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(54) REFRIGERATION SYSTEM FOR COOLING OR LIQUEFYING MIXTURES OF GASES HAVING MULTI-LEVEL BOILING POINTS

(71 We, CHIYODA CHEMICAL ENGINEERING AND CONSTRUCTION CO. LTD., of No. 1580 Tsurumi-Cho, Tsurumi-ku, Yokohama, Japan, a corporation organised under the laws of Japan, and AIR PRODUCTS AND CHEMICALS, INC., a corporation organised under the laws of the State of Delaware, United States of America, of Five Executive Mall, Swedesford Road, Wayne, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a refrigeration system for cooling or liquefying mixtures of gases having multilevel boiling points, especially to a new cascade refrigerant system related to the liquefaction of natural gas utilizing a multi-component refrigerant cycle having multi-levels of boiling point ranging from ambient temperature to a lower point than the critical temperature of the said gas, cascaded with an absorption refrigerant cycle.

In utilization of natural gas, it has become a common practice to transport and store such a gas in cryogenic liquid state, because of the greatly reduced volume, low boiling point and economy in storage space and thickness of storage vessel wall. This procedure involves liquefying natural gas prior to transportation and storage. This involves liquefying natural gas by indirect heat exchange with refrigerant having multi-level boiling points ranging from the ambient temperature to a level lower than the critical temperature of natural gas.

Since the energy required for liquefaction is the major operating cost, it is very important to reduce energy consumption as well as plant investment cost. In this respect, it has already been proposed in the French Patent, Patent No. 1557019 that the use of a multi-component refrigerant mixture refrigeration cycle is desirable. The present invention may provide an improved method of reducing energy required and plant investment required for a liquefaction plant by combining an absorption refrigeration cycle with a multi-component refrigerant mixture cycle.

The said cycles are connected with each other in such a manner that the multi-component refrigerant is cooled by absorption refrigerant, and that absorption refrigerant cycle utilizes waste exhaust energy from a driver of the multi-component refrigerant compressor.

Liquefied natural gas has become one of the important energy sources to overcome air pollution problem. There are four major liquefaction cycles, now available;

a. Joule-Thomson Expansion Cycle
b. Expansion Engine Cycle
c. Three Level Cascade Cycle
d. Multi-Component Refrigerant Cycle.

The Joule-Thomson expansion cycle has no practical applications. The expansion engine cycle will be the best process for peak shaving liquefaction plant where large portion of expanded low pressure gas can be used as base load gas to the next stage.

The three level cascade cycle gives the closest practical approach to the ideal work of liquefaction yet attained. A three level cascade cycle is known in which purified natural gas is successively cooled and liquefied by three pure refrigerants. Condensate at the outlet of the 1st stage is removed from the system to avoid plugging in downstream.

These refrigerants are propane, ethylene and methane. Each stage is divided into two or three temperature level to improve thermodynamic efficiency. The system is complicated. There are three kinds of compressor in cold duty and the piping between compressors and cold box is complex.

Multi-component refrigerant cycle proposed by Klemenko at Copenhagen in 1960

has become most promising process in ocean transportation type liquefaction plant for its capability of equipment integration. The essential feature of this cycle is that progressive cooling and liquefaction of the natural gas is obtained by successive cooling steps with a single coolant. This coolant is a mixture of hydrocarbons extracted from the natural gas itself plus nitrogen which may or may not be present in the natural gas, and is called multicomponent refrigerant (MCR). This refrigerant is compressed to certain pressure then cooled by cooling water to condense partially heavy components. Phase separated MCR vapor and liquid are further cooled in 1st. stage multi-stream heat exchanger together with natural gas against vaporizing MCR which is formed by combining subcooled MCR liquid from 1st. stage and recycling MCR stream from 2nd. stage. Natural gas is subsequently cooled from 1st. stage to 4th. stage in a same manner and finally become liquid.

As stated before, the present invention may provide an improved method of reducing energy required and plant investment required for a liquefaction plant by combining an absorption refrigeration cycle with a multicomponent refrigerant mixture cycle.

According to the present invention there is provided a refrigerating process for cooling or liquefying a mixture of gases having multilevel boiling points through combined cycles of absorption refrigeration and refrigeration by a multi-component refrigerant, which comprises cooling said gas mixture by means of an absorption refrigerant evaporating in at least two different pressure level zones and then cooling said gas mixture by means of said multi-component refrigerant, the multicomponent refrigerant being cooled first by a coolant and then by said absorption refrigerant, and utilizing in said absorption refrigeration cycle hot exhaust products of the driving means of a multi-component refrigerant compressor, said exhaust products being used in heat exchange relation with the absorbed refrigerant to remove the same from its absorbent.

