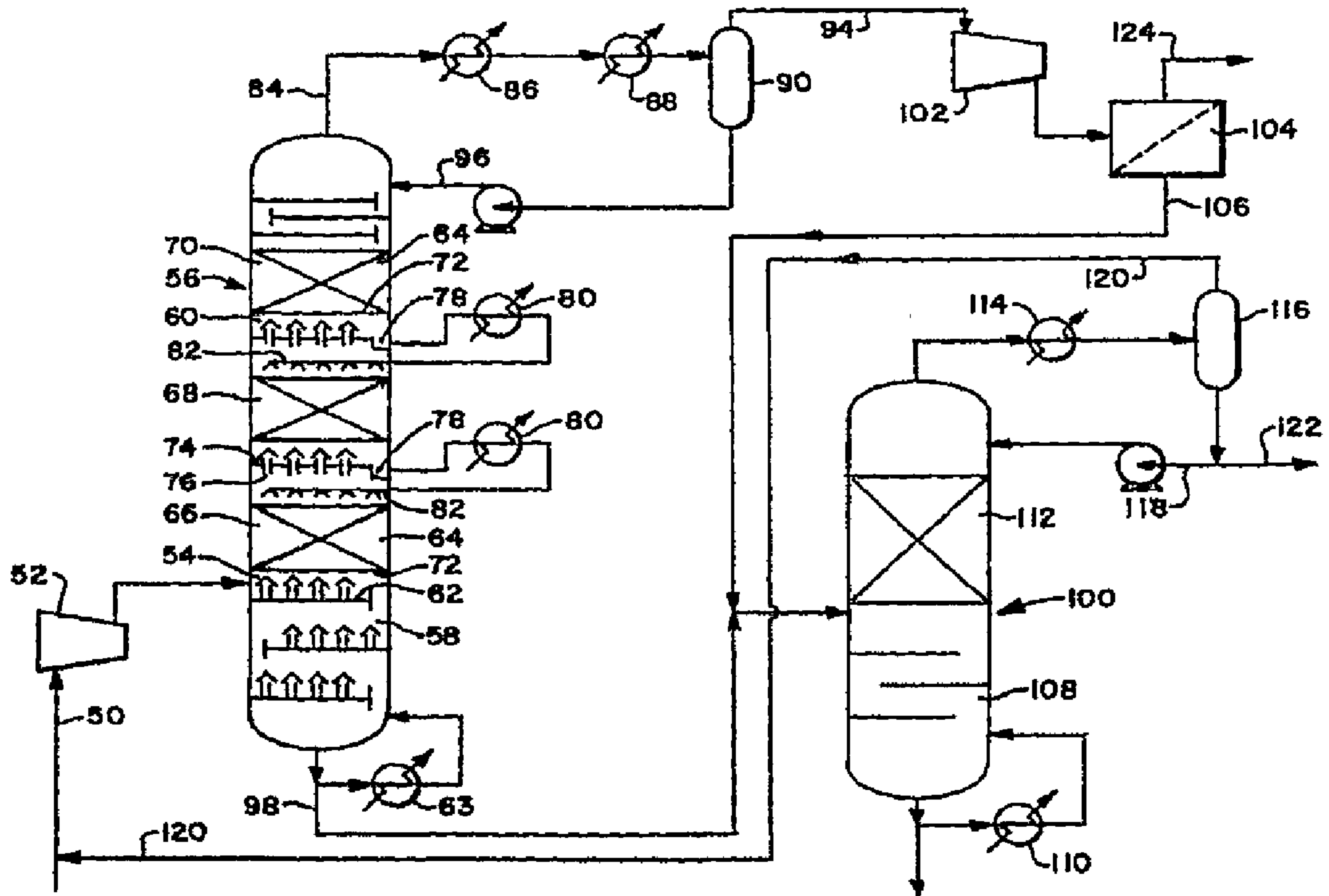




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(51) Int.Cl.⁶ C10G 70/02, C10G 45/32
(54) **SYSTEME DE RECUPERATION D'INSTALLATION DE
PRODUCTION D'OLEFINES FAISANT APPEL A LA
DISTILLATION CATALYTIQUE**
(54) **OLEFIN PLANT RECOVERY SYSTEM EMPLOYING
CATALYTIC DISTILLATION**



