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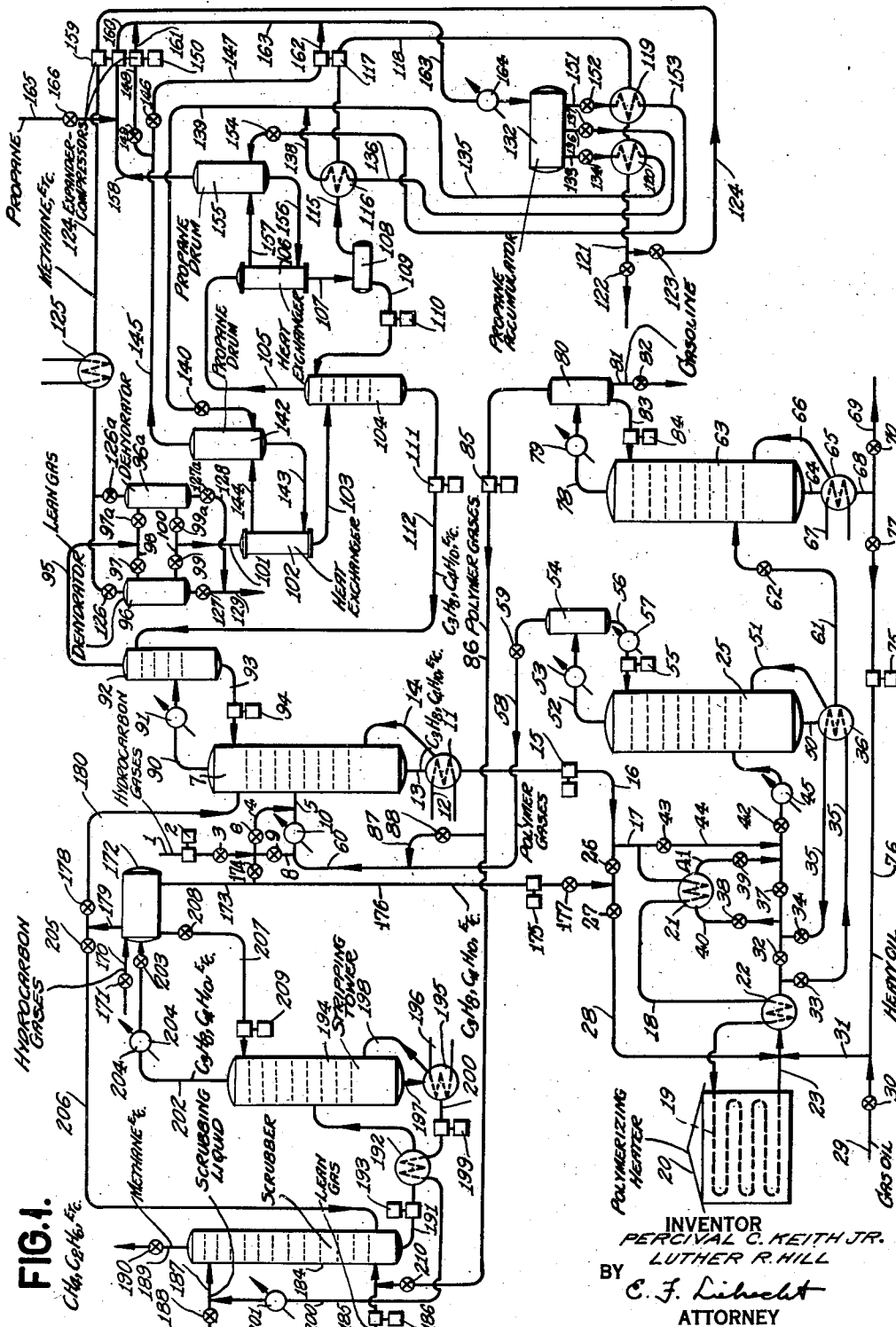
P. C. KEITH, JR., ET AL

2,258,016

TREATING HYDROCARBON FLUIDS

Filed Aug. 12, 1939

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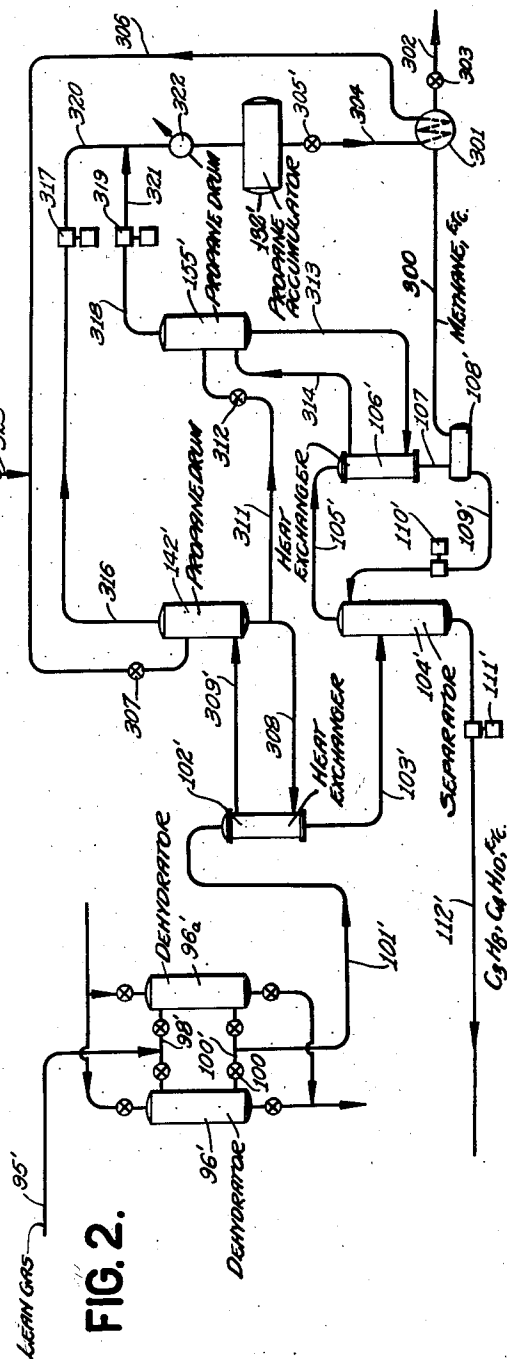
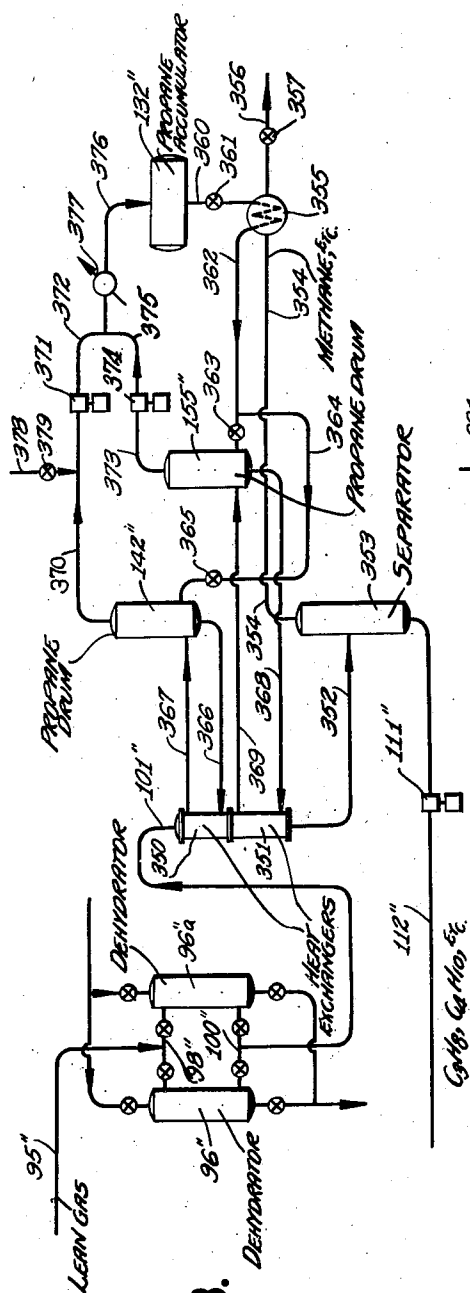
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TREATING HYDROCARBON FLUIDS