Further according to the present invention there is provided apparatus for cooling or liquefying a mixture of gases having multilevel boiling points through combined cycles of absorption refrigeration and refrigeration by a multi-component refrigerant comprising a multi-component refrigerant compressor driven by a driving means of a type producing hot exhaust products and a conduit capable of conducting said hot exhaust products from the driving means to heat exchange means where said exhaust products are placed in heat exchange relation with absorbed refrigerant to remove the same from its absorbent.

In a preferred embodiment, the process comprises of:—

(a) introducing a main feed stream of natural gas at a selected pressure,

(b) Liquefying the natural gas by successive indirect heat exchange firstly with the vaporizing absorption refrigerant prepared by the absorption refrigeration cycle, and secondly with vaporizing multi-component refrigerant;

(c) compressing the multi-component refrigerant vapor to a pressure at which the said vapor is condensed against heat exchange with the vaporizing absorption refrigerant;

(d) partially condensing the multi-component refrigerant by indirect heat exchange with the vaporizing absorption refrigerant;

(e) absorbing the absorption refrigerant by the absorbent while removing the absorption heat by the coolant;

(f) pumping up the solution to a pressure at which the generated absorption refrigerant will condense against the coolant;

(g) generating the absorption refrigerant from the solution utilizing the waste exhaust energy from the driving means of the multi-component refrigerant compressor;

(h) rectifying the generated absorption refrigerant to the extent that the absorption refrigerant is regarded as substantially a pure component to minimize the absorbent accumulation in the absorption refrigerant vaporizer;

(i) purging a small amount of liquid from an absorption refrigerant vaporizer to minimize the absorbent accumulation;

(j) removing the absorption refrigerant from the absorbent to the extent that the absorption can be done at a low pressure and under the coolant temperature;

(k) condensing the rectified absorption refrigerant by indirect heat exchange with a coolant and splitting the condensate into a reflux stream to a rectifier and into the main absorption refrigerant stream.

Further understanding of various aspects of the invention will be facilitated by referring to the accompanying flow sheet. The specific arrangements illustrated are provided by way of example only, and the scope of the invention is defined by the appended claims.

In the drawing is shown a flow sheet of an arrangement as an example according to the invention.

The treated natural gas from the acid gas removal process having a pressure of approximately 740 psia and at ambient temperature, enters the system via a Conduit 1) and is cooled to a temperature of approximately 70° F in the first Precooler 2) by indirect heat exchange with ammonia vaporizing at a temperature of approximately 65° F, after

which the condensed water is removed in the Separator 3) and the saturated gas from the separator is further allowed to dry in a Dryer 4) by an absorbent. The dried gas is then cooled to a temperature of approximately 30° in the Second Precooler 6) by indirect heat exchange with ammonia vaporizing at a temperature of approximately 25° F after which the cooled stream is fed to the Heavies Removal Column 8). The overhead vapor from the said column is further cooled to a temperature of approximately −30° F in an Overhead Condenser 10) by indirect heat exchange with ammonia vaporizing at a temperature of approximately −35° F.

The cooled stream then passes through the Reflux Accumulator 11) and the entrained condensate is removed. The lighter fraction gas from the accumulator then enters via the Conduit 12) to the Multi-component Refrigerant Heat Exchanger 16) and the heavier fraction condensate from the accumulator is recycled to the said Column 8).

The heavy components in the feed stream 7) are removed from the bottom of Column 8) to prevent them from freezing in the Exchanger 16). The Reboiler 14) is heated by stream. In Exchanger 16), the lighter fraction gas is liquefied by successive heat exchange with multi-component refrigerant vaporizing at continuously changing boiling points ranging from temperatures of approximately −30° F to −270° F. The liquefied natural gas having a pressure of approximately 650 psia and a temperature of −260° F leaves at the cold end of the Exchanger 16) and then passes through the Pressure Reducing Valve 17) and turns to a low pressure product of approximately 75 psia and at a temperature of −260° F, comprising mainly of methane, ethane and propane.

Referring now in more detail to the multi-component refrigerant circuit, the vaporized multi-component refrigerant having a pressure of approximately 40 psia and a temperature of −30° F leaves the Heat Exchanger 16) and is fed to the First Stage Compressor 19) via Suction Drum 18) and is compressed to a pressure of approximately 210 psia after which the heat of compression is removed by the Water After-cooler 21). The cooled multi-component gas then passes through the Second Stage Suction Drum 22) and is fed to the Second Stage Compressor 23) and is compressed to a pressure of approximately 620 psia after which the heat of compression is removed by the Water After-cooler 24). The cooled multi-component gas then passes through a series of two Heat Exchangers 26) and 28), respectively. In the Heat Exchanger 26) the multi-component gas is cooled down to a temperoture of approximately 25° F by ammonia boiling at the same temperature level maintained in the Heat Exchanger 6). In the Heat Exchanger 28) the multi-component gas is further cooled to a temperature of approximately −30° F and is partially condensed.

