This invention relates generally to improvements in the art of distributing and processing natural gas, and more particularly, but not by way of limitation, to an improved method of preparing liquefied natural gas for use as a fuel, or partly for use as a fuel and partly for use as raw material in the petrochemical industry.

As it is well known in the art, some localities have an abundant supply of natural gas, whereas other localities have very little or no natural gas resources. When such localities are reasonably close to one another, the natural gas may be transported from one locality to the other by means of a pipeline. However, when such localities are separated by long distances, or by substantial bodies of water, transportation by pipeline becomes impractical. A new industry is in the stage of development for the primary purpose of liquefying natural gas in a locality having an abundant supply and transporting the natural gas in liquefied form to a remote locality having a natural gas shortage. The liquefied natural gas occupies about one third the space required for natural gas in gaseous form, thereby making transportation over long distances practical. At the remote locality, the liquefied natural gas is revaporized and used as a fuel. In some of these remote localities, the natural gas can be revaporized and used directly as a fuel. In other localities, the gas specifications for existing equipment therein are different from the specifications of the revaporized natural gas, thereby requiring that the revaporized natural gas be reformed to a lower heating value and a specific gravity before use.

As it is also known in the art, natural gas usually contains a rather wide range of hydrocarbons. Ordinarily, methane comprises the major proportion of the natural gas, with the heavier hydrocarbons such as ethane, propane, butane and the like being present in the gas in minor proportions. At least some of these heavier hydrocarbons can be separated before the natural gas is liquefied and transported to the remote locations. However, it is sometimes desirable to liquefy the heavier hydrocarbons along with the methane and transport the entire natural gas composition to the remote locality in liquid form. These heavier hydrocarbons have two important uses at the remote localities. Firstly, when the natural gas must be reformed to a lower heating value and a new specific gravity to meet existing equipment specifications, the heavier hydrocarbons may be conveniently used in the formation of a carrier gas having a lower heating value and new specific gravity, with the carrier gas being subsequently mixed with methane to form the gaseous fuel having the desired heat content and specific gravity specifications. Secondly, the heavier hydrocarbons may be economically used as a raw material in the petrochemical industry in the remote locality.

The present invention contemplates a novel method of separating the heavier hydrocarbons from the liquefied natural gas, with a simultaneous revaporation of the methane. The revaporization and separation are accomplished in a fractionating zone in such a manner that a portion of the heat in vapors withdrawn from the fractionating zone may be efficiently utilized in heating the liquefied natural gas fed to the fractionating zone, and the resulting vapors will be extremely rich in methane, i.e., containing a very minor proportion of the heavier hydrocarbons. Condensate formed in said vapors by passage in heat exchange relation with the liquefied natural gas are refluxed to the fractionating zone to enhance the separation of methane in the fractionating zone. The present method also contemplates the recovery of work from the separated methane, as well as the utilization of heat from the expanded methane vapors for warming methane vapors being fed to the work-producing zone, such that the maximum energy of the separated methane may be utilized. The separated heavier hydrocarbons may be used either in forming a carrier gas or as a raw material in the petrochemical industry, as previously indicated.

An important object of this invention is to provide an efficient method of separating methane from a liquefied natural gas with a minimum of equipment and cost.

Another object of this invention is to simultaneously separate methane from liquefied natural gas and revaporize the methane.

A further object of this invention is to provide a novel method of fractionating liquefied natural gas, wherein the overhead from the fractionating zone is utilized to heat the liquefied natural gas being fed to the fractionating zone.

A still further object of this invention is to recover power in a process of revaporizing liquefied natural gas.

Other objects and advantages of the invention will be evident from the following detailed description, when read in conjunction with the accompanying drawing which illustrates this invention.

The single figure of the drawing is a flow diagram illustrating a practice of this invention.