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2 Sheets-Sheet 2



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2,258,016

TREATING HYDROCARBON FLUIDS

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3 Claims. (Cl. 62—175.5)

This invention relates to a process for the conversion of lower molecular weight hydrocarbons into hydrocarbons of higher molecular weight and is directed particularly to the conversion of normally gaseous hydrocarbons into normally liquid products suitable for use as motor fuel.

It is an object of the invention to provide a process for the polymerization of normally gaseous hydrocarbons at elevated temperatures and pressures into normally liquid products including an improved method for separating from a mixture of hydrocarbons substantially all of the normally gaseous hydrocarbons which it is desired to subject to the polymerization operation of the process.

Another object of the invention is a process for the conversion of normally gaseous hydrocarbons into normally liquid products which is especially adapted to function efficiently on hydrocarbon charging stocks varying greatly in composition.

A still further object of the invention is a process for the conversion of normally gaseous hydrocarbons into normally liquid products providing for an improved method of cooling the hot reaction products giving rise to an improved distribution of the total heat content of the hot reaction products within the system and an improved fuel economy.

In accordance with my invention a hydrocarbon mixture comprising normally gaseous hydrocarbons from any suitable source, as obtained for example in the cracking of hydrocarbon fluids or other refinery operations processing hydrocarbon fluids, is charged to a primary stripping zone wherein a lighter normally gaseous hydrocarbon fraction, comprising substantially all constituents lighter than those desired as charge to the conversion operation, for example, hydrogen, methane, ethylene and ethane, is separated from a heavier hydrocarbon fraction comprising normally gaseous hydrocarbons desired as charge to the conversion operation. This heavier hydrocarbon fraction is pumped from the primary stripping zone to a conversion zone wherein it is subjected to polymerizing conditions of temperature and pressure, for example, to temperatures of from 750° F. to 1250° F., or if suitable catalysts are employed at a lower temperature, and under a pressure in excess of about 400 pounds per sq. in. Conditions within the conversion zone are selected to produce an optimum rate of conversion of normally gaseous hydrocarbons into normally liquid products boiling within the motor fuel boiling range.

Reaction products emanating from the conver-

sion zone are quenched and cooled according to an improved method of operation fully described hereinafter. The cooled reaction products are separated into a normally liquid fraction and a normally gaseous fraction. The normally gaseous fraction of reaction products is returned to the primary stripping zone wherein it is separated, together with the fresh charge, into a lighter normally gaseous hydrocarbon fraction and a heavier normally gaseous hydrocarbon fraction comprising normally gaseous hydrocarbons suitable for recycling to the conversion zone.

The lighter normally gaseous hydrocarbon fraction separated in the primary stripping zone, even though such zone functions at optimum conditions of efficiency of a commercial operation, will contain constituents as, for example, propane and propylene, which are desirable as charge to the conversion zone. To effect the conservation and utilization of these desirable constituents of the lighter hydrocarbon fraction, the primary stripping zone is operated in intimate conjunction with a recovery system to which the lighter normally gaseous hydrocarbon fraction leaving the stripping zone is passed.

The recovery system comprises two cooling zones within which desirable constituents of the lighter hydrocarbon fraction emanating from the primary stripping zone are condensed and returned to the primary stripping zone. Such desirable constituents returned to the primary stripping zone function as reflux for the fractionating section of the primary stripping zone and the intimate operation of the primary stripping zone with the recovery system is an important feature of the invention which is made more fully apparent by the subsequent description thereof.

In its preferred embodiment the cooling zones of the recovery system consist of two indirect heat exchangers wherein the lighter hydrocarbon fraction emanating from the primary stripping zone is subjected to indirect heat exchange with a liquefied normally gaseous hydrocarbon entering the cooling side of the exchangers at, or slightly below, its boiling point. In its function as a cooling medium the liquefied normally gaseous refrigerant is vaporized in the indirect heat exchangers, drawing its latent heat of vaporization from the lighter normally gaseous hydrocarbon stream being cooled. The desired temperature of the cooling zones is maintained by controlling the pressure upon, and therefore the boiling point of, the liquefied normally gaseous hydro-

carbon refrigerant entering the cooling zones. In the preferred embodiment of the recovery system of the process of the invention the use of two independent cooling zones permits operation of the first cooling zone at a higher temperature thereby necessitating the condensation of only a minimum quantity of material in the second and cooler zone wherein the refrigerant is maintained at a lower pressure and consequently requires greater effort and expense of recompression and cooling.

A feature of the invention is the adaptability of the process to a wide variety of charging stocks. If, for example, a charge is used which comprises constituents heavier than those desired as charge to the conversion zone, the charge may be passed into an accumulating zone whence it is passed directly into the hot reaction products leaving the conversion zone. If desired a fraction of the charge comprising substantially all of those constituents heavier than those desired for the conversion operation is passed into the hot reaction products leaving the conversion zone and the remaining lighter fraction is passed into the primary stripping zone.

If the charge to the system comprises excessive quantities of constituents lighter than those desired for the conversion operation the charge may be passed into a scrubbing zone wherein it is contacted with a scrubbing medium to absorb constituents heavier than the undesired lighter constituents of the charge in the absorbing medium. The resulting rich absorbing medium comprising the absorbed desirable constituents of the charge is stripped of the desirable constituents of the charge and the desired constituents of the charge so obtained is passed into the accumulating zone whence it is passed in its entirety into the primary stripping zone, or in part into the stripping zone and in part into the hot reaction products leaving the conversion zone.

In order that the invention may be more fully set forth and more fully understood reference is made to the drawings accompanying and forming a part of this specification and which illustrate the form and manner in which the invention may be practiced.