The condensed liquid and non-condensed vapor are separated in the Separator 29), after which the separated lighter fraction vapor enters the Heat Exchanger 16) via the Conduit 30) and is then cooled to a temperature of approximately −260° F and is condensed against the vaporizing multi-component refrigerant having been expanded at valve 35. The separated heavy fraction liquid enters the Heat Exchanger 16) via the Conduit 31) and is sub-cooled to a temperature of approximately −170° F by the same vaporizing multi-component refrigerant.

The said subcooled liquid having a temperature of approximately −170° F then goes through the pressure reducing valve 32) and cools itself to a temperature of approximately −180° F. The flashed vapor and liquid enter an intermediate point of the Heat Exchanger 16). A special vapor-liquid separator can be used for separating flashed vapor and liquid before separately injecting them into heat exchanger 16). The said condensed lighter fraction liquid having a temperature of approximately −260° F then goes through a pressure reducing valve 35) and cools itself to a temperature of approximately −270° F. The flashed vapor and liquid enter the cold end of the Heat Exchanger 16). In this case the special vapor liquid separator can be used for separating flashed vapor and liquid before separately injecting them into the cold end of heat exchanger 16).

The vaporizing pressure in heat exchanger 16 is maintained at a pressure of approximately 40 psia. At this pressure, the lighter fraction vaporizes first at a lower temperature, then the heavier fraction vaporizes at a higher temperature. This results in a smooth vaporizing temperature profile in the Heat Exchanger 16). It is further observed that this smooth vaporizing temperature profile helps to ensure that the average counterflow difference is always at an optimum low value thus ensuring high thermodynamic efficiency of the refrigeration cycle.

The multi-component refrigerant is preferably a mixture of nitrogen and light hydrocarbon such as methane, ethane and propane.

The example of composition of multi-component refrigerant is shown in Table 1.

TABLE 1

	mol. per cent
nitrogen	9—11
methane	38—43
ethane	33—37
propane	13—16

The example of composition of separated lighter fraction vapor and heavier fraction liquid in separator 29 is shown in Table 2.

TABLE 2

	Lighter fraction vapor mol. per cent	Heavier fraction liquid mol per cent
nitrogen	18—21	1.5—2.5
methane	55—61	22—26
ethane	18—21	46—51
propane	2.5—3.5	23—27

In a brief summary of the multi-component refrigerant circuit, the flow through the First Stage Compressor 19) the Second Stage Compressor 23), and the Heat Exchangers 26) and 28) may be regarded as a mixture of several components of refrigerant. The Separated Stream 30) has lighter components and the Stream 31) has heavier components. It is evident that both streams are combined again in the Heat Exchanger 16) at an intermediate point and are recycled to the first stage compressor. The first and second stage compressors are driven by individual or common driving means 82) such as a steam turbine with a waste heat boiler.

Referring now in more detail to the absorption refrigeration circuit, the liquid ammonia is supplied from the Ammonia Accumulator 78) to the First Precooler 2) via the Conduit 80) the subcooler Heat Exchanger 59) and the Pressure Reducing Valve 38). In the Heat Exchanger 2), ammonia vaporizes at a pressure of approximately 130 psia and a temperature of approximately 65° F. The vaporized ammonia having a temperature of 65° F enters the Heat Exchanger 59) and is superheated to a temperature of approximately 90° F. The residual NH_3 liquid having a temperature of approximately 65° F from the Heat Exchanger 2) enters the Heat Exchanger 54) via the Conduit 40) and is subcooled to a temperature of approximately 60° F, after which the subcooled liquid enters the Second Stage Precooler 6) and the Heat Exchanger 26) via the Pressure Reducing Valves 41), respectively. In the Second Stage Precooler 6) and the Heat Exchanger 26) ammonia vaporized at a pressure of approximately 80 psia and a temperature of approximately 25° F enters the Heat Exchanger 54) and is superheated to a temperature of approximately 70° F. The residual NH_3 liquid having a temperature of approximately 25° F from the Second Stage Precooler 6) and the Heat Exchanger 26) enters the Heat Exchanger 47) via the Conduit 43) and is subcooled to a temperature of approximately 20° F after which the subcooled liquid enters the Overhead Condenser 10) and the Heat Exchanger 28) via the Pressure Reducing Valves 44) respectively. In the Overhead Condenser 10) and the Heat Exchanger 28), ammonia vaporizes at a pressure of approximately 13 psia and a temperature of approximately −35° F.