(57) Selon l'invention, des acétylènes et des diènes C₂ à C₅ et pls lourds contenus dans un courant de charge ayant subi un craquage thermique sont hydrogénés sans qu'il y ait une hydrogénation importante des oléfines C₂

(57) The C₂ to C₅ and heavier acetylenes and dienes in a thermally cracked feed stream are hydrogenated without significantly hydrogenating the C₂ and C₃ olefins. Additionally, the C₄ and heavier olefins may be



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et C₃. En outre, les oléfines C₄ et plus lourdes peuvent être hydrogénées. De façon spécifique, la charge de gaz de craquage d'une installation de production d'oléfines est hydrogénée dans une colonne de réaction de distillation contenant un catalyseur d'hydrogénation sans qu'il soit nécessaire de séparer l'hydrogène de la charge et sans hydrogénation importante de l'éthylène et du propylène. Une étape combinée de réaction-fractionnement, connue sous le nom d'hydrogénation par distillation catalytique, permet de réaliser simultanément les réactions et les séparations tout en maintenant des conditions d'hydrogénation telles que l'éthylène et le propylène restent sensiblement non hydrogénés et que pratiquement tous les autres hydrocarbures C₂ et plus lourds insaturés soient hydrogénés. Tout hydrogène n'ayant pas réagi peut être séparé par une membrane et mis à réagir avec des substances C₉ et plus lourdes séparées pour produire de l'essence de pyrolyse hydrogénée.

hydrogenated. Specifically, the cracked gas feed in an olefin plant is hydrogenated in a distillation reaction column containing a hydrogenation catalyst without the necessity of separating the hydrogen out of the feed and without any significant hydrogenation of the ethylene and propylene. A combined reaction-fractionation step known as catalytic distillation hydrogenation is used to simultaneously carry out the reactions and separations while maintaining the hydrogenation conditions such that the ethylene and propylene remain substantially unhydrogenated and essentially all of the other C₂ and heavier unsaturated hydrocarbons are hydrogenated. Any unreacted hydrogen can be separated by a membrane and then reacted with separated C₉ and heavier materials to produce hydrogenated pyrolysis gasoline.