As previously indicated, natural gas ordinarily comprises a rather wide range of hydrocarbons, and it is desirable that all of the hydrocarbons be liquefied prior to transporting the composition to a remote locality. To illustrate the present invention, it will be assumed that the liquefied natural gas to be separated and revaporized has the following analysis, although it will be understood that this composition is merely an example and that the invention may be practiced with a liquefied natural gas having substantially any composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>71.23</td>
</tr>
<tr>
<td>Ethane</td>
<td>13.65</td>
</tr>
<tr>
<td>Propane</td>
<td>9.10</td>
</tr>
<tr>
<td>Isobutane</td>
<td>2.20</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.25</td>
</tr>
<tr>
<td>Isopentane</td>
<td>0.68</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>0.33</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.34</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Referring to the drawing in detail, reference character 10 designates a line leading from a source (not shown) of the liquefied natural gas, which will ordinarily be a suitable insulated storage tank located in a coastal region where the liquefied natural gas may be received from similar insulated containers mounted aboard a ship used in transporting the gas to the remote locality. The liquefied natural gas is ordinarily stored at about atmospheric pressure, or slightly above, with a temperature of about -246° F. to -258° F., depending upon the precise composition of the gas. This low pressure and cold liquefied gas is fed to a pump 12 for pumping the liquefied natural gas through another line 14 to a fractionating tower 16 at increased pressure. It is preferred that the pump 12 provide a substantial increase in the pressure of the liquefied natural gas, with the pressure being raised to about 585 p.s.i.g. to facilitate fractionation and subsequent power recovery, as will be more fully hereinafter set forth. Also, a pair of heat exchangers 18 and 20 are interposed in the line 14 to heat the liquefied natural gas being fed to the fractionating tower 16.
until approximately the bubble point temperature of the liquefied natural gas is reached. In other words, the liquefied natural gas being fed to the tower 16 is pressurized and then heated to approximately its bubble point. The detailed operations of the heat exchangers 18 and 20 are described in detail below.

The fractionating tower 16 may be of any desired construction which provides a vertically extended fractionating zone. The liquefied natural gas is fed to the medial portion of the tower 16 and is slightly expanded, as from 585 p.s.i.g. to 535 p.s.i.g. into the tower 16 to facilitate separation of the methane from the heavier hydrocarbons. The liquid accumulating in the lower end portion of the tower 16 is circulated through a re-boiler 22 for heating the tower to such a temperature that methane enriched vapors will be directed into the upper portion of the tower, and the liquid in the lower portion of the tower will be enriched with the heavier hydrocarbons. In the example used for illustration, the liquid in the lower portion of the tower 16 is heated to a temperature of about 135°F by the re-boiler 22. The re-boiler 22 derives its heat from any suitable heating medium, such as a gaseous product from a reforming operation, to maintain the desired temperature of the liquid in the lower portion of the tower 16. The liquid accumulating in the lower portion of the tower 16 is selected or used as a raw material in a petrochemical industry.

The methane enriched vapors rising to the upper portion of the fractionating tower 16 are withdrawn through a line 30 and passed through the heat exchanger 18 interposed in the liquefied natural gas feed line 14. A typical analysis of the vapors withdrawn through the line 30 is as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>98.45</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.55</td>
</tr>
</tbody>
</table>

Also, with the temperature and pressure conditions previously indicated in the tower 16, the vapors withdrawn through the line 30 will be at about 535 p.s.i.g. and —118°F. When these vapors are passed through the heat exchanger 18, the vapors will be cooled to about —120°F before the liquefied natural gas will be slightly warmed to enhance the subsequent fractionation thereof. Cooling of the methane enriched vapors directed through the line 30 condenses a portion of the vapors. Therefore, the vapors are directed through a line 32 from the heat exchanger 18 into an accumulator 34 which also functions as a separator for collecting the condensate in the lower portion thereof. These condensates are refluxed to the upper portion of the tower 16 through a line 35. The refluxed condensates will be at about —120°F and, as it is well known in the art, will facilitate the condensation of heavier hydrocarbon vapors passing upwardly through the tower 16, as well as the vaporization of the methane component in the condensate, to facilitate a more complete separation of the methane from the heavier hydrocarbons in the tower 16. The condensates being refluxed to the tower 16 will be enriched with methane, but will contain an appreciable proportion of heavier hydrocarbons. A typical analysis thereof being as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>97.81</td>
</tr>
<tr>
<td>Ethane</td>
<td>2.19</td>
</tr>
</tbody>
</table>

