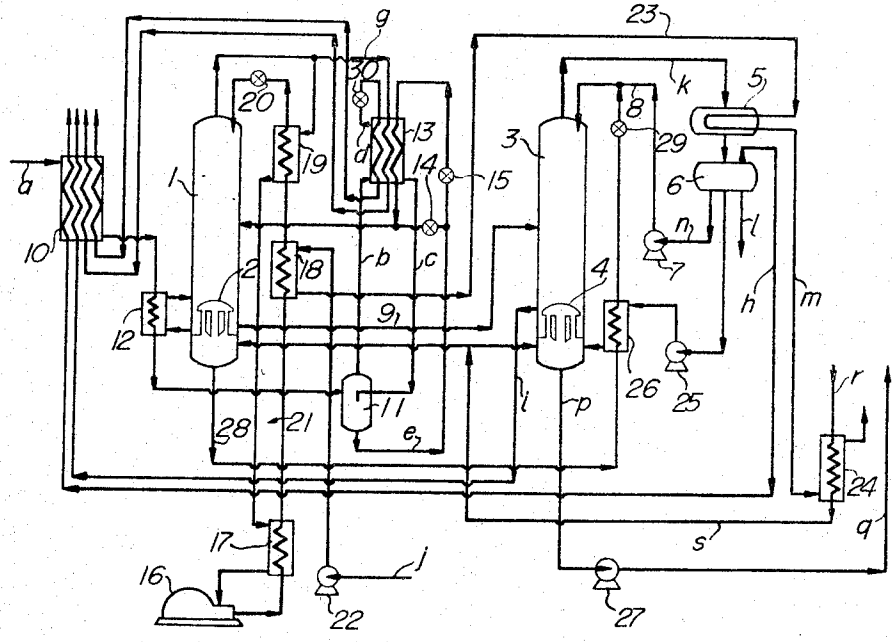
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APPARATUS FOR RECTIFICATION OF AN OLEFIN BY UTILIZATION OF REFRIGERATION SUPPLIED BY LIQUEFIED METHANE

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INVENTOR

KIYOSHI ICHIHARA

BY Paul M. Craig, Jr.

ATTORNEY

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APPARATUS FOR RECTIFICATION OF AN OLEFIN BY UTILIZATION OF REFRIGERATION SUPPLIED BY LIQUEFIED METHANE

Kiyoshi Ichihara, Hitachi-shi, Japan, assignor to Hitachi, Ltd., Tokyo, Japan, a corporation of Japan

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The present invention relates to an improved apparatus adapted for rectification olefin from an olefin-rich gas mixture by the utilization of refrigeration supplied by liquefied methane gas.

The primary object of the invention is to provide an apparatus of the above nature which is adapted to reasonably utilize coldness of liquefied methane gas for the rectification of olefin.

Generally, liquefied methane gas (L.M.G.) is carried by liquefied gas tankers and tank lorries, stored temporarily in liquefied gas storage tanks, and then heated to vaporize by a suitable method for use as fuel or raw materials for chemical industry. In this case, how the coldness held in L.M.G. is effectively utilized for other services constitutes an important factor which determines the economical value in respect of utilization of L.M.G. A problem which arises in connection with actual utilization of coldness of L.M.G. is that the degree of coldness held in 1 $Nm.^3$ (computed in terms of gaseous body at 0° C. and 760 mm. Hg) of liquid methane under atmospheric pressure is 88 kcal. at its boiling point or −161.6° C. and 65 kcal. in a temperature range between −161.6° C. and an atmospheric temperature or 20° C., and thus there is not so much difference between amounts of coldness held in the portion of latent heat and the portion of sensible heat. However, from a view point of utilization of such coldness, the coldness in the portion of sensible heat is available only in an extremely limited range since the coldness in this specific portion is spread over a wide temperature range of more than 180°, whereas the coldness in the portion of latent heat can be utilized under a definite temperature. In order, therefore, to effectively utilize the coldness in the sensible heat portion, a heat pump system comprising a compressor and a heat exchanger must be additionally provided. For this reason, the coldness in the sensible heat portion close to an atmospheric temperature has not been utilized heretofore and has been uselessly wasted in most cases.

With a view to effecting reasonable utilization of the coldness held in L.M.G., the invention provides an improved apparatus adapted to utilize such coldness of L.M.G. for rectification of olefin (mainly ethylene).