Figure 1 is a more or less diagrammatic elevational view of apparatus for carrying out the process in accordance with the invention.

Figures 2 and 3 are more or less diagrammatic views of apparatus suitable for carrying out, in a modified form, the operations effected in the recovery phase of the process in accordance with the invention and in which parts of apparatus identical with those shown in Figure 1 are identified with like reference numbers.

The following illustrative description of the process in accordance with my invention is made with reference to Figure 1 of the attached drawings. A mixture of normally gaseous hydrocarbons from any suitable source is forced by means of pump 2 through lines 1, 4 and 5, controlled by valves 3 and 6, into a primary stripping zone. The primary stripping zone may consist of a suitable fractionating tower 7. By closing valve 6 the charge may be passed from line 1 into line 8 controlled by valve 9 and through cooler 10 and line 5 into fractionator 7. Fractionator 7 is maintained at a relatively high pressure, for example, at about 350 to 450 pounds, preferably about 400 pounds. In fractionator 7 the normally gaseous hydrocarbon charge is separated into a lighter normally gaseous fraction and a heavier normally gaseous fraction. The lighter

normally gaseous fraction comprises hydrogen, methane, ethane, ethylene and some hydrocarbons having more than two carbon atoms to the molecule, for example, propane and propylene. The heavier normally gaseous hydrocarbon fraction comprises normally gaseous hydrocarbons having more than two carbon atoms to the molecule. This stripping action within fractionator 7 is aided by means of a reboiler 11 equipped with a closed coil 12 through which a suitable heating medium is passed. Liquid in the lower part of fractionator 7 circulates through line 13 into reboiler 11 and material vaporized therein returns to fractionator 7 through line 14.

The heavier normally gaseous hydrocarbon fraction, comprising hydrocarbons having more than two carbon atoms to the molecule separated in fractionator 7, is drawn continuously from reboiler 11 and forced by means of pump 15 through lines 16, 17 and 18 at a high pressure in excess of 400 pounds, for example, about 1800 to 2200 pounds, into a thermal conversion zone. The thermal conversion zone may consist of an externally heated coil 19 suitably positioned in a furnace 20 provided with suitable heating means. The invention is not limited to the use of a conversion zone comprising only one coil, for example, two or more externally heated coils positioned in suitable radiating and convection sections of a furnace may be used, through which coils the normally gaseous hydrocarbons undergoing conversion are made to pass in parallel streams.

Indirect heat exchangers 21 and 22 are positioned in line 18. By passage through heat exchangers 21 and 22, the heavier normally gaseous hydrocarbon fraction, comprising hydrocarbons having more than two carbon atoms to the molecule, is preheated to a temperature in excess of 400° F., for example, about 600° F. to 700° F. Within conversion coil 19 the preheated normally gaseous hydrocarbon stream under high pressure is raised to a high temperature of from 750° F. to 1250° F., for example, about 950° F. to 1100° F. to effect the conversion of normally gaseous hydrocarbons into normally liquid products.

Hot reaction products, comprising polymerized normally liquid hydrocarbons, leave conversion coil 19 through line 23 leading to fractionator 25. By controlled manipulation of valves 26 and 27 a part of the normally gaseous hydrocarbon stream flowing under high pressure through line 16 may be passed through line 28 into line 23 to quench the hot reaction products leaving conversion coil 19. If desired, additional quenching medium, for example, gas oil, may be drawn from an outside source and forced through line 29 controlled by valve 30, and line 31 into line 23. Sufficient quenching medium is added to the hot reaction products leaving conversion coil 19 through line 23, to lower their temperature sufficiently to arrest the progress of polymerization reactions, the temperature of the hot reaction products at this point in line 23 thereby being reduced to about 750 to 950° F., for example, 850° F.

The quenched reaction products flowing through line 23 are passed through indirect heat exchanger 22 interposed in line 23 whereby they are further cooled by indirect heat exchange with the normally gaseous hydrocarbon stream passing through line 18 to conversion coil 19. By manipulation of valves 32, 33 and 34 a part or all of the reaction products flowing through

line 23 may be drawn from line 23 after having passed through indirect heat exchanger 22 and caused to flow through line 35. Line 35 passes through reboiler 36 wherein the reaction products are further cooled by indirect heat exchange with liquid drawn from the bottom of fractionator 25, thus providing heat necessary to aid in the stripping operation in fractionator 25. After passing through reboiler 36 the partially cooled reaction products continue through line 35 and reenter line 23 at a point beyond valve 32.

Although in the present illustrative example of the invention hot reaction products are used to reboil the material from but one fractionator the process in accordance with the invention is not to be limited to this extent. Thus a part or all of the hot reaction products passed from line 23 through line 35 can be caused, if desired, to pass through additional reboilers associated with other fractionating towers of the system before being returned to line 23.

By manipulation of valves 37, 38 and 39 reaction products flowing through line 23 may, in part or in entirety, be diverted through line 40 passing to indirect heat exchanger 21 wherein they are subjected to indirect heat exchange with the normally gaseous hydrocarbon stream passing through line 18 to heat exchanger 22. Reaction products leaving heat exchanger 21 continue through line 41 to reenter line 23 at a point intermediate valve 37 and an expansion valve 42. By manipulation of valve 43 a part of the normally gaseous hydrocarbon stream flowing through line 17 may be passed through line 44 into line 23 at a point before expansion valve 42 to thereby further cool the reaction products prior to their passage through expansion valve 42.

The partially cooled reaction products in passing through valve 42 are reduced in pressure to, for example, about 350 to 450 pounds, preferably about 420 pounds. The cooled reaction products after reduction in pressure continue through line 23, passing through cooler 45 where additional cooling may be effected if desired, and enter into fractionator 25.

By careful regulation of valves 32, 33, 34, 37, 38 and 39 the quantity of reaction products passed through either reboiler 36 or heat exchanger 21, or both, may be controlled and the hot reaction products thereby cooled to a desired temperature, for example 200° F. to 450° F. prior to their entering fractionator 25. This provides an extremely flexible means for distributing in a well-balanced manner the available heat in the hot reaction products leaving conversion coil 19.

It is to be understood that this feature of the invention is not limited to the use of heat exchangers 22 and 21 as shown in the present illustrative description of the invention. Heat exchanger 21 may suitably be replaced by a plurality of indirect heat exchangers through which the normally gaseous hydrocarbon stream passing through line 18 to conversion coil 19 may be caused to flow in part or in its entirety, in parallel or in series. The hot reaction products emanating from conversion coil 19 could thus be suitably passed in its entirety or in part, in series or parallel through such a plurality of indirect heat exchangers to preheat the normally gaseous hydrocarbon charge flowing through line 18 to conversion coil 19.

In accordance with the invention it is further intended that if desired the normally gaseous hydrocarbon stream flowing through line 18 to conversion coil 19 be divided into two separate streams passing through separate pluralities of indirect heat exchangers to separate conversion coils or separate pluralities of conversion coils.

