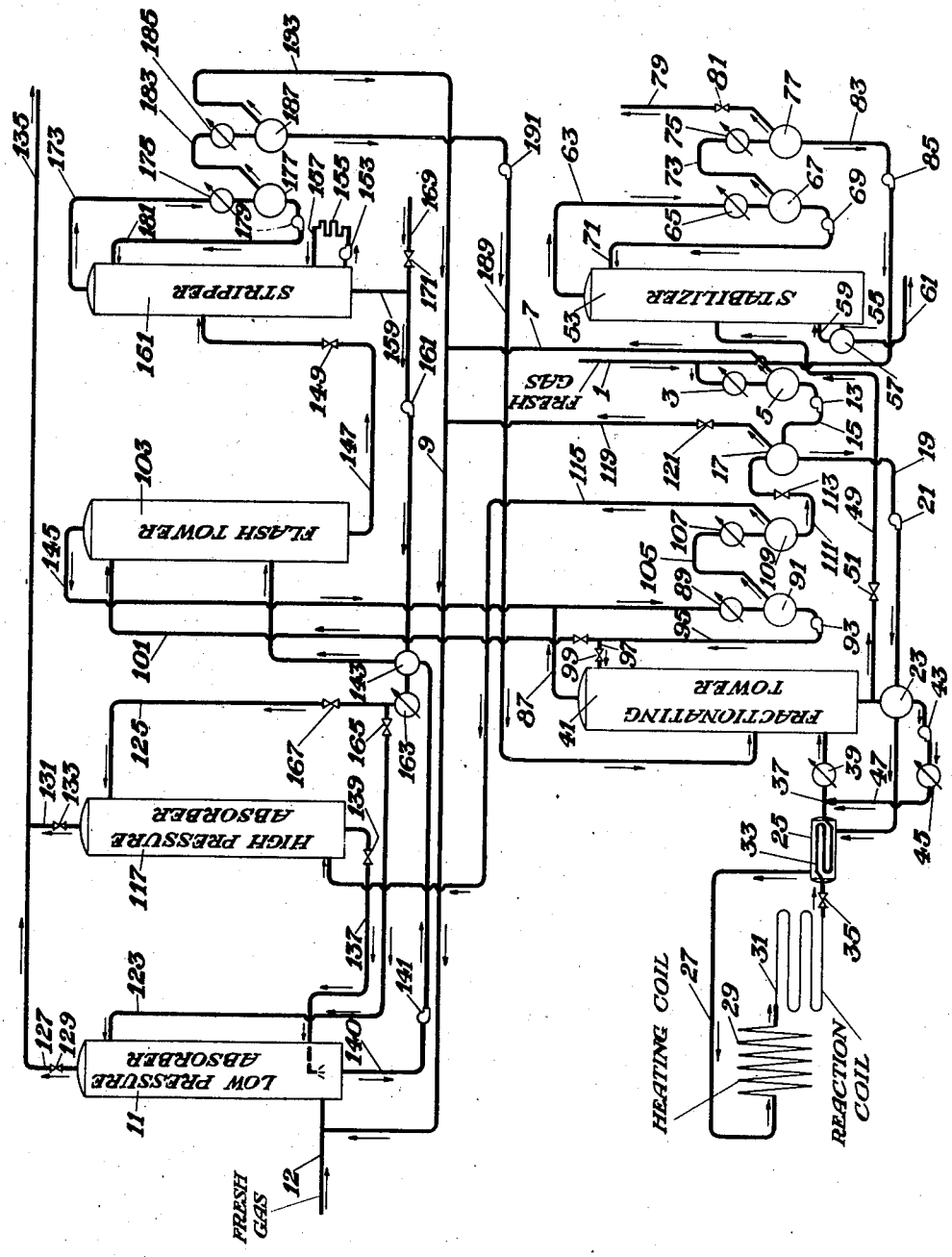
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METHOD FOR CONVERTING HYDROCARBON GASES TO LIQUID HYDROCARBONS

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METHOD FOR CONVERTING HYDROCARBON GASES TO LIQUID HYDROCARBONS

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This invention relates to conversion of hydrocarbon gases to liquid hydrocarbons and is more particularly concerned with method for thermal conversion of hydrocarbon gases to hydrocarbons boiling within the gasoline range.