For the purpose of effective utilization of externally supplied refrigeration, it is generally most advantageous to utilize it at a portion of a lowest possible temperature. In utilizing the refrigeration by L.M.G. in an olefin rectifying system, it is most desirable that the refrigeration is utilized for the production of a liquid reflux supplied to the top of a methane extracting tower since a lowest temperature appears at the top of the methane extracting tower. However, this method of utilization is not readily applicable for the following reason. Or more precisely, since so-called L.M.G. is not pure methane and contains a small fraction of such high boiling point components as ethane and propane, the boiling point of L.M.G. is relatively high or in the order of −140° C. to −150° C. Therefore, even when L.M.G. is made to vaporize at atmospheric pressure, the methane extracting tower must be operated at a working pressure of 2.5 atmospheres at the boiling point of −150° C. and more than 6.5 atmospheres at the boiling point of −140° C. Due to such high working pressure, operating temperature becomes higher as a whole with the result that loss of ethylene increases and greater wall thickness of the rectifying tower is required. Since, in an apparatus of the kind, an amount of refrigeration required for the production of a liquid reflux for a methane extracting tower is usually one third or one fourth that for an ethylene tower due to relative amount of reflux involved in the operation, and a great advantage can not be derived when L.M.G. is diverted in the form of gas to other services for the purpose of making up for a refrigeration loss in the ethylene separator. When, therefore, L.M.G. is diverted in the form of gas to other services in prior systems, the coldness of L.M.G. must be also utilized for the production of the liquid reflux for the ethylene tower with the result that L.M.G. is thereby gasified. This is apparently disadvantageous in that the coldness of L.M.G. is utilized for a service at a relatively high temperature.

The present invention provides an improvement in the prior defective utilization of L.M.G. and provides an improved apparatus in which L.M.G. is pressurized by a pump to thereby raise its boiling point up to a temperature of −110° to −120° C. so that a liquid reflux to a methane extracting tower can be produced by the sensible heat of L.M.G. developed up to such boiling point.

According to the invention, there is provided an apparatus for the rectification of olefin from an olefin-rich gas mixture by the utilization of refrigeration by externally supplied liquefied methane gas comprising a methane extracting tower, an olefin tower, a methane recirculating cycle including a methane compressor, heat exchangers and an expansion value for recirculating a portion of methane delivered from said methane extracting tower again into said methane extracting tower, and a pump for conducting at an increased pressure said liquefied methane gas to one of the heat exchangers in said methane recirculating cycle for refrigeration by the sensible heat of said liquefied methane gas, wherein the manner of operation is such that recirculating methane is first liquefied by the refrigeration by the sensible heat of said liquefied methane gas and subsequently said liquefied methane gas is used to refrigerate a liquid reflux for said olefin tower.

There are other objects and particularites of the invention which will become obvious from the following description with reference to the accompanying drawing, in which the sole figure is a diagrammatic arrangement of a preferred embodiment of an apparatus according to the invention.

In the drawing, reference numeral **1** denotes a methane extracting tower which includes therein a reboiler **2**. Reference numeral **3** denotes an ethylene tower which includes therein a reboiler **4**. An ethylene condenser **5** and a receiver **6** therefor are associated with the ethylene tower **3**, and a pump **7** is provided to recirculate a liquid reflux of ethylene from the receiver **6** into the top of the ethylene tower by way of a conduit **8**. The methane extracting tower **1** is connected with the ethylene tower **3** by way of a conduit **9**. A heat exchanger **10** is provided to effect heat exchange between raw gas and product gases delivered from the methane extracting tower **1** and the ethylene tower **3**. The heat exchanger **10** is connected with a gas-liquid separator **11** through a reboiler **12**. A heat exchanger **13** is provided to effect further cooling of noncondensed gas in the gas-liquid separator **11**. An expansion valve **14** is interposed in a line between the methane extracting tower **1** and the gas-liquid separator **11**, while an expansion valve **15** is interposed in another line connecting the methane extracting tower **1** with the gas-liquid separator **11** through the heat exchanger **13**.

According to the invention, a portion of methane delivered from the top of the methane extracting tower **1** is recirculated through a methane recirculating cycle **21** which comprises a methane compressor **16**, heat exchangers **17**, **18** and **19**, and an expansion valve **20**. Externally supplied liquefied methane gas (L.M.G.) is pressurized by a pump **22** and supplied to the heat exchanger **18** in the methane recirculating cycle **21** to thereby liquefy the recirculating methane by refrigeration with its sensible heat portion, then L.M.G. is diverted to refrigerate the liquid reflux for the ethylene tower **3**.

