ABSTRACT

Process for the removal of methane from a hydrocarbon feed containing ethylene, methane and higher boiling hydrocarbons with minimum loss of ethylene. Methane is separated overhead from the feed in a separation zone at a first lower pressure; a first portion of this overhead vapor is expanded through an expansion motor producing an energy output; a second portion of the overhead vapor is compressed to a second pressure greater than the first pressure in a compressor driven by the motor output. The compressed vapor portion is then cooled to condense the major portion of the methane and the condensed methane is returned to the separation zone as reflux and recovering ethylene as bottoms from the separation zone. The methane vapor is recovered as fuel gas.

16 Claims, 1 Drawing Figure
LOW PRESSURE ETHYLENE RECOVERY PROCESS

REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our copending application, Ser. No. 800,875, filed Feb. 20, 1969.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention is concerned with the processing of cracked gases derived from hydrocarbon feedstocks and specifically with processes for separation having as their ultimate objective the economical recovery of maximum quantities of ethylene from such feedstocks. The present invention provides a process adapted to the recovery of ethylene from ethylene-containing feeds which typically contain as well as hydrogen, appreciable quantities of methane and various heavier ends such as ethane, propane and propylene. Particularly significant in the present development is the effective separation of methane from the ethylene at relatively low pressures and at moderate refrigeration temperatures whereby much high pressure equipment is obviated and/or expensive methane refrigeration plant requirements are avoided.

2. Prior Art

Recovery of ethylene from ethylene-containing gases is widely practiced in industry. Most operations have as their central facility a demethanizer column from which methane is passed overhead and ethylene is taken as bottoms. Typical operating conditions include 450 psia pressure in the column and accumulator temperatures of about -140°F. This combination keeps ethylene loss low (<1 percent) but is disadvantageous in that the high pressure in the demethanizer results in a greater than necessary total compressor energy requirement for refrigeration and raw gas compressors. Increased demethanizer pressure is even counterproductive as methane/ethylene separation is relatively more difficult at increased pressures.

Some ethylene recovery plants have so-called low pressure demethanizers. These, however, have been combined with expensive methane refrigeration cycles to produce a sufficiently low temperature for minimizing ethylene losses with the separation method. Thus the pressure-temperature problem referred to above is shifted but not resolved.

SUMMARY OF THE INVENTION

A different approach to the ethylene recovery problem is taken by the present invention where the methane/ethylene separation is achieved at relatively low pressures, but still with the application of moderate refrigeration temperatures. The present invention eliminates the use of the demethanizer. In this manner the high pressure facilities required in the plant are much reduced and operating costs are similarly lessened. As a particular feature, motor energy from an expander such as turbo-expander, driven by expansion of a portion of demethanizer overhead vapors is used to compress a second portion of the overhead vapors, which are cooled by external ethylene refrigeration and partially condensed, thus providing reflux for the demethanizer without external methane refrigeration being required.

Specifically, the invention provides a process for the removal of methane from a hydrocarbon feed containing ethylene, hydrogen, methane and higher boiling hydrocarbon components with low loss of ethylene. The process includes effecting in a methane separation zone at a first pressure between about 200 and 350 psia, a separation overhead of methane-rich vapor which may contain up to 4 percent hydrogen and less than 2 percent ethylene by volume, expanding a first portion of the overhead vapor through an expansion motor producing an energy output from the vapor expansion, compressing a second portion of the overhead vapor to a second pressure greater than the first pressure in a compressor driven by the energy output of the motor, cooling the compressed overhead vapor portion sufficiently to condense the major portion of the methane therein, separating methane vapor from the condensed methane, returning the condensed methane to the methane separation zone as reflux and recovering ethylene and heavier components of the feed as bottoms from the methane separation zone. The first vapor portion generally will comprise not less than 50 percent by volume of the methane separation zone overhead and the second overhead vapor portion accordingly will be less than 50 percent by volume of the methane separation zone overhead vapors. The expansion of the first overhead vapor portion is carried out to produce an energy output which will effect the desired compression of the second overhead vapor portion. In particular embodiments, the overhead first vapor portion is expanded to a pressure less than 100 psia while the second portion of the overhead vapor is compressed to a pressure above about 450 psia.

In preferred embodiments the first vapor portion is centrifugally expanded through a turbine type expansion motor.

The process further includes flashing hydrogen and methane from the hydrocarbon feed in advance of the methane separation zone and heat exchanging the flash vapor and flash liquid with incoming feed to cool the feed before flashing hydrogen and methane therefrom. In addition, heat exchanging the expanded overhead vapor portion with the feed to cool the feed further prior to said flashing may also be accomplished in the process. Further included is heat exchanging the bottoms from the methane separation zone with the feed to cool the feed prior to flashing methane and hydrogen therefrom. The second vapor portion may be compressed to a pressure above about 450 psia and thereafter be cooled by external refrigeration to a temperature below about -135°F, to effect liquefaction of from 50 to 95 percent of the methane content in the portion.