In thermal gas conversion processes it is necessary to cool the reaction products leaving the reaction zone in order to stop conversion. This may be done either by indirect heat exchange or by direct quenching with liquid. Both methods of cooling have their advantages and disadvantages. Indirect heat exchange permits utilization of the heat remaining in the reaction products to preheat the charging stock to a comparatively high temperature, thereby reducing fuel requirements for heating the charge to reaction temperature. A great disadvantage of indirect cooling is that carbon and carbonaceous deposits build up rapidly in the transfer line and heat exchanger, necessitating frequent shutdowns for cleaning. Another disadvantage of indirect heat exchange is the high cost of the exchangers, particularly in high pressure processes.

Direct quenching with liquid eliminates or greatly lessens the deposition problem, but the quenched mixture is necessarily at a lower temperature level than the unquenched reaction products and therefore cannot possibly preheat the charging stock to as high a temperature as can be obtained with the unquenched reaction products.

It has been discovered that by a proper combination of indirect heat exchange and direct quenching, the disadvantages of either method of cooling can be obviated and the advantages of both in a large measure realized.

In accordance with the present invention, the pressure on the hot reaction products leaving the reaction zone is partially reduced and the reaction products under the lower superatmospheric pressure but before reduction in temperature are passed in indirect heat exchange relation with the charging stock. The cooling by means of heat exchange with the charging stock or other cooling medium is regulated so that the reaction products are not cooled to a temperature substantially below the dew point of the mixture. The dew point is that temperature at which droplets of condensible material form and deposit out of the reaction mixture under the pressure conditions being maintained. By limiting the cooling to a temperature not substantially below the dew point, deposition of carbon or carbonaceous matter from the reaction products is substantially prevented. Immediately following the cooling by the indirect heat exchange with the charging stock, the reaction products are then cooled to a temperature substantially below the dew point by direct contact with liquid cooling medium. The cooling medium used for the quenching should be an inert liquid which has the ability to dissolve or maintain in suspension material such as gum, resin, tar and asphalt which may condense from the reaction products. In this manner deposition of carbon or carbonaceous material in the transfer line is prevented and the material which would otherwise deposit in the heat exchanger or transfer line is removed from the system in liquid solution or suspension.

It is an object of this invention to provide method for utilizing the heat in reaction products from a gas conversion process operated at high pressures without causing harmful deposition of carbon and carbonaceous material.

It is a further object of the invention to provide method for preheating charging stock in a high pressure gas conversion process by means of high temperature reaction products in such manner as to reduce the cost of the apparatus involved and also to prevent clogging of the apparatus due to carbon deposition.

Other objects of the invention will appear from the following description taken in conjunction with the accompanying drawing of which the single figure is a diagrammatic side-elevational view of apparatus suitable for carrying out the invention.

Referring to the drawing, numeral 1 indicates a line through which fresh gas may be charged to the system under pressure by means of a suitable compressor not shown. The fresh gas may be stabilizer gas from either or both catalytic and pyrolytic oil cracking processes mixed or unmixed with the higher boiling fractions of natural gas. The fresh gas is passed through water cooler 3 where the temperature may be reduced to approximately 75° to 100° F. The partially condensed gases pass to accumulator 5 which may be maintained at a pressure of approximately 200–250 lbs. per square inch. That portion of the gas which is not condensed is withdrawn from accumulator 5 through the line 7 and passes from line 7 through line 9 to the lower portion of a low pressure absorber 11. Fresh gas may be fed into absorber 11 through line 12. This gas may be residual gas from oil cracking units. That portion of the gas which does liquefy is withdrawn from the accumulator 5 by means of pump 13 through line 15 into feed tank 17. The feed tank 17 may be maintained at a pressure of

approximately 225 to 300 lbs. per square inch and at a temperature of approximately 75° to 100° F.