The hot reaction products emanating from such separate conversion coils can thus be caused to flow in dual flow through the separate pluralities of indirect heat exchangers to preheat the normally gaseous hydrocarbons flowing to the conversion coils.

Within fractionator 25, maintained at a pressure of, for example, 350 to 450 pounds, preferably about 410 pounds, products emanating thereto through line 23 and comprising products resulting from conversion reactions effected within conversion coil 19 are separated into a normally gaseous fraction comprising hydrocarbons having four carbon atoms to the molecule and less and hydrogen, and a normally liquid fraction comprising hydrocarbons having five or more carbon atoms to the molecule. By means of line 50 liquid in the bottom of fractionator 25 is passed into reboiler 36 wherein, by control of valves 32, 33 and 34, sufficient heat is absorbed from the hot reaction products passing through line 35 to effectively aid in stripping of constituents having less than five carbon atoms to the molecule from the normally liquid fraction separated from the reaction products in fractionator 25. Such stripped constituents are returned to fractionator 25 through line 51.

The normally gaseous fraction separated in fractionator 25 is passed from fractionator 25 through line 52 and cooler 53 into accumulator 54. In cooler 53 the hydrocarbon stream is cooled to a temperature, for example, not exceeding 210° F. resulting in the condensation of heavier constituents of the hydrocarbon stream, which condensed material, comprising, for example, hydrocarbons having four carbon atoms to the molecule, is separated from the remaining uncondensed stream in separator 54 and forced by means of pump 55 through line 56 and cooler 57, as reflux, into the top of column 25.

Normally gaseous hydrocarbons are passed from accumulator 54 through line 58 controlled by valve 59 and lines 60, cooler 10 and line 5 into fractionator 7 wherein they are separated, together with the fresh charge, into a lighter normally gaseous hydrocarbon fraction and a heavier normally gaseous hydrocarbon fraction.

The normally liquid fraction, separated in fractionator 25, is continuously drawn from reboiler 36 and passed through line 61 and expansion valve 62 into fractionator 63. In passing through expansion valve 62 the stream flowing through line 61 to fractionator 63 is substantially reduced in pressure so that it enters fractionator 63 at a pressure of, for example, not exceeding 100 pounds. Within fractionator 63 constituents boiling above the motor fuel boiling range are separated as a liquid fraction from lighter constituents comprising polymerized products boiling within the gasoline boiling range. Heat required to effectively aid in the substantially complete stripping within fractionator 63 of the gasoline from the heavier constituents is provided by passage of liquid from the bottom of fractionator 63 through line 64, into reboiler 65. Reboiler 65 is equipped with a closed coil 67 through which a suitable heating medium, which may suitably be part of the hot reaction products flowing through line 35, is caused to

flow. Stripped gasoline constituents are returned to fractionator 63 through line 66.

Liquid comprising constituents boiling above the motor fuel boiling range is drawn continuously from fractionator 63 through line 64, reboiler 65, line 68 and line 69 controlled by valve 70 and eliminated from the system. If desired a part of the liquid so drawn from fractionator 63 through reboiler 65, may be forced by means of pump 75 through line 76, controlled by valve 77, and line 31 into line 23 carrying the hot reaction products leaving conversion coil 19.

The gasoline fraction separated within fractionator 63, comprising lighter constituents which may have passed into fractionator 63, leaves the upper part of fractionator 63, through line 78 and passes through cooler 79, wherein normally liquid products are condensed, into accumulator 80. Within accumulator 80 the condensed normally liquid products are separated from any remaining normally gaseous constituents. Liquid comprising desired constituents boiling within the motor fuel boiling range is drawn from accumulator 80 through line 81 controlled by valve 82 and eliminated from the system as a desired final product. A part of the liquid separated in accumulator 80 is forced through line 83 by means of pump 84 as reflux to the top of fractionator 63.

Normally gaseous constituents, for example, hydrocarbons having less than five carbon atoms to the molecule, separated in accumulator 80 are forced by means of pump 85 through line 86, line 87 controlled by valve 88, and line 60, cooler 10 and line 5, into fractionator 7.

The lighter normally gaseous hydrocarbon fraction comprising hydrocarbons having less than three carbon atoms to the molecule and hydrogen, separated in fractionator 7 will comprise some quantity of hydrocarbons having more than two carbon atoms to the molecule as, for example, hydrocarbons having three carbon atoms to the molecule, which it is desired to include in the charge to the polymerization zone. It is the purpose of the subsequent stage of the operation of the process in accordance with the invention to effect the substantial recovery of hydrocarbons having more than two carbon atoms to the molecule from the lighter normally gaseous hydrocarbon fraction separated in fractionator 7. Accordingly the lighter normally gaseous hydrocarbon fraction is passed overhead from fractionator 7 through line 90 and cooler 91 into a separator 92. Separator 92 may suitably consist of a column provided with baffles or trays.

In passing through cooler 91 the gaseous stream will be cooled to a temperature, for example, below 130° F., and preferably about 100° F. thereby effecting condensation of heavier constituents in the gaseous stream comprising some hydrocarbons having three carbons to the molecule and any heavier constituents which may have passed over into line 90. In separator 92 further liquefaction of the heavier components of the normally gaseous hydrocarbon stream is brought about by the introduction into the top of separator 92 of cold recovered liquefied hydrocarbons having more than two carbon atoms to the molecule. Liquefied normally gaseous hydrocarbons are taken from the bottom of separator 92 and pumped through line 93 by means of pump 94 into the upper part of fractionator 7. The liquid so introduced into the top of fractionator 7 through line 93 functions as reflux for fractionator 7.

Normally gaseous products comprising hydro-

carbons having three and less carbon atoms to the molecule and hydrogen leave separator 92 through line 95 at a temperature of, for example, not exceeding about 85° F., preferably about 60° F., and at a pressure of, for example, about 340 to 440 pounds, preferably about 400 pounds. The gaseous stream passing through line 95 enters dehydrators 96 and 96a which are arranged so that the gas may pass therethrough in series or in parallel by judicious manipulation of valves 97, 97a, in line 98 and valves 99, 99a in line 100. For example, the gaseous stream may flow from line 95 through line 98, valve 97 into dehydrator 96, valve 97a being closed. Dehydrators 96, 96a may be of any desired type and in the present illustration of the invention consist of chambers charged with a suitable dehydrating agent such as, for example, alumina and silica gel. In dehydrator 96 water is removed from the gaseous stream to avoid subsequent freezing of constituents in the gaseous stream and difficulties resulting therefrom. From dehydrator 96, the dehydrated gaseous stream passes through line 100, valve 99, valve 99a being closed, and line 101 into indirect heat exchanger 102.

In indirect heat exchanger 102 the gaseous stream is subjected to indirect heat exchange with a refrigerating medium, for example, boiling propane, resulting in the cooling of the stream to, for example, 30° to 40° F., preferably to below 35° F., and effecting liquefaction of hydrocarbons having more than two carbon atoms to the molecule. The cooled stream is passed from exchanger 102 through line 103 into a separating zone which may suitably consist of a fractionator 104. Within fractionator 104, separation of additional liquefied hydrocarbons from remaining uncondensed components is effected.