On the other hand, the vapors withdrawn through a line 36 from the top of the reflux accumulator 34 will have a smaller percentage of heavier hydrocarbons, with a typical analysis thereof being as follows:

<table>
<thead>
<tr>
<th>Component</th>
<th>Mol. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>99.05</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.95</td>
</tr>
</tbody>
</table>

It may also be noted that the vapors discharged through the line 36 will be at about 355 p.s.i.g. and about —120°F. These vapors are passed through heat exchangers 38, 40 and 42 to provide a substantial warming of the vapors. It is preferred that the methane vapors be warmed by passage through the heat exchangers 38, 40 and 42 to a temperature of about 700°F. Whereupon, the gas is expanded through a suitable expander 44 down to about 100 p.s.i.g. for the recovery of a substantial amount of work from the revaporized methane. The device 44 may be of any suitable form, such as a turbine, which will form a work-producing zone through which the methane may be expanded to produce work. In a typical installation, where about 235,398 pounds per hr. of liquefied natural gas are fed to the tower 16, and having a composition as previously described, the expander 44 should produce about 7400 B.H.P.; whereas the pump 12 for increasing the pressure of the liquefied natural gas will require only about 790 B.H.P., thereby resulting in a substantial power recovery from the system.

The exhaust from the expander 44 is fed through a line 46 to the heat exchanger 40 to provide heating of the feed to the expander, as previously described. After the revaporized methane has been passed through the heat exchanger 40, it may be used directly as a fuel, or reformed to a lower heat content and new specific gravity, as previously indicated. In the example disclosed, the revaporized methane discharged from the heat exchanger 40 will be at about 100 p.s.i.g. and 100°F.

The methane vapors passing from the line 36 to the heat exchanger 38 on their way to the expander 44 are initially heated by a heating medium passed through the heat exchanger 38. The heating medium passed through the heat exchanger 38 may be of any suitable form having a temperature higher than the temperature of the methane vapors in the line 36. When the present method is being used in combination with a reforming process, the heating medium for the heat exchanger 38 may conveniently be a hot fluid from the reforming operation. For the temperature and pressure conditions previously described, the heating medium passed through the heat exchanger 38 should have a temperature of about 81°F. This heating medium may then be transferred through a line 48 to the heat exchanger 20 used for heating the liquefied natural gas to the fractionating tower 16. It will be understood, however, that separating mediums may be used in the exchangers 20 and 38, it being only necessary that the liquefied natural gas being fed to the tower 16 be raised approximately to its bubble point temperature, and the revaporized methane in the line 36 be at a temperature for efficient heat transfer with the expanded methane vapors in the line 36 to a temperature which will provide the most
efficient expansion of the methane through the expander 44 and permit use of this expanded methane for heat exchange with the feed to the expander, it is required that an additional heating medium of rather high temperature be passed through the heat exchanger 42. Any desired heating medium may be used with the heat exchanger 42, it only being necessary that the revaporized methane be fed to the expander 44 be increased in temperature for an efficient expansion. When the present method is being used in combination with a reforming operation, a hot gas from the reforming operation at about 840° F. may be passed through the heat exchanger 42. Thus, the revaporized methane may be raised to a temperature of about 700° F. before passing through the expander 44.

From the foregoing it will be apparent that the present invention provides an efficient method for separating methane from liquefied natural gas by using the minimum of apparatus, and with a minimum of cost. It will be further apparent that the separation of the methane from the heavier hydrocarbon components of a liquefied natural gas stream is accomplished simultaneously with revaporization of the methane, such that the separated components will be in proper form for use as a fuel or for further processing. The method may be performed in such a manner that a substantial amount of work may be recovered from the revaporized methane. It will also be apparent that the present invention provides a novel method of fractionating liquefied gases, wherein the overhead vapors from the fractionating zone are passed in heat exchange relation with the liquefied gases being fed to the fractionating zone, and wherein the resulting condensates are refluxed to the fractionating zone, to provide an efficient fractionation without the necessity of using a separate reflux condenser and refrigerant.

Changes may be made in the combination and arrangement of steps and procedures, as well as the form and arrangement of apparatus, heretofore set forth in specification and shown in the drawing, it being understood that changes may be made in the precise embodiment disclosed without departing from the spirit and scope of the invention as defined in the following claims.