Liquefied gas is withdrawn from feed tank 17 through line 19 by means of pump 21 in which the pressure may be increased to 750–2000 or more lbs. per square inch, then passed through heat exchangers 23 and 25 and line 27 to the inlet of the heating coil 29. In the heat exchanger 23 the charging stock may be preheated to a temperature in the neighborhood of 200° F. and in the heat exchanger 25 the charging stock may be further preheated to a temperature in the neighborhood of 450° to 550° F. The preheated gas is further heated in the heating coil 29 to a reaction temperature of 900° to 1200° F. and then passed to a reaction coil 31 in which the temperature of the gases is maintained for a sufficient period of time to bring about the desired conversion of hydrocarbon gases to liquid hydrocarbons. The conversion coil 31 is preferably of greater cross-sectional area than the heating coil in order to decrease the velocity of the gases undergoing reaction and give the gases sufficient time to react. The reaction coil 31 is preferably placed in a zone where its temperature can be maintained at the desired reaction temperature either by heating or cooling, as required. When the charging stock has a high concentration of olefins, the reaction is exothermic in character, necessitating cooling of the mixture undergoing reaction. However, where the concentration of olefins is low, the reaction is endothermic in character, necessitating heating of the reaction zone to maintain the temperature. Where the gas is rich in olefins, lower temperatures of reaction are preferable and the same is true where the reaction mixture is composed chiefly of C_4 hydrocarbons with minor proportions of C_3 and C_2 hydrocarbons.

The hot reaction products leaving the reaction zone 31 pass through the coil 33 of heat exchanger 25 wherein the reaction products are partially cooled by indirect heat exchange with the charging stock. One of the outstanding features of this invention is the reduction of pressure on the hot reaction products prior to their passage to the heat exchanger, by means of the slide valve 35. The pressure may be reduced at the slide valve to approximately 500–600 lbs. per square inch without obtaining any substantial amount of carbon deposition. By reducing the pressure before the reaction products enter the heat exchanger 25, it is possible to utilize a heat exchanger of comparatively low cost of construction instead of an expensive heat exchanger which would otherwise be required to withstand the high pressure and temperatures to which it would be subjected. In the heat exchanger the temperature of the reaction products is reduced to a temperature not substantially below the dew point of the mixture. At pressures of 500 lbs. per square inch and higher the dew point will be within the temperature range of approximately 400° to 750° F. It will be understood that it is not necessary to reduce the temperature of the reaction products in the heat exchanger 25 to the dew point, but in order to obtain the benefit of as much of the heat in the reaction products as possible for preheating the charging stock, it is preferred that the temperature of the reaction products at this stage should be reduced as close to the dew point as possible.

Immediately upon leaving the heat exchanger coil 33, the partially cooled reaction products are further cooled by injecting cooling fluid into the stream of reaction products at the point 37. The temperature to which the reaction products are quenched by injection of cooling liquid is substantially below the dew point of the reaction mixture and in practice is preferably between 250° and 500° F. Sufficient quenching fluid of high enough boiling point must be used in order to have a substantial body of liquid present to carry in solution or in suspension any high boiling material of a gummy, resinous, tarry, asphaltic or carbonaceous nature which precipitates from the reaction mixture.

The reaction mixture which has been cooled below its dew point may be further cooled if necessary, by passing through water cooler 39 in which the temperature is lowered to approximately 250° to 350° F. From the cooler 39 the products pass into the lower part of fractionating tower 41. The fractionating tower 41 is maintained under such conditions that only C_4 and lighter gases pass overhead. To accomplish this fractionation, the tower may be maintained under the pressure to which the reaction products are reduced at the valve 35, allowing for pressure drop through the line, with a bottom temperature of 250° F. and a top temperature of about 200° F. The pressure in the tower may be in the neighborhood of 400 lbs. per square inch. Under these conditions substantially all the C_5 and heavier hydrocarbons as well as a part of the lighter hydrocarbons condense as a liquid in the bottom of the tower. A portion of the condensate is withdrawn from the bottom of the tower through heat exchanger 23 by means of pump 43, passed through water cooler 45 and line 47 and injected as the quenching liquid into the reaction stream at the point 37. In passing through the heat exchanger 23 and cooler 45 the condensate used for quench may be cooled to a temperature of approximately 150° to 200° F. The remainder of the condensate is withdrawn from the bottom of fractionating tower 41 through line 49, controlled by valve 51 and passed to stabilizer 53. The pressure is somewhat reduced at the valve 51, but the pressure in the stabilizer is preferably mainatined above 100 lbs. per square inch to insure liquefaction of the recycle gas. In the stabilizer 53 any gases lighter than C_4 and a portion or all of the C_4 hydrocarbons are removed from the condensate. Heating of the condensate in the stabilizer is accomplished by passing it from the lower portion of the stabilizer through line 55 into reboiler 57. Vapors from the reboiler are returned to the stabilizer through line 59. The stabilizer condensate is withdrawn from the reboiler through line 61 and is sent to storage or to a re-run operation of make finished gasoline. The vapors from the stabilizer which are composed chiefly of C_3 and C_4 hydrocarbons, with small amounts of lighter boiling material, pass overhead through line 63 through cooler 65 wherein a portion of the gas condenses and then passes to accumulator 67. The liquid from the accumulator 67 is recycled by means of pump 69 and line 71 to the top of the stabilizer 53 as reflux liquid. The gases from the accumulator 67 are taken off through line 73 to another water cooler 75 where the temperature is reduced to approximately 75° to 100° F. and substantially all of the gas condenses to liquid and is collected in the accumulator 77. The small amount of gas which does not condense is withdrawn through line 79, controlled by 81, and may be recycled to the low pressure absorber or withdrawn