The apparatus of the invention with the above arrangement operates in the following manner. Raw gas, from which water, CO_2 and high boiling point hydrocarbons including C_3 and more carbon have been eliminated, is supplied into the apparatus by way of a line *a* and made to pass through the heat exchanger **10** and the reboiler **12** wherein it is cooled to a temperature of the order of −90° C. by the refrigeration supplied by separated gases to turn into a condensate. The condensate thereby formed is separated in gas-liquid separator **11**, while non-condensed gas is led by way of a line *b* into the heat exchanger **13** wherein it is cooled to a temperature of −130° C. to −140° C. Condensate formed in the heat exchanger **13** is led back into the gas-liquid separator **11** by way of a line *c*, while remaining gas mainly of hydrogen is led through a line *d* into an expansion valve **30** wherein it is expanded to a pressure close to atmospheric pressure and lowered in its temperature. The gas is then made to flow inversely through the heat exchangers **13** and **10** to make heat exchange with the raw gas, warmed up to a temperature of −43° C. to −45° C. and discharged outwardly of the system.

The condensate collected in the gas-liquid separator **11** is taken out thereof by way of a line *e* and expanded by the expansion valves **14** and **15** to a pressure of 0.5 kg./cm.² G. The condensate expanded at the expansion valve **15** is made to flow through the heat exchanger **13**, vaporizes by cooling the raw gas and is fed into the methane extracting tower **1**, while the condensate expanded at the expansion valve **14** is supplied in its liquid form into the methane extracting tower **1**. Methane in the methane extracting tower **1** is led by way of a line *f* to the methane compressor **16**, wherein it is pressurized up to a pressure of the order of 20 kg./cm.² G. Then, methane is led through the heat exchangers **17**, **18** and **19** for being cooled therein, expanded by the expansion valve **20** to a pressure of 0.5 kg./cm.² G and recirculated into the methane extracting tower **1**. In the methane extracting tower **1**, methane collects at the top thereof, while ethylene and ethane collect at the bottom thereof. A portion of the methane component is fed back into the methane compressor **16** by way of the line *f*, while the remaining portion or product methane is made to flow inversely through the heat exchangers **13** and **10** by way of a line *g* for heat exchange with the raw gas, warmed up to a temperature of −43° C. to −45° C., and discharged outwardly of the system. The ethylene and ethane components separated at the bottom of the methane extracting tower **1** are fed into the ethylene tower **3** by way of the line **9** under pressure differential.

A manner of rectification in the ethylene tower **3** which is operated at a working pressure of 0.3 kg./cm.² G is similar to that of the methane extracting tower **1**. In the ethylene tower **3**, ethylene collects at the top thereof and ethane at the bottom thereof. The ethylene component is led through a line *k*, ethylene condenser **5**, ethylene receiver **6**, and a line *h* into the heat exchanger **10**, in which it makes counter flow with the raw gas for heat exchange therewith, is warmed up to a temperature of −43° C. to −45° C., and discharged outwardly of the system. The ethane component is led through a line *i* into the heat exchanger **10**, in which it makes counter flow with the raw gas for heat exchange therewith, is warmed up to a temperature of −43° C. to −45° C., and likewise discharged outwardly of the system.

A manner of heating the bottom of the methane extracting tower **1** and the ethylene tower **3**, and a manner of cooling for the production of the liquid reflux therefor are as follows: L.M.G. is admitted into the system by way of a line *j* and pressurized to a pressure of the order of 15 kg./cm.² G by the pump **22**. L.M.G. is then fed into the heat exchanger **18** for heat exchange with methane pressurized in the methane compressor **16** and recirculating through the methane recirculating cycle **21**. By liquefying the recirculating methane, L.M.G. is heated up to a temperature of −110° C. to −120° C. and led to the ethylene condenser **5** by way of a line **23**. L.M.G. fed into the ethylene condenser **5** is effective to liquefy a major portion of ethylene led out of the top of the ethylene tower **3** and into the ethylene condenser **5** by way of the line *k*. (The amount of ethylene to be liquefied corresponds to a required amount of reflux. When product ethylene is to be obtained in the form of liquid, the entire amount is liquefied. In this case, product ethylene is directly taken out of the system by way of a line *l*.) L.M.G. thereby vaporized is led into a heat exchanger **24** by way of a line *m*, makes heat exchange with compressed ethylene returned into the heat exchanger **24** by way of a line *r* after having been used as a refrigerating medium in other services, is warmed up to a temperature of −45° C. to −50° C., and discharged outwardly of the system.

Ethylene liquefied in the ethylene condenser **5** flows down into the receiver **6**, and a major portion of liquefied ethylene is led by way of a line *n* into the pump **7**, by which it is fed back to the top of the ethylene tower **3** by way of the line **8**. A portion of liquefied ethylene is led by way of a line *o* into a pump **25** by which it is pressurized by an amount more than 3.5 to 4 kg./cm.², for example, pressurized up to 10 kg./cm.² G, warmed up to a certain degree through heat exchange with pressurized liquid ethylene at a relatively high temperature, and fed into the reboiler **4** of the ethylene tower **3**. Liquid ethylene under pressure of 10 kg./cm.² G, which is liquefied by heating the ethylene tower **3**, is led by way of a line *p* into a pump **27**, which compensates with its head for any pressure loss due to resistance during flow in the piping and diverts liquid ethylene by way of a line *g* to any other services requiring refrigeration. Refrigeration temperature available for other services depends upon the working pressure of the ethylene tower reboiler **4**, but, in the present case, it is in the order of −45° C. to −50° C.