The remaining gaseous components, still containing hydrocarbons having three or less carbon atoms to the molecule and hydrogen, is passed from fractionator 104 through line 105 into a second indirect heat exchanger 106 wherein the gaseous stream is further cooled to a temperature of, for example, -10° F., thus effecting liquefaction of remaining hydrocarbons having more than two carbon atoms to the molecule. The cooled stream is passed from exchanger 106 through line 107 into separator 108. From the bottom of separator 108 the liquefied constituents are forced through line 109 by means of pump 110 into the upper part of fractionator 104.

Liquid products comprising hydrocarbons having more than two carbon atoms to the molecule are drawn from the bottom of fractionator 104 and forced by means of pump 111 through line 112 into the upper part of separator 92.

Gaseous products substantially free of hydrocarbons having more than two carbon atoms to the molecule and comprising hydrogen, methane, ethane and ethylene leave separator 108 through line 115 at a temperature of, for example, 0 to -10° F. and a pressure of about 325 to 425 pounds, for example, about 385 pounds.

The low temperature and high pressure of the gaseous stream leaving separator 108 through the line 115 is utilized to cool and compress at least a part of the refrigerant used as the cooling medium in indirect heat exchangers 102 and 106.

For this purpose the cold gaseous stream leaving separator 108 through line 115 is passed through indirect heat exchanger 116 and thereafter expanded in the expansion side of compressor 117 to a pressure below, for example, 100 pounds preferably about 60 pounds. The ex-

panded stream leaving expansion side of compressor 117 will, as a result of the expansion, have lowered its temperature to a temperature of, for example, -25 to -35° F. This low temperature of the expanded gaseous stream is utilized by passage through indirect heat exchangers 119 and 120 wherein it serves to cool a part of the refrigerating medium destined to cool indirect heat exchangers 102 and 106. From exchanger 120 the expanded gaseous stream passes through line 121 controlled by valve 122 to be eliminated from the system.

A part of the gaseous stream to be eliminated from the system through line 121 may be used to dry the dehydrating material in dehydrators 96, 96a after the latter has become charged with moisture removed from the hydrocarbon stream treated. By the proper manipulation of valves 122 and 123 a part or all of the gas passing from exchanger 120 through 121 may be diverted through line 124 to dehydrators 96, 96a. A heater 125 is interposed in line 124 to heat the gas to a temperature suitable to the dehydrating operation, for example, about 300° F. The heated gas leaving heater 125 continues through line 124 and by the closing of valves 126, 97a, 99a, 127, and opening of valves 126a and 127a, is passed through dehydrator 96a to dehydrate the dehydrating material therein. The gas containing moisture removed from the dehydrating material flows out of dehydrator 96a through line 128 controlled by valve 127a and is eliminated from the system through line 129. Similarly by closing of valves 126a, 97, 99, 127a and opening of valves 126 and 127 the heated gas leaving heater 125 through line 124 may be caused to flow through dehydrator 96, to dehydrate the dehydrating material therein and be eliminated therefrom through line 129 controlled by valve 127. It is thus possible to dehydrate one of the dehydrators 96, 96a while the other remains in operation.

A liquefied normally gaseous refrigerating medium for example, a liquefied normally gaseous hydrocarbon, is drawn from an accumulator 132. Although propane is a preferred refrigerant and is used in the present description of an illustrative example of the invention, the process according to the invention is not limited to the use of this particular hydrocarbon as the refrigerating medium and other normally gaseous hydrocarbons or any other suitable refrigerating medium may suitably be used.

Accumulator 132 containing the liquefied propane is maintained at a suitably high pressure, for example, 185 to 250 pounds. From accumulator 132 liquefied propane is passed through line 133 controlled by valve 134 to indirect heat exchanger 120 wherein it is subjected to indirect heat exchange with cold expanded gaseous products emanating from the expansion side of compressor 117 through line 118, and indirect heat exchanger 119 to exchanger 120. In passing through exchanger 120 and into line 135 the temperature of the liquefied propane will be lowered to a temperature below 100° F., for example, about 70° F. A further quantity of propane is drawn from accumulator 132 through line 136 controlled by valve 137 and passed into indirect heat exchanger 116 wherein it is subjected to indirect heat exchange with cold normally gaseous products emanating from separator 108 through line 115. In passing through exchanger 116 and into line 138 the temperature of the propane refrigerant will be reduced to a temperature below 50° F., for example, about 20° F. The cooled pro-

pane refrigerant emanating from exchanger 116 through line 138 is combined with the propane refrigerant flowing through line 135 resulting in a combined stream having a temperature below about 70° , for example, 45° F. flowing through line 139 to propane drum 142.

In passing through valve 140 in line 139 the liquefied cooled propane refrigerant is reduced to a pressure below 50 pounds, preferably 37 pounds, before entering drum 142, thereby insuring a liquid in the bottom of drum 142 at a temperature below 20° F., for example, 15° F. From the bottom of drum 142 propane refrigerant is passed through line 143 into the cooling side of indirect heat exchanger 102 wherein the propane refrigerant is brought to its boiling point and vaporized by heat transferred to it from the hydrocarbon stream entering indirect heat exchanger 102 through line 101. The vaporized propane refrigerant is returned through line 144 from exchanger 102 to drum 142.

Vaporized propane leaves the top of drum 142 through line 145 and is passed in part through valve 146 into line 147 leading to the compression side of compressor 117 wherein it is compressed to a pressure of about 200 to 250 pounds, for example, about 230 pounds. The remainder of the vaporized propane refrigerant flowing through line 145 is passed through line 148, controlled by valve 149, to compressor 150 wherein it is compressed to a pressure of about 200 to 250 pounds, for example, about 230 pounds.

Another stream of liquefied propane refrigerant is drawn from accumulator 132 and passed through line 151, controlled by valve 152, into indirect heat exchanger 119 wherein its temperature is lowered to a temperature below 50° F., for example, 15° F., by indirect heat exchange with the expanded hydrocarbon stream emanating from the expansion side of compressor 117 through line 118 to exchanger 119. From exchanger 119 the cooled propane refrigerant is passed through line 153 and valve 154 into drum 155. In passing through valve 154 the propane refrigerant is reduced in pressure to a pressure below the maintained in drum 142, for example, 35 pounds, preferably 10 pounds, to assure liquid propane refrigerant at the bottom of drum 155 at a temperature below that of the liquid propane refrigerant within drum 142, for example, below 10° F., preferably -20° F. From the bottom of drum 155 liquefied propane refrigerant is passed through line 156 to the cooling side of indirect heat exchanger 106. In cooling the hydrocarbon stream entering indirect heat exchanger 106 through line 105 the propane refrigerant is brought to the boiling point and vaporized. The vaporized propane refrigerant is passed from exchanger 106 to drum 155 through line 157. Vaporized propane refrigerant is passed from the top of drum 155 through line 158 to compressor 159 where it is compressed to a pressure of about 200 to 250 pounds, for example, about 230 pounds.