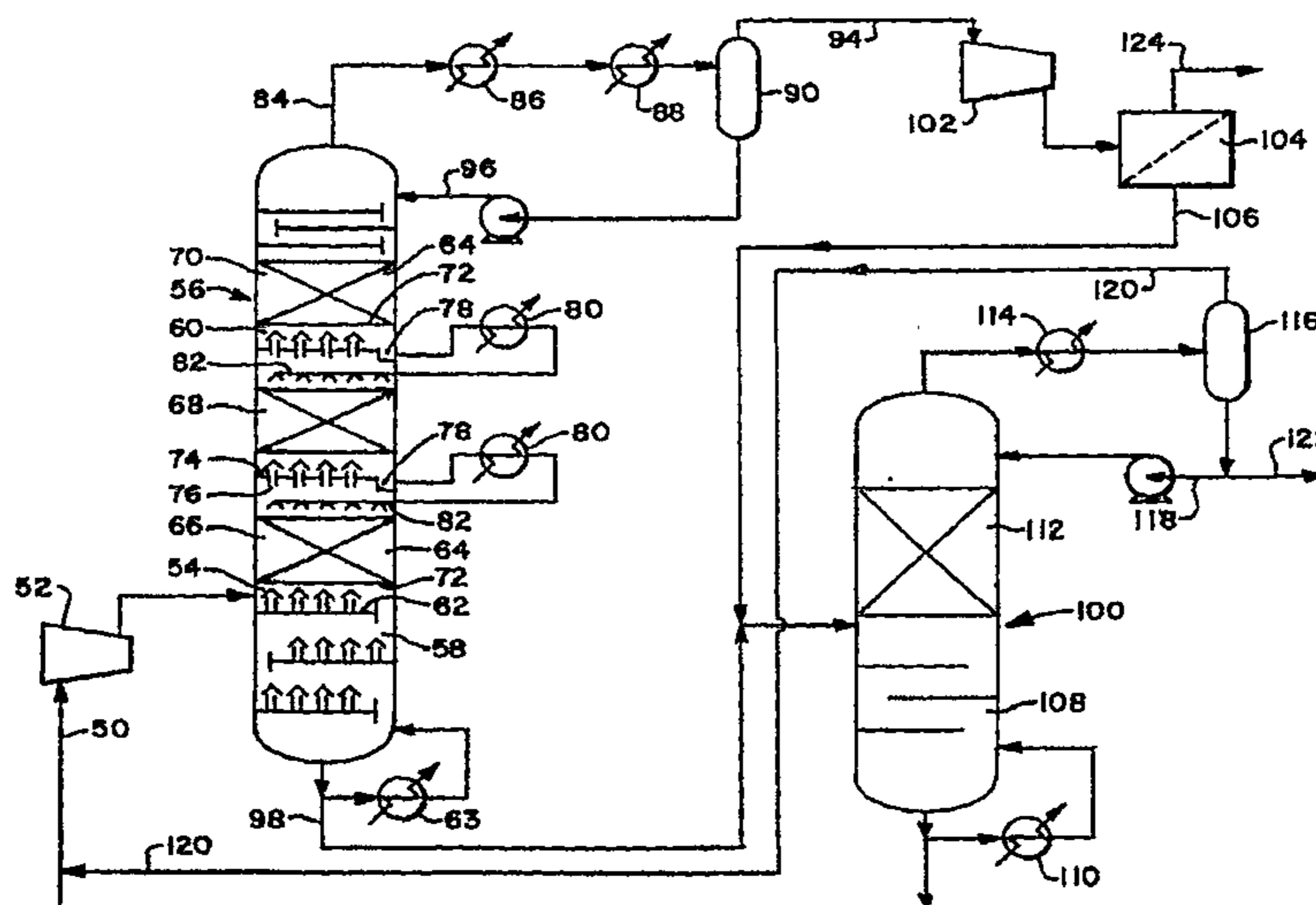
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<p>(21) International Application Number: PCT/US97/01932</p> <p>(22) International Filing Date: 19 February 1997 (19.02.97)</p> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/442,954 (CIP) Filed on 17 May 1995 (17.05.95)</p> <p>(71) Applicants (for all designated States except US): ABB LUMMUS GLOBAL INC. [US/US]; 1515 Broad Street, Bloomfield, NJ 07003 (US). CHEMICAL RESEARCH & LICENSING COMPANY [US/US]; 10100 Bay Arena Boulevard, Pasadena, TX 77507 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): STANLEY, Stephen, J. [US/US]; 319 B. Morganville Road, Matawan, NJ 07747 (US). McCARTHY, Francis, D. [US/US]; 151 Warbler Drive, Wayne, NJ 07470 (US). SUMNER, Charles [US/US]; 3 Stratford Drive, Livingston, NJ 07039 (US). GILDERT, Gary, Robert [CA/US]; 14507 Windy Ridge Lane, Houston, TX 77062 (US).</p> <p>(74) Agents: BERNEIKE, Richard, H. et al.; Alix, Yale & Ristas, LLP, 750 Main Street, Hartford, CT 06103 (US).</p>	<p>(81) Designated States: AU, BR, CA, CN, KR, MX, RU, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>	