The vaporized ammonia having a temperature of −35° F enters the Heat Exchanger 47) and is superheated to a temperature of approximately 30° F. A small quantity of ammonia liquid may be withdrawn from the Overhead Condenser 10) and the Heat Exchanger 28) to avoid water accumulation in the boiling ammonia. The withdrawn liquid from the Condenser 10) and the Heat Exchanger 28) returns to the intermediate stage of the Rectifyer 70) via the Conduit 46) and the Pump 49). The superheated low pressure ammonia vapor from the Heat Exchanger 47) enters the low Pressure Absorber 50) via the Conduits 45) and is absorbed by lean water under a pressure of approximately 9 psia while removing the absorption heat by cooling water. Lean solution is pumped by the Low Pressure Pump 52) to an intermediate pressure of approximately 75 psia and enters the intermediate Absorber 55). Superheated intermediate pressure ammonia vapor from the Heat Exchanger 54) enters the intermediate pressure absorber via the Conduit 42) and is absorbed by the lean solution while removing absorption heat by cooling water. Intermediate solution is pumped by the Intermediate Pump 57) to a high pressure of approximately 120 psia and enters the High Pressure Absorber 62).

Superheated high pressure ammonia vapor from the Heat Exchanger 59) and the Heat Exchanger 66) enters a high pressure absorber via the Conduits 39), 60) and 61) and is absorbed by an intermediate solution while removing the absorption heat by cooling water.

Rich solution from the High Pressure Absorber 62) is pumped by the Rectifier Feed Pump 64) to a pressure of approximately 230 psia and enters the Solution Preheater 68) via the Heat Exchangers 65) and 66). Rich solution is preheated by steam in preheater 68) to a temperature of approximately 250° F and enters the rectification column 70). The ammonia vapor is generated in the High Pressure Generator 71) by waste exhaust energy from the driving means 82) connected directly to the Compressors 23) and 19) by the Coupling 84). Trace ammonia contained in the lean water from the High Pressure Generator 71) is removed in the Low Pressure Generator 73) and sent to absorber 62) via heat exchanger 66). The temperature of the exhaust steam of a steam turbine or temperature of the waste heat boiler steam of the gas turbine is selected to balance the duty of both refrigeration cycles. The rectified ammonia is cooled by cooling water and is condensed in the Condenser 77) and enters the Accumulator 78). Part of the condensed ammonia is recycled to the rectifying column via the Conduit 79). Most of the ammonia becomes a refrigerant.

To summarize the absorption circuit, ammonia recycles through a circuit compris-

ing of the Accumulator 78), the Heat Exchangers 59), 2), 54), 6), 26), 47), 10), and 28), the Absorbers 50), 55), 62), the Heat Exchangers 65), 66), and 68), the Column 70) and the Condenser 77). Absorbent water recycles through the Absorbers 50), 55), 62) and the Heat Exchangers 65), 66), 68), 71), 73) and 65).

It should be noted that although this description deals with an arrangement for liquefying a specific gas (natural gas) utilizing a certain refrigerant (ammonia and hydrocarbons), other refrigerant could also be employed for other services.

Other available refrigerants for the absorption cycle are methanol-ammonia, lithium bromide-water, hexane-propane etc.

Other available refrigerants for the multi-component refrigerant cycle are halogenated hydrocarbons.

It should also be noted that the selection of the types of driver, and the number of stages and operating conditions do not restrict the limitation of this invention.

Relative merits of these processes are shown in Table 3. The process design calculations are complicated and need the help of high speed digital computer. It is the purpose of this study to develop process design calculation program of this cycle.

TABLE 3
Relative Merits

Prior Art		
Expansion Engine	Cascade	MCR
1. Simple cycle	1. Highest thermal efficiency	1. No pure refrigeration
2. No need of recompression at dispensable case of expanded gas	2. Process calculation is simple	2. One kind of compression at warm duty
		3. Simple piping between compressor and cold box
		4. Flexibility
		5. Lower initial investment

Present Invention
(MCR—Abs)

1. One kind of compression at medium temperature duty
2. Flexibility
3. Low initial investment
4. Low power consumption

WHAT WE CLAIM IS:—

1. A refrigerating process for cooling or liquefying a mixture of gases having multi-level boiling points through combined cycles of absorption refrigeration and refrigeration by a multi-component refrigerant, which comprises cooling said gas mixture by means of an absorption refrigerant evaporating in at least two different pressure level zones and then cooling said gas mixture by means of said multi-component refrigerant, the multi-component refrigerant being cooled first by a coolant and then by said absorption refrigerant, and utilizing in said absorption refrigeration cycle hot exhaust products of the driving means of a multi-component refrigerant compressor, said exhaust products being used in heat exchange relation with the absorbed refrigerant to remove the same from its absorbent.