Compressed propane refrigerant leaving compressors 117, 150 and 159 through lines 162, 161 and 160, respectively, is combined into a single stream flowing through line 163, provided with cooler 164, to propane accumulator 132. In passing through cooler 164 the compressed propane refrigerant is cooled by means of a suitable cooling medium to a temperature below 120° F., for example, about 100° F. to liquefy it.

Propane refrigerant may be introduced from

an outside source into line 158 through line 165 controlled by valve 166.

The process in accordance with the invention is in no wise limited to the temperatures and pressures of the propane refrigerant set forth herein as illustrative of the method of carrying out the recovery phase of the process. The temperatures and pressures to be selected for the refrigerating medium are dependent upon the particular refrigerating medium used and the degree of recovery to be effected in the recovery phase of the process in accordance with the invention. It must be pointed out that the latent heat of vaporization of the propane refrigerant is relied upon to effect a substantial part of the cooling in indirect heat exchangers 162 and 166. Valves 140 and 154 are therefore controlled to expand the cold, compressed, liquefied, propane refrigerant to a pressure which is slightly below the vapor pressure of boiling propane at the temperatures which are to be maintained in indirect heat exchangers 162 and 166.

A feature of the process in accordance with the invention is its adaptability to the processing of hydrocarbon mixtures in which the normally gaseous hydrocarbons which it is desired to subject to the conversion operation are in admixture with a substantial proportion of hydrocarbons heavier or lighter than those normally gaseous hydrocarbons which it is desired to subject to the conversion operation.

If, for example, a hydrocarbon mixture to be processed in accordance with the invention, from any suitable source, comprises normally gaseous hydrocarbons in admixture with an appreciable proportion of hydrocarbons having more than four carbon atoms to the molecule, it is charged to the system through line 170, controlled by valve 171, into accumulator 172. Such charge may optionally be introduced simultaneously with separate introduction of normally gaseous hydrocarbons through line 1.

The pressure maintained in accumulator 172 will be governed by the type of operation carried out and may vary from, for example, about 300 pounds to a pressure substantially higher than that maintained in fractionator 7. Normally gaseous hydrocarbons may be drawn from accumulator 172 through line 173 and passed through lines 4 and 5 into fractionator 7, valves 174 and 6 being open. If desired the hydrocarbon stream may, by closing valve 6, be passed from line 173, through line 8 controlled by valve 9 and through cooler 10 and line 5 into fractionator 7.

When the hydrocarbons drawn from accumulator 172 through line 173, comprise hydrocarbons having more than four carbon atoms to the molecule it is preferred to force them by means of pump 175 through line 176 controlled by valve 177, and through line 28 controlled by valve 27 into line 23 carrying the hot conversion products emanating from conversion coil 19.

By control of valves 26 and 27 a part or all of the hydrocarbon stream flowing through line 176 may be passed from line 176 through lines 28 and valve 26 into line 17 and combine therein with the normally gaseous hydrocarbon stream emanating from fractionator 7 through line 16 by means of pump 15.

If desired valve 178 may be opened to pass normally gaseous hydrocarbons from accumulator 172 through lines 179 and 180 into fractionator 7 while drawing liquids comprising normally gaseous hydrocarbons and some hydro-

carbons having more than four carbon atoms to the molecule from accumulator 172 through line 173.

If the hydrocarbons to be processed in the process in accordance with the invention consist of hydrocarbons comprising substantial amounts of normally gaseous hydrocarbons having less carbon atoms to the molecule than those desired to be subjected to the conversion operation they are introduced into the system through line 185. When, for example, it is desired to process such a mixture the normally gaseous hydrocarbon mixture is drawn from an outside source and forced by means of pump 186 through line 185 into the lower part of scrubber 184 wherein the charge so introduced is scrubbed with a suitable scrubbing medium, for example, gas oil, capable of absorbing hydrocarbons having more than two carbon atoms to the molecule which is introduced through line 187, controlled by valve 188, into the top of scrubber 184. Substantially all hydrocarbons having less than three carbon atoms to the molecule and hydrogen is passed from the top of scrubber 184 through line 189 controlled by valve 190 and eliminated from the system.

Rich scrubbing medium, comprising absorbed normally gaseous hydrocarbons having more than three carbon atoms to the molecule, is taken from the bottom of scrubber 184 and forced by means of pump 193 through line 191, provided with indirect heat exchanger 192, into stripping column 194. In stripping column 194 absorbed normally gaseous hydrocarbons are stripped from the absorbing medium. Heat necessary to the stripping operation is provided by means of reboiler 195 equipped with heating coil 196 through which a suitable heating medium is passed. Liquid from the bottom of stripping column 194 is circulated through line 197, reboiler 195 and the stripped constituents are returned through line 198. Lean scrubbing medium stripped of absorbed hydrocarbons is continuously taken from reboiler 195 and forced by means of pump 199 through line 200 into line 187 entering the top of scrubber 184. Lean scrubbing medium passing from reboiler 195 through line 200 passes through heat exchanger 192 wherein it is cooled by indirect heat exchange with the rich absorption medium flowing to stripping tower 194. A cooler 201 interposed in line 200 beyond exchanger 192 further cools the lean scrubbing medium to a temperature, for example, below 100° F.

Normally gaseous hydrocarbons stripped from the rich scrubbing medium in stripping tower 194 leave the top of stripping column 194 through line 202 controlled by valve 203 and pass into accumulator 172. A cooler 204 is interposed in line 202 to cool and condense hydrocarbons passing therethrough to accumulator 172. From accumulator 172 any uncondensed gases, which may comprise hydrocarbons having less than three carbon atoms to the molecule can, by control of valves 178 and 205 be passed either through line 206 to the bottom of scrubber 184 or through line 180 to the top of fractionator 7. A part of the liquid in accumulator 172 is drawn therefrom through line 207, controlled by valve 208 and sent by means of pump 209 as reflux to the top of stripping column 194.

When scrubber 184 is used in conjunction with the process in accordance with the invention, gases leaving separator 80 and pumped through line 86 may, by closing valve 88 in line 87 and opening of valve 210 be passed into line 185 leading into lower part of scrubber 184.

In accordance with the invention the charge to the system may consist solely of a hydrocarbon mixture comprising substantial amounts of constituents lighter than those desired to be converted and which charge is introduced into the system as described through line 185. It is to be understood, however, that simultaneously with the charging of hydrocarbon mixtures comprising substantial amounts of hydrocarbons having less than three carbon atoms to the molecule to the system through line 185, separate streams of hydrocarbons comprising normally gaseous hydrocarbons taken from an outside source may be charged to the system in accordance with the invention through line 1 or line 170 or through both line 1 and line 170.