from the system. Accumulator 77 is preferably maintained under a pressure of 100 to 200 lbs. per square inch in order to assure condensation of the gas taken from the top of the stabilizer. The liquefied gas collected in accumulator 77 is withdrawn through line 83 by means of pump 85 and returned to accumulator 5 together with the fresh feed.

Returning to the main fractionating tower 41, the C_4 and lighter gases are taken overhead through line 87, cooled by passing through water cooler 89 to a temperature of approximately 150° F. and then passed to accumulator 91. A portion of the gases are condensed in passing through cooler 89. The liquefied gas is withdrawn from the accumulator 91 by means of pump 93 and recycled through lines 95 and 97, controlled by valve 99, to the top of the fractionating tower 41 as reflux liquid. A portion of the liquefied gas from accumulator 91 may be passed through line 101 to the top of flash tower 103 as reflux liquid. The uncondensed gas from accumulator 91 is withdrawn through line 105 to a second water cooler 107 where the temperature is further reduced to approximately 90° to 100° F. In the cooler 107 a large portion of the gas condenses to liquid under the existing pressure which is substantially that maintained in the fractionating tower 41. The cooled products pass from cooler 107 to accumulator 109 from which the liquefied gas is withdrawn through line 111, controlled by valve 113, to feed tank 17. The pressure differential between accumulator 109 and feed tank 17 is maintained by means of valve 113. The uncondensed gas is withdrawn from accumulator 109 through line 115 and charged to the lower portion of high pressure absorber 117. This absorber is maintained at substantially the same pressure as the high pressure accumulator 109, being slightly lower because of pressure drop through the line. When the fractionating tower 41 is maintained at a pressure of about 410 lbs. per square inch, the high pressure absorber will operate at approximately 385 lbs. per square inch. Any gas which escapes from the feed tank 17 is withdrawn through line 119, controlled by valve 121, and is returned through line 9 to low pressure absorber 11. This absorber is preferably run at a pressure of approximately 175 to 250 lbs. per square inch and is generally slightly below the pressure maintained on the feed tank 17.

Absorption menstruum such as light gas oil or mineral seal oil is charged to the upper portion of absorbers 11 and 117 through lines 123 and 125, respectively. Absorption menstruum passes downwardly through the absorbers countercurrent to the gas passing upwardly therethrough. The major portion of the C_4 and C_3 gases as well as a substantial portion of the C_2 hydrocarbons and a small amount of methane is absorbed by the absorption menstruum in the two absorbers. The unabsorbed gas consisting chiefly of methane, hydrogen and C_2 hydrocarbons is withdrawn from absorber 11 through line 127, controlled by valve 129, and from absorber 117 through line 131, controlled by valve 133, and eliminated from the system through line 135. The rich menstruum from the bottom of high pressure absorber 117 is passed through line 137, controlled by valve 139, into the bottom of low pressure absorber 11 where it is mixed with the rich menstruum in the bottom of that absorber. The valve 139 maintains the pressure differential between the low and high pressure absorbers. The combined rich menstruum is withdrawn from the bottom of low pressure absorber 11 through line 140 by means of pump 141 and passed through heat exchanger 143 to the lower portion of flash tower 103. The pressure on the rich menstruum is raised in the pump 141 to a pressure slightly higher than that maintained in the accumulator 91. In passing through the heat exchanger 143 the temperature of the rich menstruum is raised sufficiently to cause vaporization in the flash tower 103 of the lighter gas constituents absorbed. This temperature may be between 350° and 400° F. The gases are taken from the top of the flash tower 103 through line 145 and passed through cooler 89 to high pressure accumulator 91 together with the gases from the top of fractionating tower 41. The partially denuded menstruum is withdrawn from the bottom of flash tower 103 through line 147, controlled by valve 149, and passed to the mid-portion of stripper 151. The pressure on the partially denuded menstruum is substantially reduced at the valve 149 so that the stripping tower may be maintained at a pressure only sufficient to enable return of gases to the low pressure absorber without compression. The liquid in the bottom of the stripper 151 is withdrawn by means of pump 153, heated in coil 155 and returned to the stripper through line 157. In the coil 155 the liquid is heated to a sufficiently high temperature to completely denude the absorption menstruum of absorbed gases. This temperature may be in the neighborhood of 600° F. By maintaining the top of the stripper at a temperature of 300° F. or less, only the absorbed gases pass overhead and the absorption menstruum is substantially all condensed. The hot absorption menstruum, which may be at a temperature slightly below 600° F., is withdrawn from the bottom of the stripper through line 159 by means of pump 161 and returned through heat exchanger 143 and cooler 163 to lines 123 and 125 leading to the absorbers 11 and 117. The control of the absorption menstruum to the two absorbers is effected by means of valve 165 in line 123 and valve 167 in line 125. Make-up absorption menstruum may be charged to the system through line 169, controlled by valve 171, as required.

