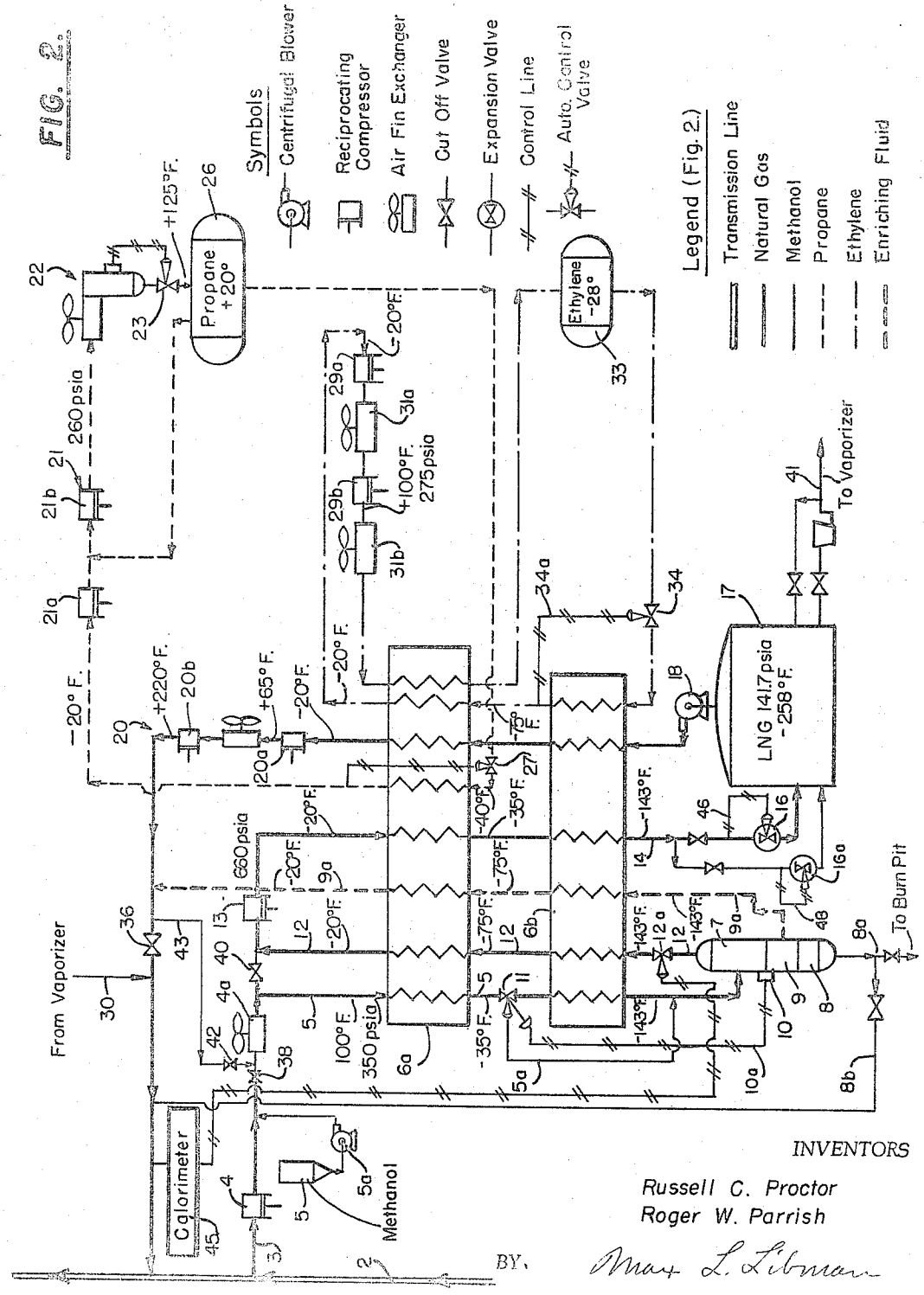
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Filed March 22, 1965 2 Sheets-Sheet 2

FIG. 2.