That phase of the process wherein hydrocarbons having more than two carbon atoms to the molecule are recovered from the light normally gaseous hydrocarbon fraction separated in fractionator 7 is not limited in its application to the above illustrative example of carrying out the invention. Figures 2 and 3 of the drawings illustrate simplified forms of apparatus suitable for carrying out this phase of the invention wherein parts of apparatus identical with those shown in Figure 1 are indicated by the same reference numerals, these reference numerals being primed in Figure 2 and double primed in Figure 3.

Referring to Figure 2, the dehydrated normally gaseous hydrocarbon stream, comprising three and less carbon atoms to the molecule and hydrogen, emanating from dehydrators 96', 96'a through line 101', passes into indirect heat exchangers 102'. This stream is subjected to indirect heat exchange with boiling propane, resulting in the cooling of the normally gaseous stream to, for example, 30° F. to 40° F., preferably below 35° F., and effecting liquefaction of hydrocarbon constituents having more than two carbon atoms to the molecule. The cooled and condensed normally gaseous hydrocarbons are passed from indirect heat exchanger 102' through line 103' into fractionator 104'. Within fractionator 104', separation of condensed hydrocarbons having more than two carbon atoms to the molecule from remaining gaseous components is effected and the remaining gaseous components comprising hydrocarbons having three or less carbon atoms to the molecule and hydrogen is passed from fractionator 104' through line 105' into a second indirect heat exchanger 106', wherein it is further cooled to a temperature of, for example, -10° F., thus effecting liquefaction of remaining hydrocarbons having more than two carbon atoms to the molecule.

The cooled stream is passed from indirect heat exchanger 106' through line 107' into separator 108'. From the bottom of separator 108' the liquefied gases are forced through line 109' by means of pump 110' into the upper part of fractionator 104'.

Liquefied gases are drawn from the bottom of fractionator 104' and forced by means of pump 111' through line 112' into the upper part of separator 92 (Figure 1).

Gaseous products substantially free of hydrocarbons having more than two carbon atoms to the molecule and comprising hydrogen, methane, ethane and ethylene leave separator 108' through line 300 at a temperature of, for example, zero to -10° F. and a pressure of, for example, 325 to 425 pounds.

The low temperature of the gaseous stream leaving separator 108' through line 300 is utilized

to cool the refrigerant used as the cooling medium in exchangers 102' and 106'. To this purpose the cold gaseous stream leaving separator 108' through line 300 is passed through indirect heat exchanger 301 wherein it is subjected to indirect heat exchange with the refrigerating medium, thereby cooling the refrigerating medium. The gaseous stream flowing through line 300 leaves the system through line 302 controlled by valve 303. In a preferred method of operation the gaseous stream flowing through line 300 is reduced in pressure before entering exchanger 301 to thereby reduce the temperature of the stream before it enters indirect heat exchanger 301.

Liquefied propane is drawn from a propane accumulator 132', maintained at a suitably high pressure of, for example, 185 to 250 pounds. From accumulator 132' the liquefied propane is passed through line 304, controlled by valve 305, to indirect heat exchanger 301 wherein it is subjected to indirect heat exchange with the cold gaseous stream flowing through line 300. In passing through exchanger 301 the temperature of the liquefied propane will be lowered to a temperature below 50° F., for example, about 20° F. The cooled liquefied propane is passed from exchanger 301 through line 306 to drum 142'. In passing valve 307 in line 306 the pressure of the cooled liquefied propane is reduced to a pressure below 50 pounds, for example, 37 pounds, thereby providing a liquid propane in drum 142' having a temperature below 20° F., for example, 15° F. From the bottom of drum 142' liquid propane is drawn through line 308 and passed as cooling medium to exchanger 102' wherein the liquefied propane is brought to its boiling point and vaporized by heat transferred to it from the gaseous stream entering indirect heat exchanger 102' through line 101'. The vaporized propane refrigerant is returned from exchanger 102' to drum 142' through line 309'.

A part of the liquefied propane drawn from drum 142' through line 308 is passed through line 311 and valve 312 into drum 155'. In passing through valve 312 the pressure on the liquefied propane is reduced to a pressure of, for example, about 10 pounds to provide a liquid propane refrigerant in drum 155' having a temperature of, for example, about -20° F. Liquid propane is drawn from the bottom of drum 155' through line 313 and passed into indirect heat exchanger 106' as the cooling medium therefor. Within indirect heat exchanger 106' the liquid propane refrigerant is brought to its boiling point and vaporized by heat extracted from the gaseous stream entering exchanger 106' through line 105'. Vaporized propane refrigerant is returned to drum 155' from exchanger 106' through line 314.

Vaporized propane refrigerant is drawn from the top of drum 142' and passed through line 316 to compressor 317 wherein it is compressed to a pressure of about 185 to 250 pounds. Similarly vaporized propane refrigerant is drawn from the top of drum 155' and passed through line 318 to compressor 319 wherein it is compressed to a pressure of about 185 to 250 pounds. Compressed propane refrigerant leaves compressor 317 through line 320 and compressor 319 through line 321 into line 320. The combined stream of compressed propane refrigerant flowing through line 320 passes through cooler 322 to propane refrigerant accumulating drum 132'. In cooler 322 the compressed propane refrigerant is cooled

to a temperature of, for example, about 100° F. to liquefy it.

Additional propane refrigerant may be drawn from an outside source through line 323 controlled by valve 324 discharging into line 306.

In the further modification of the recovery phase of the process in accordance with the invention as shown in Figure 3, the stream of normally gaseous hydrocarbons from which hydrocarbons having more than two carbon atoms to the molecule are to be separated, is passed consecutively through the two refrigerating zones of the recovery phase of the process without separation of any liquefied material from the stream between the two refrigerating zones.

The dehydrated normally gaseous hydrocarbon stream comprising hydrocarbons having three and less carbon atoms to the molecule and hydrogen emanating from dehydrators 96'', 96''a through line 101'' passes into indirect heat exchanger 350 wherein it is subjected to indirect heat exchange with boiling propane. In indirect heat exchanger 350 the gaseous stream is cooled to, for example, 30° F. to 40° F., preferably below 35° F., resulting in liquefaction of hydrocarbons having more than two carbon atoms to the molecule. The cooled gaseous stream passes from heat exchanger 350 directly into indirect heat exchanger 351. In indirect heat exchanger 351 the stream is further cooled to a temperature of, for example, -10° F., thus effecting liquefaction of remaining hydrocarbons having more than two carbon atoms.

The cooled stream is passed from exchanger 351 through line 352 into fractionator 353 wherein separation of liquefied normally gaseous hydrocarbons from uncondensed cooled gaseous products is effected. From the bottom of fractionator 353 the liquefied normally gaseous hydrocarbons having more than two carbon atoms to the molecule are withdrawn through line 112'' and forced therethrough by means of pump 111'' to separator 92 (Figure 1).