The stripped gases are removed from the top of stripper 151 through line 173, cooled to a temperature of approximately 200° F. by passing through water cooler 175, and run into accumulator 177. A portion of the gases are condensed to liquid in accumulator 177 and these are recycled by means of pump 179 and line 181 to the top of the stripper 151 as reflux liquid. The remaining gases are taken from the accumulator 177 through line 183, and passed through a second cooler 185 wherein the temperature may be reduced to approximately 90° to 100° F., whereby a large portion of the gas condenses to liquid. From the cooler 185 the partially condensed material passes to low pressure accumulator 187. The liquefied gas from the accumulator 187 is charged through line 189 by means of pump 191 to the main fractionating tower 41 at a point above the discharge of the reaction products into the tower. The uncondensed gas is withdrawn from the low pressure accumulator 187 and returned through line 193 to the low pressure absorber 11. The accumulator 187 is preferably maintained at sufficient pressure to enable return of the gas to the low pressure absorber 11 without compression.

As an example of actual operating conditions, residue and stabilizer gas from high pressure pyrolytic cracking of hydrocarbon oil is used as the fresh charge to the system. The stabilizer gas is cooled in cooler 3 to a temperature of 95° F. and the accumulator 5 is maintained at a pressure of 230 lbs. per square inch. Feed tank 17 is maintained at a temperature of 90° F. and a pressure of 265 lbs. per square inch. Residue gas is charged to the low pressure absorber 11. The analysis of the combined stabilizer and residue gas charged to the process in mol. percent is as follows:

Hydrogen	3.6
Methane	28.6
Ethylene	3.7
Ethane	19.5
Propene	9.5
Propane	17.7
Butenes	7.5
Butanes	8.2
Pentanes and pentenes	0.9
Hexanes and hexenes	0.8

The olefine content of the combined gas is approximately 20% before treatment in the absorbers and the olefin content of that portion of the combined fresh gas which is charged to the reaction coil is 40.75%.

Liquefied gas from the feed tank 17 having the following composition in mol. percent:

Hydrogen	0.
Methane	2.79
C_2 hydrocarbons	13.69
C_3 hydrocarbons	53.90
C_4 hydrocarbons	29.40
C_5 hydrocarbons	0.22
Total olefins	20.8

is charged to the heating coil 29 under a pressure of 1250 lbs. per square inch and preheated to a temperature of 500° F. by passage through the exchangers 23 and 25. In the heating coil 29 the temperature of the charge is raised to 1060° F. and this temperature is maintained in the reaction coil 31. The pressure at the slide valve 35 is reduced to 570 lbs. per square inch and the temperature is reduced in the heat exchanger 25 to 700° F. A pressure drop takes place through the heat exchanger coil 33 so that the pressure on the outlet is only 420 lbs. per square inch. The partially cooled reaction products are quenched to a temperature of 450° F. by means of condensate withdrawn from the fractionating tower which had been cooled to 180° F. and the temperature of the reaction products is further lowered in the cooler 39 to 320° F. The fractionating tower 41 is held at a pressure of 410 lbs. per square inch with a bottom temperature of 250° F. and a top temperature of 195° F. The accumulator 91 is held at a temperature of 155° F. and accumulator 109 at a temperature of 95° F. The pressure in both is 400 lbs. per square inch. Accumulator 5 is held at a pressure of 230 lbs. per square inch and a temperature of 95° F. Stabilizer 53 is maintained at a pressure of 125 lbs. per square inch with a bottom temperature of 330° F. and a top temperature of 140° F.