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United States Patent Office 3,331,214 Patented July 18, 1967

3,331,214

METHOD FOR LIQUEFYING AND STORING NATURAL GAS AND CONTROLLING THE B.t.u. CONTENT

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Filed Mar. 22, 1965, Ser. No. 441,768
9 Claims. (Cl. 62—20)

This invention relates to the storage of natural gas supplied from a pipeline, by converting it to liquid natural gas, and to the control of the B.t.u. content of natural gas supplied back to the pipeline from said storage. The present invention relates to the same problem as is dealt with in the copending application of Bodle and Young, Ser. No. 282,727, assigned to the assignee of the present invention, over which it has the following advantages: (1) It eliminates the need for removing acid gases and water from the feed gas. (2) It reduces the number of heat exchanges needed for liquefaction. (3) It moves a greater proportion of hydrocarbon and CO_2 at a low pressure, after which the gas is recompressed to a high pressure for liquefaction of the entire stream. (4) It is simpler in construction and can be readily designed for construction into relatively small units which are suitable for skid mounting, and hence can be made transportable. An antifreeze agent which is injected to prevent riming is not lost, but adds its fuel value to the heavies used for B.t.u. control.

A recent development in the pipeline transportation of natural gas is the introduction of "peak shaving," by which is meant the storage of surplus gas delivered by the pipelines during periods of low demand near the point of ultimate use, for addition to the local gas supply during periods of high use. For this purpose, the stored gas is preferably in liquid form, since this enables very large quantities of gas to be stored in a reasonable and relatively economical storage reservoir. One preferred form of such storage is to maintain the liquid in suitably insulated or underground containers at substantially atmospheric pressure, and at its natural boiling point, which at this pressure is in the neighborhood of —258° F. Because natural gas is a mixture of low molecular weight hydrocarbons and other substances, the exact boiling point of the mixture is a function of the composition. Since the stored liquid is boiling under these conditions due to heat leakage from the warmer surroundings, the boil-off vapor contains a larger proportion of lighter constituents, and the residual stored liquid tends to gradually accumulate a larger and larger percentage of heavier hydrocarbons, which have a higher heating value than the lighter hydrocarbons. However, customer requirements call for a supply of gas at a constant or pre-agreed B.t.u. value, both for heat requirements and for proper operation of the gas-utilization equipment. It is a major object of the present invention to supply this need by providing means for automatically and continuously maintaining the B.t.u. value of the gas supplied from the storage pipeline at a constant B.t.u. value.

Another object is to eliminate the need for removing carbon dioxide and water from the feed gas, as this is accomplished easily as part of the present method.

Still another object is to separate out a substantial proportion of the heavier hydrocarbons at a relatively low pressure, for use in reconstituting the B.t.u. value of gas supplied fom the storage reservoir.

Still another object is to prevent riming and clogging of the lines by water and CO_2 which would otherwise tend to occur at the low temperatures employed.

The above and other objects are achieved in accordance with the invention by initially compressing the natural gas stream from the transmission line only sufficiently so that upon cooling liquid containing hydrocarbons heavier than methane, CO_2, and methanol or other suitable antifreeze agent is condensed; the methanol is added as necessary to prevent riming of the exchangers by water and CO_2 which would tend to clog the system. The condensed liquid is then separated from the gas stream, while the uncondensed portion is recompressed to a sufficiently higher pressure so that upon subsequent cooling it will liquefy, the LNG is then expanded into a suitable container. The methanol-water mixture and absorbed CO_2 are removed plus some heavy hydrocarbons; and these can be disposed of into the boil-off line in order to control its B.t.u. and utilize its fuel value. The water-methanol mixture may be separated from the hydrocarbon liquid layer for later reconcentration by distillation. The condensed heavy hydrocarbons are vaporized by passing them in heat exchange with the initially compressed NG stream, and combined with gas vaporized from the stored LNG in the correct proportions to maintain the initial B.t.u. content of the gas in the transmission line. The amount of heavy hydrocarbons condensed is varied to maintain the B.t.u. balance by controlling the compressor interstage pressure or bypassing around a heat exchanger.