Gaseous products substantially free of hydrocarbons having more than two carbon atoms to the molecule and comprising hydrogen, methane, ethane and ethylene leave the upper part of fractionator 353 through line 354 at a temperature of, for example, zero to -10° F. The low temperature of the gaseous stream leaving fractionator 353 through line 354 is made use of to cool the propane refrigerant used as the cooling medium in indirect heat exchangers 350 and 351. To this purpose the gaseous stream flowing through line 354 is passed through heat exchanger 355 wherein it is subjected to indirect heat exchange with the propane refrigerating medium. After passing through heat exchanger 355 the normally gaseous stream is eliminated from the system through line 356, controlled by valve 357. If desired, the gaseous stream flowing through line 354 may be reduced in pressure prior to its entry into heat exchanger 355 to thereby further lower its temperature prior to its entry into heat exchanger 355.

Liquefied propane refrigerating medium is drawn from accumulator drum 132'' maintained at a suitably high pressure, for example, 185 to 250 pounds and passed through line 360 controlled by valve 361 to indirect heat exchanger 355. Within indirect heat exchanger 355 the propane refrigerant is cooled to a temperature below about 50° F., for example, about 20° F. The cooled liquefied propane refrigerant is passed from indirect heat exchanger 355 through line

362 and valve 363 into propane drum 155''. In passing through valve 363 the cooled propane is reduced in pressure to a pressure below 37 pounds, for example, 10 pounds, thereby providing a liquid propane in drum 155'', having a temperature of, for example, about -20° F.

A part of the propane refrigerant flowing through line 362 is drawn therefrom before passage through valve 363 and passed through line 364 and valve 365 into propane drum 142''. In passing through valve 365 the pressure of the propane refrigerant is reduced to a pressure below 50 pounds, for example, about 37 pounds, thereby providing a liquid propane in drum 142'', having a temperature below 20° F., for example, 15° F.

From the bottom of drum 142'' liquid propane refrigerant is passed through line 366 into indirect heat exchanger 350 as cooling medium. In indirect heat exchanger 350 the propane refrigerant is raised to its boiling point and vaporized by heat withdrawn from the normally gaseous stream entering indirect heat exchanger 350 through line 101''. The vaporized propane refrigerant is drawn from heat exchanger 350 and passed through line 367 to propane drum 142''.

Similarly, liquid propane refrigerant is withdrawn from the bottom of propane drum 155'' and passed through line 368 into indirect heat exchanger 351 as cooling medium. Within indirect heat exchanger 351 the propane refrigerant is raised to the boiling point and vaporized by heat withdrawn from the normally gaseous stream passed to indirect heat exchanger 351 from indirect heat exchanger 350. Vaporized propane refrigerant is drawn from indirect heat exchanger 351 and passed through line 369 to propane drum 155''.

Vaporized propane refrigerant is drawn from the top of propane drum 142'' and passed through line 370 to compressor 371 wherein it is compressed to a pressure of, for example, 185 pounds to 250 pounds. The compressed propane refrigerant leaves compressor 371 through line 372. Similarly, vaporized propane refrigerant is withdrawn from propane drum 155'' and passed through line 373 to compressor 374 wherein it is compressed to a pressure of, for example, 185 to 250 pounds. The compressed propane refrigerant leaves compressor 374 through line 375. Compressed propane refrigerant flowing through lines 372 and 375 is combined into a single stream flowing through line 376 to propane accumulator drum 132''. Line 376 is provided with a cooler 377 wherein the compressed propane refrigerant is cooled to a temperature below 120° F., for example, 100° F. to liquefy it.

Additional propane refrigerant may be added to the system from an outside source through line 378, controlled by valve 379, discharging into line 370.

While the recovery systems shown in the drawings are especially adapted for removing desired hydrocarbon constituents from gases and vapors passing overhead from separator 92, the recovery systems may be used for separating desired hydrocarbons, such as C₃ and C₄ hydrocarbons, from gaseous mixtures containing hydrocarbons and derived from other sources. For example, gaseous mixtures containing higher and lower molecular weight hydrocarbons, such as, cracking still gases or natural gas may be introduced into any one of lines 93, 95' and 95'' and passed through either one of the dehydrators 96 or 96a,

96' or 96'a or 96'' or 96''a to dry the gaseous mixture and the dried gaseous mixture is then passed through the rest of the recovery system to cool and liquefy higher molecular weight hydrocarbons. The liquefied hydrocarbons are separated from unliquefied gases and are passed through line 112 or line 112' or line 112'', associated, respectively, with dehydrators 96—96a, 96'—96'a or 96''—96''a, and may be withdrawn from the system and further treated as desired or they may be passed to the separator 92. Where natural gasoline is recovered from natural gas, it is preferably withdrawn from the system.

While the invention has been described hereinabove with respect to specific examples of the mode of operation, it will be understood by those skilled in the art that the invention is not limited to such illustrative examples but may variously be practiced and embodied within the scope of the claims hereinafter made.

We claim:

1. A process for separating heavier normally gaseous hydrocarbons from a mixture of normally gaseous hydrocarbons wherein normally gaseous hydrocarbons are charged to a fractionating zone, separating said normally gaseous hydrocarbons in said fractionating zone into a fraction comprising lighter normally gaseous hydrocarbons and a fraction comprising heavier normally gaseous hydrocarbons, passing said fraction comprising lighter normally gaseous hydrocarbons through a drying zone, passing said dried fraction through a cooling zone wherein it is indirectly contacted with a liquefied refrigerant under high pressure to cool said fraction and condense additional heavier normally gaseous hydrocarbons therefrom, passing said cooled fraction through a second cooling zone wherein it is indirectly contacted with a liquefied refrigerant under lower pressure than said refrigerant

in said first cooling zone to further cool said fraction and condense additional heavier normally gaseous hydrocarbons therefrom, said refrigerant being vaporized at least in part during said cooling process in said cooling zones, separating said condensed hydrocarbons from uncondensed normally gaseous hydrocarbons after each of said cooling zones, passing said condensed hydrocarbons to said fractionating zone, withdrawing vaporized refrigerant from said cooling zones, expanding said cooled uncondensed normally gaseous hydrocarbons, utilizing the energy made available by said expansion to compress at least a part of said vaporized refrigerant, to a high pressure, cooling said compressed refrigerant to liquefy it, passing said liquefied refrigerant to a common source of supply, withdrawing a portion of liquefied refrigerant from said common source of supply, cooling said portion of liquefied refrigerant by indirect contact with said cooled uncondensed normally gaseous hydrocarbons prior to said expansion step, withdrawing a second portion of liquefied refrigerant from said common source of supply, cooling said second portion of liquefied refrigerant by indirect contact with said expanded normally gaseous hydrocarbons and using said cooled portions of liquefied refrigerant as the refrigerant in said cooling zones.

2. Process in accordance with claim 1 wherein said cooled refrigerant compressed to high pressure is reduced in pressure before entering said cooling zones to a reduced pressure which will maintain said refrigerant entering said cooling zones in a liquefied state and permit vaporization of said liquefied refrigerant during the cooling process in said cooling zones.

3. A process in accordance with claim 1 wherein liquefied propane is used as said refrigerant.

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