Ethylene having been used as a refrigerating medium at other services returns in the form of gas into the system by way of the line *r*, is partly re-liquefied in the heat exchanger **24**, and fed into the ethylene tower reboiler **4** and the methane extracting tower reboiler **2** by way of a line *s*. It will be understood that the rate of admission of ethylene must be determined from a viewpoint of a heat balance in the system. Ethylene liquefied by heating the methane extracting tower **1** at the reboiler **2** is fed through a line **28** and the heat exchanger **26** into an expansion valve **29**, in which it is expanded to a pressure approximately equal to the working pressure of the ethylene tower **3**, or 0.3 kg./cm.² G, joins the ethylene reflux from the pump **7**, and is supplied to the ethylene tower **3**.

As described in detail in the foregoing, according to the invention, the temperature of refrigeration available for other services is the boiling point of ethylene corresponding to the working pressure of the ethylene tower reboiler **4**, and the working pressure can be freely set at any value more than 3.5 to 4 kg./cm.² Therefore, the invention provides prominent effects that coldness of L.M.G. can be utilized for the separation of ethylene and its surplus coldness can be practically conveniently utilized in a considerably wide temperature range, while at the

same time L.M.G. is finally obtained in the form of gas at a pressure above 10 kg./cm.^{2} G. L.M.G. is mainly utilized by gas producing companies and these companies are also producing oil gas. Therefore, application of L.M.G. to the separation of olefin from the oil gas will provide an extremely great advantage, since L.M.G. obtained in the form of gas after such process can readily be supplied to a town gas system.

Further since refrigeration to provide the required amount of reflux for the methane extracting tower **1** is only one third or one fourth the refrigeration to provide the required amount of reflux for the ethylene tower **3**, it will be apparent that the amount of refrigeration for the production of the reflux for the methane extracting tower **1** can sufficiently be provided by the sensible heat contained in the required amount of liquefied methane gas (L.M.G.) which is vaporized at a temperature of —110° C. to —120° C. to produce the liquid reflux for the ethylene tower **3**. Because of a widened temperature range for the utilization of refrigeration by L.M.G. in the methane extracting tower **1**, the methane recirculating cycle is additionally incorporated in the apparatus of the invention for compressing methane by the methane compressor **16** for recirculation to the extracting tower **1**, as in case of prior apparatus wherein refrigeration by L.M.G. is not utilized. However, in the apparatus of the invention, boosting up to a pressure of the order of 20 atmospheres is only sufficient as against 50 atmospheres in prior apparatus, since the refrigerating temperature is relatively low, or in the order of —110° C. to —120° C. Therefore, the addition of such recirculating cycle is not a drawback when compared with an increased yield of ethylene owing to low temperature operation, effective utilization of coldness of liquefied methane gas, and other advantageous factors.

The invention, further, is very advantageous in that the methane compressor at a high compression efficiency can be easily manufactured in view of the low degree of pressurization of 20 atmospheres, which compressor is generally of a labyrinth type structure in order to avoid mixture of oil into compressed gas.

In the invention, a so-called refrigeration cycle is formed and utilized for the separation of olefin for the purpose of pressurizing and recirculating a component such as ethylene having a higher boiling point than methane by means of a pump or compressor, liquefying ethylene by surplus coldness and utilizing for other services the refrigeration provided by vaporization of liquefied ethylene. Thus, the surplus coldness in the apparatus working at an elevated temperature level and a major portion of coldness derived from the sensible heat portion of L.M.G. can be utilized for refrigeration at a predetermined temperature, and a great degree of utilization of such coldness can thereby be attained.

What is claimed is:

Apparatus for the rectification of olefin from an olefin-rich gas mixture by the utilization of refrigeration by externally supplied liquefied methane gas comprising a methane extracting tower, an olefin tower, a methane recirculating cycle including a methane compressor, heat exchangers and an expansion valve for recirculating a portion of methane delivered from said methane extracting tower again into said methane extracting tower, and a pump for conducting at an increased pressure said liquefied methane gas to one of the heat exchangers in said methane recirculating cycle for refrigeration by the sensible heat of said liquefied methane gas, wherein the manner of operation is such that recirculating methane is first liquefied by the refrigeration by the sensible heat of said liquefied methane gas and subsequently said liquefied methane gas is used to refrigerate a liquid reflux for said olefin tower.

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