BRIEF DESCRIPTION OF THE DRAWING

The single FIGURE schematic flow sheet illustrates one embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It will be apparent from the foregoing and as the description proceeds that the present invention provides separation of methane during ethylene recovery at temperatures no lower than those realizable with ethylene refrigerants at ordinary pressures, e.g. -145°F and with a minimum of high pressure equipment. Moreover, this process effectively balances power outputs and demands, and heating and cooling requirements, to secure high efficiency in operation.

Thus, and with reference to the accompanying flow sheet drawing, the feed enters along line 1 at a temperature generally of -40°F to +60°F and at pressures typically between 235 and 550 psia for example 420 psia. The cold process streams available from subsequent operations, to be described, are used to advantage to cool the feed, prior to fractionation of the feed, to temperatures at which hydrogen and methane may be flashed from the feed e.g. -120°F to -140°F. Feed from line 1 is split to send a first portion to heat exchanger 2 along line 3. In passage along line 3, this first portion of the feed is heat exchanged in heat exchanger 4 with the product recovery stream in line 53 prior to passing the product stream to subsequent processing equipment, e.g. a deethanizer (not shown). The first portion of the feed may also be cooled with auxiliary cooling means such as propylene refrigeration in heat exchanger 5, ethylene refrigeration in heat exchanger 6 as required to achieve the desired temperature in the feed.

The second portion of the feed controlled by valve 7 bypasses heat exchangers 4, 5 and 6 and passes along line 8 to heat exchanger 9 where this feed portion is cooled by heat exchange with exiting hydrogen and methane gas streams in lines 10 and 11 respectively. The off-gas cooled, second feed portion is returned along line 12 to line 3 for recombination with the cooled feed first portion at 13.
Thus preliminarily cooled, the feed passes to a gas-liquid separator 14 having level control valve 14a, so that the feed enters separator 14 at approximately −120°F. In separator 14, gas and liquid phases are flash separated at a pressure of approximately 405 psia. The flash liquid from this phase separation is taken as bottoms from separator 14 along line 15 and forms the main feed to the demethanizer zone, after reheating by topping to temperature in heat exchanger 2, as was described. The flash vapor from separator 14 is taken overhead in line 16 and cooled drastically in heat exchanger 17 e.g. to −210°F at 400 psia by heat exchange therein with very cold methane gas and liquid e.g. −218°F in line 11 from the vapor expansion hereinafter described and passed along line 18 to be flashed in gas-liquid separator 19 having a pressure control valve 19a. The flash vapors from separator 19 constitute a cold, hydrogen-rich gas stream which may be passed along line 10 as a refrigerating stream to be heat exchanged with the feed in heat exchanger 9 before leaving the system e.g. at +52°F.

The flash liquid from the second flash in separator 19 is passed from the separator along line 20a having level control valve 20a, reheated against the first flash vapors in heat exchanger 17 and thereafter combined at 21 with the gross demethanizer column overhead stream in line 28.

Considering again the first flash separator 14, flash liquid taken off in line 15 controlled by level control valve 14a is passed through heat exchanger 2 for warming e.g. to −75°F and is then passed to fractionating column 22 at feed point 23 in the column. Column 22 is operated as the demethanizer first stage. Pressure in bottoms section 24 of column 22 is relatively low for a demethanizing operation e.g. between 200 and 350 psia and suitably about 265 psia. Bottoms temperature is maintained with reboiler 25 by condensation of propylene refrigeration vapors from line 26 at a level sufficient to boil the bottoms mixture of C4H10 and heavier hydrocarbons e.g. −5°F.

The upper section of column 22 above the feed point 23 is operated at a slightly lower pressure and at a lower temperature than the column bottom section 24, e.g. at 260 psia and −110°F. Temperatures in upper section 27 may be between −70° and −130°F and pressures may range between 195 and 340 psia. The gross demethanizer overhead from column upper section 27 comprising predominantly methane and some minimum quantity of ethylene e.g. 4 to 7 percent is passed in line 28 to rectification in rectifier 29. The gross demethanizer overhead is cooled in heat exchanger 30 with −147°F ethylene prior to introduction into the rectifier. As previously described, the flash liquid from separator 19 is added to the gross demethanizer overhead at point 21 in line 28, following heat exchanger 30. The gross demethanizer overhead is passed into the bottom of rectifier 29 which is suitably maintained at a pressure of 255 psia and a temperature of −140°F, both below their corresponding values in upper section 27 of column 22. Liquid bottoms from the rectifier 29 is passed by pump 31 along line 32 through valve 32a to the upper section 27 of demethanizer column 22, as reflux.