(54) Title: OLEFIN PLANT RECOVERY SYSTEM EMPLOYING CATALYTIC DISTILLATION



(57) Abstract

The C₂ to C₅ and heavier acetylenes and dienes in a thermally cracked feed stream are hydrogenated without significantly hydrogenating the C₂ and C₃ olefins. Additionally, the C₄ and heavier olefins may be hydrogenated. Specifically, the cracked gas feed in an olefin plant is hydrogenated in a distillation reaction column containing a hydrogenation catalyst without the necessity of separating the hydrogen out of the feed and without any significant hydrogenation of the ethylene and propylene. A combined reaction-fractionation step known as catalytic distillation hydrogenation is used to simultaneously carry out the reactions and separations while maintaining the hydrogenation conditions such that the ethylene and propylene remain substantially unhydrogenated and essentially all of the other C₂ and heavier unsaturated hydrocarbons are hydrogenated. Any unreacted hydrogen can be separated by a membrane and then reacted with separated C₉ and heavier materials to produce hydrogenated pyrolysis gasoline.

Olefin Plant Recovery System Employing Catalytic Distillation

Background of the Invention

5 The present invention relates to a process for the production of olefins and particularly to processing the charge gas feed to more effectively recover the product and process the by-products.

Ethylene, propylene and other valuable petrochemicals are produced by the thermal cracking of a variety of hydrocarbon feedstocks ranging from ethane to heavy vacuum gas oils. In the thermal cracking of these feedstocks, a wide variety of products are produced ranging from hydrogen to pyrolysis fuel oil. The effluent from the cracking step, commonly called charge gas or cracked gas, is made up of this full range of materials which must then be separated (fractionated) into various product and by-product streams followed by reaction (hydrogenation) of at least some of the unsaturated by-products.

The typical charge gas stream, in addition to the desired products of ethylene and propylene, contains C_2 acetylenes, C_3 acetylenes and dienes and C_4 and heavier acetylenes, dienes and olefins as well as a significant quantity of hydrogen. In the majority of prior processes, the C_2 acetylenes and C_3 acetylenes and dienes and the C_5 and heavier dienes, acetylenes and olefins are catalytically hydrogenated in fixed bed reactors using a series of commercially available catalysts. In a growing number of applications, the C_4 acetylenes, dienes, and olefins are also catalytically hydrogenated in fixed bed reactors. These separate hydrogenation steps take place in one of two process sequences. In the first sequence, the charge gas is compressed to between 2.76 and 4.14 MPa (400 and 600 psia). It is then progressively chilled condensing the C_2 and heavier components. Hydrogen is cryogenically recovered and methane is fractionated out of the stream. The remaining C_2 and heavier stream enters a series of fractionation towers. The first tower produces an overhead stream containing the C_2 acetylenes, olefins, and paraffins. This stream is sent to a fixed bed, vapor phase reactor where the C_2 acetylene

is selectively hydrogenated using the hydrogen cryogenically separated earlier from the charge gas stream.

The second tower in this sequence produces an overhead stream containing the C₃ acetylenes, dienes, olefins and paraffins. This stream is sent to a fixed bed, vapor or liquid phase reactor where the C₃ acetylenes and dienes are selectively hydrogenated using the hydrogen cryogenically separated earlier from the charge gas stream.

The third tower in this first sequence produces an overhead stream containing the C₄ acetylenes, dienes, olefins, and paraffins. This stream is then sent either to battery limits as a final product or to a fixed bed, liquid phase reactor where the dienes, acetylenes, and in some instances the olefins are hydrogenated using the hydrogen cryogenically recovered previously from the charge gas.

The bottoms of the third tower contains the C₅ and heavier dienes, acetylenes, olefins and paraffins. This stream is sent to a series of two fixed bed, liquid phase reactors. In the first, the acetylenes and dienes are catalytically hydrogenated. The olefins are catalytically hydrogenated in the second reactor. Both reactors utilize the hydrogen cryogenically recovered previously from the charge gas. In some applications, the third tower produces an overhead stream containing both the C₄ and C₅ acetylenes, dienes, olefins, and paraffins. These are hydrogenated as discussed previously for the C₄'s alone, in a single fixed bed, liquid phase reactor. The C₆ and heavier dienes, acetylenes, olefins and paraffins exit in the bottoms of the third tower and are hydrogenated as discussed previously in two fixed bed, liquid phase reactors.