The specific nature of the 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. 1 is a highly simplified schematic flow chart showing the principle of the invention;

FIG. 2 is a more detailed flow chart showing a system in accordance with the invention; and

FIG. 3 is a flow chart of the vaporizer used in connection with the system of FIG. 2.

Referring to FIG. 1, the transmission line **2** is a main supply line for natural gas, typically at a pressure from 115–315 p.s.i.a. In accordance with the invention, the gas is taken from the transmission line in feeder line **3** and is compressed by compressor **4** to a suitable pressure, e.g., 350 pounds, which is however still a lower pressure than that required for the ultimate liquefaction of all the gas. The gas is then cooled in heat exchanger **6** to —143° F. At this temperature and pressure, some of the higher hydrocarbons will begin to condense out of the gas, and are trapped in knock-out drum **7**, together with water and methanol (if any is added) which sink to the bottom as shown at **8**, and can be removed in line **8***a*, together with a certain amount of CO_2, which becomes dissolved in the methanol-water under these conditions, or can be added in line **8***b* to the flow in line **9***a* and thence to the transmission line **2**. If the CO_2 is present in a concentration of less than a few percent, substantially all of the CO_2 will be removed by this step. The heavier hydrocarbons remain in layer **9**, and are kept at a suitable level in the knock-out drum by control apparatus as will be shown below. The lighter uncondensed hydrocarbons (together with a certain percentage of the heavies) are passed in line **11** back through heat ex-

changer 6, warmed, and recompressed by compressor 12, then cooled again in passage through heat exchanger 6, from which they emerge as a liquid at a temperature of —143° F. and a pressure of approximately 660 p.s.i.a., so that upon expansion through valve 14 to atmospheric pressure in tank 16, most of the gas remains liquefied for storage in the tank 16. The flash and boil-off gases in tank 16 are passed through line 18 to heat exchanger 6, and then compressed by compressor 20 to the transmission line pressure, and fed into the transmission line. When a peak demand occurs and more gas is needed, it is taken from storage tank 16 through pump 32 on line 24 and vaporized in vaporizer plant 26, then supplied on lines 28 and 30 back to the transmission line. Line 9*a* returns the condensed enriching liquid in layer 9 back to return pipe 35 to maintain the B.t.u. level constant. To maintain the necessary temperature conditions in heat exchanger 6, external refrigeration is needed, as schematically indicated by external refrigerating circuit 40, described in more detail below.

FIGS. 2 and 3 show a more detailed flow sheet of the above system. In practice, an air-fin heat exchanger 4*a* is inserted after compressor 4 to cool the compressed gas by heat exchange with ambient air. Between compressor 4 and exchanger 4*a*, or at any other suitable point in this line, methanol is injected from container 5 by means of a suitable pump 5*a*, in order to prevent freezing of the CO_2 and water, and consequent riming of the pipes, especially in heat exchangers 6*a* and 6*b*. If the pipeline gas is adequately dry for the process, it may not be necessary to inject the methanol. However, with the typical conditions shown, the methanol is necessary to inhibit the formation of gas hydrates in the cooling of the gas and the freezing of the CO_2. The gas at the outlet of exchanger 4*a* is at a temperature of 100° F. and a pressure of 350 p.s.i.a., and is now conducted in pipe 5 to successive stages of heat exchanger 6, identified in this case as 6*a* and 6*b*, from which it emerges at a temperature of —143° F. At this temperature and pressure, some of the heavier hydrocarbons will condense out of the gas, and these are trapped in knock-out drum 7, together with condensed water and methanol solution, which forms a bottom layer 8, and can be drawn off in line 8*a* to a burn pit for disposal or to a reconcentration apparatus, or alternatively can be sent back on line 8*b* for ultimate addition to the fuel line, thus utilizing the heat content of the methanol. The heavier hydrocarbons which are condensed form a layer 9 in knock-out drum 7, the level of which is maintained within desired limits by sensing device 10, which through control line 10*a* acts upon three-way valve 11, which is also controlled thereby to divert a portion of the stream in line 5 around the heat exchanger 6*b* so that there is not more hydrocarbon liquid made in knock-out drum 7 than is necessary for the enrichment of the boil-off gas from the storage tank.