The overhead from rectifier 29 comprising methylene and 2 to 4 percent hydrogen and minimum ethylene e.g. 0 to 2 percent and preferably <1 percent by weight and typically at a temperature of −165°F is passed along line 33 to a turbo-expander 34 through heat exchanger 46 for warming. The turbo-expander includes an expander section 35, typically a centrifugal expander which is operated as an expansion motor and a compressor section 36 also centrifugal, which is operated as a compressor, driven by the expander section to which it is directly coupled, as by a motor. The term "expansion motor" herein is used to describe devices producing mechanical energy through gas or vapor expansion. While turbine motors are preferred reciprocating motors may be used.

The rectifier overhead line 33 communicates along line 37 with the inlet 38 of expander section 35 and along line 39 with the suction inlet 40 of the compressor section 36, whereby the rectifier overhead vapors in line 33 are divided into two portions, at 41, for passage to either the expander or compressor sections 35, 36 along line 37 or 39 respectively. Moreover, by control valve 42 operation a portion of the rectifier overhead can bypass the expander and pass directly to line 11 e.g. in heat exchanger 17 as shown.

Post-fractionation compression of a portion of the rectifier overhead vapors provides a capability in the present process for minimum ethylene recovery without operating the fractionation column 22 at critical values of temperature or unacceptably high pressure. Thus in compressor section 35, the rectifier overhead vapors are compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

Incompressor section 36, the rectifier overhead vapors are compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.

In compressor section 35, the rectifier overhead vapor is compressed to a pressure at which the major portion i.e. 50 percent by volume and above, e.g. 50 to 75 percent up to 95 percent of the methane component thereof is condensible against readily available streams such as cold ethylene, e.g. ethylene at −147°F. Total condensation is not economically feasible due to the necessary inclusion of small concentrations of hydrogen in the methane overhead from rectifier 29, which in turn results from solutions of minor components in the feed.
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psia to secure a hydrogen rich by-product gas in separator 19 which is taken off along line 10. Liquid from the −120°F flash is exchanged against the feed in heat exchanger 2 and fed to the demethanizer column 22 at −75°F. Demethanizer column bottom pressure is maintained at 260 psia and the temperature of material therefrom at −5°F. Overhead vapors from the demethanizer column 22 at −110°F and 255 psia are rectified in rectifier 29. Rectifier overhead vapors at −165°F and 250 psia are first heated in exchanger 46 to −147°F and then split and less than 50 percent is passed to the intake of compressor 36 to be compressed to 500 psia at −60°F. The energy for the compression is obtained from the expansion in expander 36 of the balance (greater than 50 percent) of the rectifier overhead, the expansion being from a pressure of 250 psia and a temperature of −147°F to 70 psia and −218°F. The expansion energy is balanced with the compression energy at these conditions. Liquid methane from separator 45 is returned to the rectifier 29 as reflux.

A typical material balance for the process is given in the table.

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Liquid</th>
<th>Vapor</th>
<th>Liquid</th>
<th>Vapor</th>
<th>Methane of gas</th>
<th>Demethanizer bottoms</th>
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<tr>
<td>Hydrogen</td>
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<td>88.20</td>
<td>1,356.80</td>
<td>9.96</td>
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<td>96.18</td>
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<tr>
<td>CO</td>
<td>5.90</td>
<td>3.15</td>
<td>6.41</td>
<td>0.80</td>
<td>6.81</td>
<td>4.08</td>
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</tr>
<tr>
<td>Methane</td>
<td>2,623.80</td>
<td>1,871.05</td>
<td>752.33</td>
<td>432.42</td>
<td>520.91</td>
<td>2,591.18</td>
<td>0.29</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>3,962.14</td>
<td>2,843.63</td>
<td>138.55</td>
<td>136.47</td>
<td>3.96</td>
<td>27.68</td>
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<tr>
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<td>696.41</td>
<td>666.15</td>
<td>2.25</td>
<td>2.38</td>
<td></td>
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<td>226.42</td>
<td>226.41</td>
<td>0.01</td>
<td>0.1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Total</td>
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<td>6,798.63</td>
<td>2,367.36</td>
<td>573.03</td>
<td>1,964.33</td>
<td>2,612.12</td>
<td>6,858.54</td>
</tr>
</tbody>
</table>