The low pressure absorber is maintained at a pressure of 175 lbs. per square inch and the high pressure absorber is maintained at 385 lbs. per square inch. Flash tower 103 is maintained at a pressure of 410 lbs. per square inch with the incoming rich menstruum heated to a temperature of 390° F. The stripper 151 is maintained at a pressure of 190 lbs. per square inch with a bottom temperature of 590° F. and a top temperature of 290° F. The accumulator 177 is maintained at a temperature of 210° F. and the low pressure accumulator 187 maintained at a temperature of 95° F. and a pressure of 180 lbs. per square inch.

The total residue gas leaving the system will have the following composition in mole percent:

Hydrogen	5.5
Methane	47.5
C_2 hydrocarbons	30.3
C_3 hydrocarbons	15.16
C_4 hydrocarbons	1.51

This recycle ratio, that is, the ratio of the liquid volume of the gas charged to the conversion zone, to the liquid volume of C_3 and C_4 hydrocarbons converted per pass to gasoline and higher boiling hydrocarbons, will be 5 to 1.

It will be seen that in accordance with this invention it is possible to operate under extremely high pressure conditions and utilize the heat of the reaction products for heating the charge without the necessity of using expensive heat exchangers, due to the discovery that reduction in pressure on the reaction products can be accomplished before cooling without causing excessive deposition and clogging in the transfer line and heat exchanger.

It is claimed:

1. In the process of converting hydrocarbon gases to liquid hydrocarbons at high superatmospheric pressures and at high temperatures between approximately 900 and 1200° F., the steps of reducing the pressure on the reaction products at the outlet of the reaction zone to a lower superatmospheric pressure, then cooling the reaction products to a temperature below conversion temperature close to but not below the dew point of the reaction products by indirect heat exchange with charging gases, then suddenly cooling the reaction products from a temperature not substantially below the dew point of the mixture to a temperature substantially below the dew point by direct contact with cooling liquid of such nature as to hold suspended material contained in the reaction products in solution or suspension.

2. Method in accordance with claim 1 in which the hydrocarbon gases are cooled by indirect heat interchange to a temperature not less than approximately 650° F. and the partially cooled reaction products cooled substantially below 650° F. by direct contact with cooling liquid.

3. Method in accordance with claim 1 in which the gases are converted at a pressure above 750 lbs. per square inch and the pressure on the products at the outlet of the reaction zone is reduced to a pressure not in excess of 600 lbs. per square inch.

4. Method in accordance with claim 1 in which the gases are converted at temperatures above 900° F. and pressures above 750 lbs. per square inch, the pressure on the reaction products is reduced at the outlet of the reaction zone to a pressure substantially below 750 lbs. per square inch, the reaction products are thereafter partially cooled to a temperature below conversion but not substantially below 650° F. by indirect heat exchange and the partially cooled products further cooled to a temperature substantially below 650° F. by direct contact with cooling liquid.

5. In a process for converting hydrocarbon gases to liquid hydrocarbons under high pressure and temperature of the order of 900–1200° F. in a conversion zone and in which the reaction prod-

ucts are fractionated into gases and liquid condensate, the steps of reducing the pressure on the products leaving the conversion zone, prior to cooling thereof, thereafter partially cooling the reaction products to a temperature close to but not below the dew point of the mixture by indirect heat exchange with charging stock, further cooling the reaction mixture from a temperature not substantially below the dew point of the reaction mixture to a temperature substantially below the dew point by direct contact with cooled liquid condensate.

6. Process in accordance with claim 5 in which the conversion zone is maintained at a pressure above 750 lbs. per square inch and the pressure is reduced below approximately 600 lbs. per square inch prior to cooling.

7. Process in accordance with claim 5 in which the reaction products are cooled to a temperature between 650° and 800° F. by indirect heat exchange with charging stock and the reaction products are chilled substantially below 650° F. by direct contact with cooled condensate.

8. Method in accordance with claim 5 in which the condensate used for cooling the reaction products is cooled by indirect heat exchange with charging stock prior to passing the charging stock in indirect heat exchange with reaction products.

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