The uncondensed gas in drum 7 is returned in line 12 gas is admitted again to heat exchangers 6*a* and 6*b* and from which it emerges at a temperature of —20° F., and is now admitted to second-stage feed-gas compressor 13 where it is compressed to 660 p.s.i.a. At this level, the gas is admitted again to heat exchangers 6*a* and 6*b* and is in a fully liquefied condition as it emerges in line 14 at —143° F. and 660 p.s.i.a. The LNG is then admitted through the back-pressure control valve 16 to the storage tank 17 at atmospheric pressure and its temperature is reduced to approximately —258° F.

Boil-off and flash gases from the storage tank are compressed in single-stage centrifugal blower 18 (to overcome the pressure drop in the heat exchanger) and are admitted to the boil-off compressors 20*a* and 20*b* at —20° F. for recompression to the transmission line pressure.

The above-described process requires some additional refrigeration capacity to be added to the heat exchangers, and this is supplied by a propane loop and an ethylene loop of refrigeration which will now be described.

The propane loop includes compressors 21*a* and 21*b* (a two-stage reciprocating compressor) which compresses propane vapors from essentially atmospheric pressure to 260 p.s.i.a. where the propane vapor is condensed in heat exchanger 22 (air-fin type) for admission through valve 23 to storage tank 26 at +20° F. The temperature in the storage tank is maintained at 20° F. by the interstage pressure between the two stages of compressor.

Propane leaving tank 26 goes through valve 27 to heat exchanger 6*a* and the propane liquid is flashed to its equilibrium temperature of —40° F. and superheated to —20° F. for return to the inlet of compressor 21*a* (first stage).

The ethylene cycle also has a two-stage reciprocating compressor 29*a* and 29*b* with air-fin intercooling and aftercooling as shown at 31*a* and 31*b* respectively. After the ethylene vapors are cooled with air in heat exchanger 31*b*, they are condensed by exchange against the propane circuit in heat exchanger 6*a*. The liquid ethylene is stored at —28° F. in tank 33. This ethylene is admitted through valve 34 into heat exchanger 6*b* and valve 34 is controlled by temperature control on the outlet of the ethylene vapors leaving 6*b*, as indicated at 34*a*. These vapors are superheated in exchanger 6*a* to —20° F. for admission to the inlet of compressor 29*a*.

By compressing the feed gas to 350 p.s.i.a. in line 5 and with the injection of methanol as described, approximately 85% of the CO_2 is condensed and removed in knock-out drum 7. Assuming that the amount of CO_2 in the feed gas was 1 mol percent, the CO_2 in the gas being condensed at 660 p.s.i.a at the discharge of compressor 13, is well within the solubility limit of CO_2 in liquid methane at this level of pressure and temperature, and there will therefore be no CO_2 condensing out in heat exchangers 6*a* and 6*b* prior to the liquefaction of the gas for storage in tank 17.

It will at times be necessary or desirable not to add any net feed to the storage, and for this purpose a holding circuit is arranged which will now be described. During holding, the feed gas compressor 4 will be shut down, and the boil-off compressor will recirculate vapors from the tank through the holding circuit. This is done by closing valves 36 and 38, and opening valves 40 and 42, so that the boil-off vapors now circulate through line 43, and air-fin exchanger 4*a*. It will be seen that the exchanger 4*a* thus serves the dual purpose of being the air-fin cooler for the first stage of compressor 4 under normal liquid operation and also serves as the after-cooler for compressors 20*a* and 20*b* during the holding operation. The boil-off gases are free of contaminants such as CO_2 and H_2O vapor, and these gases are recirculated through heat exchanger 4*a*, and through compressor 13 to follow the same course as before. As an alternative to the three-way diversion valve 11, it is possible to control the hydrocarbon level in knock-out drum 7 equally well by controlling a valve in the gas line 5 between exchangers 6*a* and 6*b*, which would accordingly change the discharge pressure on compressor 4 and consequently control the amount of condensed liquid in the knock-out drum by controlling this pressure, or alternatively controlling the pressure through adjusting the capacity of compressor 4 by unloading or bypassing.