| STAGE | −120°F flash | −210°F flash |

In summary and in its preferred form the present process for the removal of methane from a hydrocarbon feed containing ethylene, hydrogen, methane and higher boiling hydrocarbon components with low loss of ethylene includes removing hydrogen from the feed, fractionating the hydrogen-lean feed in a column having a bottoms temperature less than about 10°F and a bottoms pressure between 250 and 275 psia to provide a methane-rich overhead vapor comprising methane and up to 4 percent by volume hydrogen, and not more than 2 percent by volume ethylene at a temperature below about −140°F and a bottoms stream essentially free of methane, dividing said overhead vapor into a first portion equal to less than 50 percent by volume of the column overhead vapor and a second portion conversely equal to less than 50 percent of the overhead vapor, expanding the first portion through a turbine to lower the pressure of the first portion to less than about 150 psia and to lower the temperature of the first portion to less than about −200°F and producing an energy output from the expansion, heating the expanded first portion with the feed to cool the feed temperatures about −120°F and a portion of the feed to −200°F or lower suitable for removal of hydrogen therefrom, and recovering the heat exchanged expanded first portion as fuel gas; compressing the second portion of the overhead vapor to a pressure greater than about 450 psia in a compressor driven by the energy output of the turbine, cooling the compressed second vapor portion to a temperature less than about −135°F at which least 50 to 95 percent by weight of the methane therein condenses, separating condensed methane from the compressed second vapor portion with said feed to cool the feed before flashing hydrogen and methane hydrocarbons as bottoms from said column.

We Claim:

1. Process for the removal of methane from a hydrocarbon feed containing ethylene, methane and higher boiling hydrocarbon components with low loss of ethylene which includes effects in a methane separation zone at a first pressure

2. Process according to claim 1 in which said second portion of the overhead vapor is compressed to a pressure above about 450 psia.

3. Process according to claim 1 in which said first vapor portion is compressed to a pressure less than about 150 psia.

4. Process according to claim 5 in which said second vapor portion is compressed to a pressure above about 450 psia and is thereby cooled by external refrigeration to a temperature below about −135°F to effect liquefaction from 50 to 95 percent of the methane in said portion.

5. Process according to claim 6 including also returning the liquid methane obtained from said second vapor portion to the methane separation zone as reflux.

6. Process according to claim 7 in which said first vapor portion comprises less than 50 percent by volume of the methane separation overhead.

7. Process according to claim 8 and including also compressing said second vapor portion sufficiently to utilize the energy output of the expansion.

8. Process according to claim 1 including also centrifugally expanding said first vapor portion through a turbine.

9. Process according to claim 9 including also centrifugally expanding said first vapor portion through a turbine.

10. Process according to claim 11 including also cooling the compressed second vapor portion to a temperature liquefying the methane therein.

11. Process according to claim 12 including also heat exchanging said expanded overhead vapor portion with said feed to cool said feed prior to said flashing.

12. Process according to claim 13 including also heat exchanging said expanded overhead vapor portion with said feed to secure a hydrogen rich by-product gas in separator 19 which is taken off along line 10. Liquid from the −120°F flash is exchanged against the feed in heat exchanger 2 and fed to the demethanizer column 22 at −75°F. Demethanizer column bottom pressure is maintained at 260 psia and the temperature of material therefrom at −5°F. Overhead vapors from the demethanizer column 22 at −110°F and 255 psia are rectified in rectifier 29. Rectifier overhead vapors at −165°F and 250 psia are first heated in exchanger 46 to −147°F and then split and less than 50 percent is passed to the intake of compressor 36 to be compressed to 500 psia at −60°F. The energy for the compression is obtained from the expansion in expander 36 of the balance (greater than 50 percent) of the rectifier overhead, the expansion being from a pressure of 250 psia and a temperature of −147°F to 70 psia and −218°F. The expansion energy is balanced with the compression energy at these conditions. Liquid methane from separator 45 is returned to the rectifier 29 as reflux.

13. Process according to claim 4 including also hea...
16. Process for the removal of methane from a hydrocarbon feed containing ethylene, hydrogen, methane and higher boiling hydrocarbon components with low loss of ethylene which includes hydrogen removal from the feed, fractionating said feed in a column having a bottoms temperature less than about 10°F and a bottoms pressure between 250 and 275 psia to provide a methane-rich overhead vapor comprising methane, up to 4 percent by volume hydrogen and not more than 2 percent by volume ethylene at a temperature below about 140°F and a bottoms stream essentially free of methane; dividing said overhead vapor into a first portion equal to not less than 50 percent by volume of said overhead vapor and a second portion conversely equal to less than 50 percent of said overhead vapor; expanding said first portion through a turbine to lower the pressure of said first portion to less than about 150 psia and to lower the temperature of said first portion to less than about -200°F producing an energy output from said vapor expansion, heat exchanging said expanded first portion with said feed to cool the feed to temperature about -120°F and a portion of the feed to -200°F or lower suitable for hydrogen removal therefrom, and recovering the heat exchanged expanded first portion as fuel gas; compressing the second portion of the overhead vapor to a pressure greater than about 450 psia in a compressor driven by said energy output of said turbine, cooling said compressed second vapor portion to a temperature less than about -135°F at which at least 50 to 95 percent by weight of the methane therein condenses separating condensed methane from the compressed second vapor portion and returning the condensed methane to the column as reflux; and recovering ethylene and higher boiling hydrocarbons as bottoms from said column.