We claim:
1. In a method of separating the heavier hydrocarbons from liquefied natural gas containing a substantial proportion of methane, the steps of:
   (a) feeding the liquefied natural gas into the media portion of a fractionating zone;
   (b) heating the contents of the lower portion of the fractionating zone to a temperature to produce methane enriched vapors in the upper portion of the fractionating zone;
   (c) withdrawing vapors from the upper portion of the fractionating zone and directly passing said vapors in heat exchange relation with the liquefied natural gas being fed to the fractionating zone, to heat said feed and cool said vapors;
   (d) separating condensates from said vapors, after they have been used in heat exchange relationship with the liquefied natural gas,
   (e) refluxing said condensates to the upper portion of the fractionating zone for in the upper portion of the fractionating zone and inducing downward movement of heavier hydrocarbon enriched liquefied gas into the lower portion of the fractionating zone, and
   (f) withdrawing the heavier hydrocarbon enriched liquefied gas from the lower portion of the fractionating zone.

2. A method as defined in claim 1 characterized further in expanding said methane enriched vapors, after removal of the condensates therefrom, through a work-producing zone.

3. A method as defined in claim 1 characterized further in compressing the liquefied natural gas being fed to the fractionating zone.

4. A method as defined in claim 1 characterized further in compressing the liquefied natural gas being fed to the fractionating zone, and heating the compressed liquefied natural gas to approximately its bubble point temperature.

5. A method as defined in claim 1 characterized further in compressing the liquefied natural gas being fed to the fractionating zone, and heating the compressed liquefied natural gas to approximately its bubble point temperature.

6. In a method of separating the heavier hydrocarbons from liquefied natural gas containing a substantial proportion of methane and stored at about atmospheric pressure, the steps of:
   (a) pumping the liquefied natural gas into the medial portion of a fractionating zone at an increased pressure,
   (b) heating the lower portion of the fractionating zone to a temperature to produce methane enriched vapors in the upper portion of the fractionating zone,
   (c) withdrawing the methane enriched vapors from the upper portion of the fractionating zone and directly passing said vapors in heat exchange relation with the pressurized liquefied natural gas being fed to the fractionating zone for heating said feed and cooling said vapors,
   (d) separating the condensates from said vapors, after they have been used in heat exchange relationship with the liquefied natural gas,
   (e) refluxing said condensates to the upper portion of the fractionating zone to cool the upper portion of the fractionating zone and enhance the accumulation of heavier hydrocarbon enriched liquid in the lower portion of the fractionating zone,
   (f) withdrawing liquid from the lower portion of the fractionating zone, and
   (g) expanding said vapors, after removal of said condensates, through a work-producing zone.

7. A method as defined in claim 6 characterized further in passing the expanded vapors in heat exchange relation with said vapors between removal of condensates from said vapors and expansion of said vapors.

8. A method as defined in claim 6 characterized further in heating the liquefied natural gas being fed to the fractionating zone to approximately the bubble point temperature thereof.

9. A method as defined in claim 6 characterized further in that the liquefied natural gas being fed to the fractionating zone is raised in pressure to about 585 p.s.i.g and heated to its bubble point temperature before entering the fractionating zone.

10. A method as defined in claim 6 characterized further in heating said vapors to about 700° F. before expansion in said work-producing zone.

11. In a method of separating the lower boiling temperature component from a liquefied gas mixture by use of a fractionating tower, the improvement which comprises feeding the liquefied gas mixture into the medial portion of the tower, re-boiling the contents of the lower portion of the tower to such a temperature to produce vapors enriched with the lower boiling temperature component in the upper portion of the tower, directly passing said vapors in heat exchange relation with the liquefied gas mixture being fed to the tower, separating condensates from said vapors, and refluxing said condensates back to the upper portion of the tower.

References Cited in the file of this patent

UNITED STATES PATENTS
1,465,599 De Brey Aug. 21, 1923
2,526,996 Crawford Oct. 24, 1950
2,583,090 Cost Jan. 22, 1952
2,600,110 Hachmuth June 10, 1952
2,666,019 Winn Jan. 12, 1954