Control of the liquid in the knock-out drum 7 is accomplished by controlling the discharge pressure on compressor 4 through a signal from the calorimeter 45 which reads the heating value of the boil-off and flash gases admitted back to the transmission lines. The level of enriching liquid in the knock-out drum is controlled by a valve 12*a* in the gas line 12 controlling the discharge pressure on compressor 4.

It is expected that there would be some formation of solid CO_2 in the valve 16 during operation, and an alternative route with a similar valve 16*a* is therefore provided so that these two valves can be cycled alternatively should the pressure drop across either valve increase because of the build-up of solid CO_2 in the valve. This is accomplished by pressure control devices 46 and 48 so

that when the valves are being cycled, the valve that is not in operation can be electrically derimed by conventional means (not shown).

FIG. 3 shows the vaporizer, which may be of any desired construction, but in one practical form consists of an indirect exchanger between LNG which comes from the tank in line **41**, and isopentane in exchanger **42**. The isopentane is circulated through a direct fired heater **43**, by pump **44**, and is heated to 300° F. in the heater. LNG is exchanged in exchanger **42** for admission to the pipeline. The primary advantage of this vaporizer is that the heat medium may be circulated by pump **44**, the heater **43** started up, and control of the temperature of the isopentane leaving the heater **43** will modulate the fire in the heater. The thermal inertia of the total quantity of heat medium liquid is such that this control is easily maintained and it is not a critical operating procedure to start up the heater and circulate the isopentane. When LNG is admitted to exchanger **42**, it may be started through the exchanger gradually, which will reduce the temperature of the heat medium liquid and bring up the fire as more and more LNG is admitted through the heat exchanger up to its designed capacity.

The LNG in the tank will have the same B.t.u. content as the incoming gas stream because the enriching separator will have stripped out sufficient high B.t.u. components to maintain the boil-off stream at the same B.t.u. as the incoming stream.

Although the heavier hydrocarbons were condensed out in vessel **7** at a relatively low pressure (350 pounds), this is still higher than the initial pressure in line **2** (approximately 315 pounds maximum) by virtue of compressor **4**, and therefore no additional pumping is required to return the heavies on line **9***a* into the main line **2**.

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 liquefying natural gas containing heavy hydrocarbons and CO_2 for storage of the liquefied natural gas for use during peak load periods, which comprises

(a) compressing the natural gas stream,

(b) injecting methanol into the natural gas stream,

(c) cooling the compressed natural gas stream containing methanol to a point at which sufficient of the heavy hydrocarbons and a portion of CO_2 are condensed and the uncondensed level of CO_2 will be well within the solubility range when further compressed and cooled,

(d) separating the liquid heavy hydrocarbons from the gas stream,

(e) vaporizing the liquid heavy hydrocarbons by passing it in heat exchange with the compressed natural gas stream containing methanol to effect in part the cooling of step (c),

(f) recompressing the gas stream from step (d), cooling it such that the stream is totally condensed at the increased pressure and flashing it to storage at substantially atmospheric pressure,

(g) using the gas boiling off from storage due to heat leak into the system together with the flash gas from the expansion in step (f) to effect in part the cooling in steps (c) and (f) and then recompressing the same and mixing with it the vaporized liquid from step (e) so as to adjust the B.t.u. content of the mixed stream to essentially that of the incoming stream, and

(h) passing said mixed stream to the gas delivery line.