2. A process according to claim 1 which comprises the use of ammonia as a single component refrigerant in said absorption cycle.

3. A process according to claim 1 or 2 wherein said absorption refrigeration cycle comprises a series of cascade heat exchangers through which the gas mixture and multi-component refrigerant are sequentially passed in heat exchange with a single component liquid absorption refrigerant which is thus vaporized and said absorption refrigerant which is thus vaporized and said absorption refrigerant vapour is then passed through a series of absorption stages and then in heat exchange with said exhaust products.

4. A process according to any one of the preceding claims, wherein said exhaust products are derived from the exhaust steam of a steam turbine or exhaust gas of a gas tur-

ing of the Accumulator 78), the Heat Exchangers 59), 2), 54), 6), 26), 47), 10), and 28), the Absorbers 50), 55), 62), the Heat Exchangers 65), 66), and 68), the Column 70) and the Condenser 77). Absorbent water recycles through the Absorbers 50), 55), 62) and the Heat Exchangers 65), 66), 68), 71), 73) and 65).

It should be noted that although this description deals with an arrangement for liquefying a specific gas (natural gas) utilizing a certain refrigerant (ammonia and hydrocarbons), other refrigerant could also be employed for other services.

Other available refrigerants for the absorption cycle are methanol-ammonia, lithium bromide-water, hexane-propane etc.

Other available refrigerants for the multi-component refrigerant cycle are halogenated hydrocarbons.

It should also be noted that the selection of the types of driver, and the number of stages and operating conditions do not restrict the limitation of this invention.

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Present Invention (MCR—Abs)
1. One kind of compression at medium temperature duty
2. Flexibility
3. Low initial investment
4. Low power consumption

WHAT WE CLAIM IS:—

1. A refrigerating process for cooling or liquefying a mixture of gases having multi-level boiling points through combined cycles of absorption refrigeration and refrigeration by a multi-component refrigerant, which comprises cooling said gas mixture by means of an absorption refrigerant evaporating in at least two different pressure level zones and then cooling said gas mixture by means of said multi-component refrigerant, the multi-component refrigerant being cooled first by a coolant and then by said absorption refrigerant, and utilizing in said absorption refrigeration cycle hot exhaust products of the driving means of a multi-component refrigerant compressor, said exhaust products being used in heat exchange relation with the absorbed refrigerant to remove the same from its absorbent.

2. A process according to claim 1 which comprises the use of ammonia as a single component refrigerant in said absorption cycle.

3. A process according to claim 1 or 2 wherein said absorption refrigeration cycle comprises a series of cascade heat exchangers through which the gas mixture and multi-component refrigerant are sequentially passed in heat exchange with a single component liquid absorption refrigerant which is thus vaporized and said absorption refrigerant which is thus vaporized and said absorption refrigerant vapour is then passed through a series of absorption stages and then in heat exchange with said exhaust products.

4. A process according to any one of the preceding claims, wherein said exhaust products are derived from the exhaust steam of a steam turbine or exhaust gas of a gas tur-

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bine or waste heat boler steam of said gas turbine, and are conditioned to balance the requirements of both refrigeration cycles.

5. A process according to claim 1 wherein said absorption cycle uses lithium bromide as the refrigerant and water as solvent.

6. A process according to any one of the preceding claims, wherein the multi-component refrigerant is a mixture of nitrogen, methane, ethane and propane.

7. A process according to claim 1 wherein the refrigerant of the absorption cycle is ammonia-water, ammonia-methanol, lithium bromide-water or hexane-propane.

8. Apparatus for cooling or liquefying a mixture of gases having multi-level boiling points through combined cycles of absorption refrigeration and refrigeration by a multi-component refrigerant comprising a multi-component refrigerant compressor driven by a driving means of a type producing hot exhaust products and a conduit capable of conducting said hot exhaust products from the driving means to heat exchange means where said exhaust products are placed in heat exchange relation with absorbed refrigerant to remove the same from its absorbent.

9. The refrigerating process substantially as hereinbefore described.

10. The apparatus of for cooling or liquefying a mixture of gases, substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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