2. A process for liquefying or partially liquefying natural gas containing methane and heavier hydrocarbons and CO_2 for storage of the liquefied natural gas for use during peak load periods, which comprises

(a) compressing the natural gas stream,

(b) injecting an anti-freeze agent into the natural gas stream,

(c) cooling the compressed natural gas stream containing the anti-freeze agent sufficiently to cause a portion of the heavy hydrocarbons and CO_2 to condense, and then separating the portion of the hydrocarbons heavier than methane, CO_2, and the anti-freeze agent,

(d) vaporizing the liquid heavy hydrocarbons so separated by passing it in heat exchange with the compressed natural gas stream containing the anti-freeze agent to effect in part the cooling referred to in step (c),

(e) recompressing the gas stream from step (c), cooling it such that the stream is totally condensed at the increased pressure and flashing it to storage at substantially atmospheric pressure,

(f) using the gas boiling off from storage due to heat leak into the system together with the flash gas from the expansion in step (e) to effect the cooling in steps (c) and (e) and then recompressing the same and mixing it with such a proportion of the vaporized liquid from step (d) as to adjust the B.T.U. content of the mixed stream to essentially that of the incoming stream, and

(g) passing said mixed stream to the gas delivery line.

3. A process for liquefying natural gas supplied by pipe line and consisting mostly of methane, for storage and use during peak load periods, said natural gas containing less than one mol percent CO_2 and some heavy hydrocarbons, which comprises

(a) compressing the natural gas from the pipe line,

(b) cooling the compressed natural gas stream to a point at which the heavy hydrocarbons and CO_2 are largely condensed,

(c) separating out a portion of the condensed heavier hydrocarbons and CO_2,

(d) recompressing the uncondensed gas stream from step (b), cooling it below its liquefaction temperature and flashing it to substantially atmospheric pressure for storage,

(e) storing the liquefied natural gas in a reservoir, at a pressure and temperature such that some gas is normally boiling out of the liquid due to heat leak through the storage vessel,

(f) using said boil-off gas from step (e) together with the flash gas from the expansion of step (d), to effect in part the above cooling steps (b) and (d),

(g) recompressing said boil-off and flash gas and mixing with it vaporized heavier hydrocarbons from step (c) in such proportion as to adjust the B.t.u. content of the mixed stream to essentially that of the incoming stream, and

(h) passing said mixed stream back to the pipe line.

4. The process as claimed in claim **1**, including the steps of

(a) withdrawing liquefied natural gas from said reservoir,

(b) heating said withdrawn liquefied natural gas by heat exchange interchange with a liquid heat exchange medium to convert the liquefied natural gas to vapor, and

(c) passing said vapor back to the pipe line.

5. The process as claimed in claim **4**, wherein said liquid heat exchange medium is isopentane, including the step of circulating the heat exchange medium through a direct fired heater to raise its temperature to the order of 300° F.

6. The process as claimed in claim **5**, wherein the isopentane is first heated up by the heater in starting the system and its temperature rise is used to control the operation of the heater, while LNG is admitted gradually to the heat exchanger to reduce the temperature of the heated isopentane and thereby increase the heat input to the heater.

7. The process as claimed in claim **1**, including the

following steps for use during holding periods when no NG is to be returned to the pipe line,

(a) diverting said mixed stream in step (h) of claim **1** from the gas delivery line and passing it through a heat exchanger to lower its temperature to ambient temperature,

(b) passing said stream from step (a) above through recompression and low-temperature heat exchange means to produce step (d) of claim **1**, and recirculating said stream through steps (e) through (g) inclusive of claim **1**.

8. The process as claimed in claim **1**, in which the low-temperature heat exchange means is cooled by external refrigeration.

9. The process as claimed in claim **8**, in which the low-temperature heat exchange means is in two separate stages,

the external refrigeration for the first stage being a propane refrigeration cycle, and the external refrigeration for the second stage being an ethylene refrigeration cycle.

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