In the second process sequence, the cracked gas is compressed to between 2.07 and 3.45 MPa (300 and 500 psia) and sent to a fractionation tower. The overhead of the tower is the C₃ and lighter portion of the charge gas. It is sent to a series of fixed bed, vapor phase reactors where the C₂ acetylene and a portion of the C₃ acetylenes and dienes are hydrogenated using a small portion (typically less than 10%) of the hydrogen contained in the C₃ and lighter stream. The unhydrogenated

portion of the C₃ acetylenes and dienes as well as the C₄ and heavier acetylenes, dienes, and olefins are hydrogenated in a fashion similar to that described above for the first process sequence. This still leaves over 90% of the hydrogen to be recovered cryogenically.

5 Also in such a system, it is necessary to fractionate out the C₄ and heavier materials from the charge gas prior to the hydrogenation step. Otherwise, the heat of the hydrogenation reaction would be excessive and there would be a high rate of hydrogenation catalyst fouling. Since such a fractionation occurs in a high hydrogen and
10 methane environment, the energy requirements are high.

 In most prior processes, the C₂ and C₃ acetylenes and C₃ dienes are hydrogenated after the hydrogen separation/recovery step. The hydrogenation of the C₄ and heavier acetylenes, dienes, and olefins always occurs after the hydrogen separation step and will consume up
15 to 80% of the total available hydrogen. This hydrogenation also occurs in fixed bed catalytic reactors using catalysts chosen for the selectivity and degree of hydrogen saturation dictated by the particular process.

 While widely practiced, both process sequences described above have a number of disadvantages. First, the cracked gas must be chilled
20 and condensed in the presence of hydrogen. Due to the high partial pressure of the hydrogen, the mechanical refrigeration requirements to accomplish the condensation of the C₂ and heavier material are high thereby increasing the energy consumption and capital investment in the process. Also, the hydrogen must be cryogenically separated to supply
25 the hydrogen for the various downstream reactors which is both energy and capital intensive. Further, the hydrogenation steps occur in a series of fixed bed reactors requiring between 3 and 6 separate reactor systems thereby increasing the capital investment and complexity of the plant.

30 Various prior art hydrogenation processes and features are shown in U.S. Patents 3,692,864; 4,020,119; 4,404,124; 4,443,559 and

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4,973,790. Also a selective catalytic hydrogenation process is disclosed in published International Patent Application WO 95/15934.

Summary of the Invention

5 An object of the present invention is to hydrogenate in the liquid phase in a boiling point reactor the C₂ to C₅ and possibly heavier

acetylenes and dienes in a feed stream without hydrogenating the C₂ and C₃ olefins in the feed stream. Additionally, the C₄, C₅ and some or all of the heavier olefins may be hydrogenated still without hydrogenating the C₂ and C₃ olefins.

5 More specifically, an object of the present invention is to provide a system and method for hydrogenating the cracked gas in an olefin plant prior to the separation of hydrogen and methane from the cracked gas in a manner so as to hydrogenate the by-products, C₂ acetylenes, C₃ acetylenes and dienes and C₄ and heavier acetylenes and dienes and, if
10 desired, the C₄ and heavier olefins, without significant hydrogenation of the ethylene and propylene. This involves the use of a combined reaction-fractionation step known as catalytic distillation hydrogenation upstream of the chilling and condensation of the C₂ and heavier material to simultaneously carry out the reactions and separations in a manner so as
15 to prevent or minimize the hydrogenation of the desired main products and to consume the hydrogen without the need for costly hydrogen separation.

The hydrogenation of the C₄ and heavier acetylenes, dienes and olefins increases the hydrogen removal to between 70% and 100% and most typically 90% to 95%. This high removal of hydrogen reduces the
20 hydrogen partial pressure thereby lowering the mechanical refrigeration requirements to chill and condense the C₂ and heavier material thereby saving energy and capital investment. The cryogenic separation of the hydrogen from the cracked gas is eliminated. Since all of the hydrogenation reactions occur upstream of the hydrogen-methane
25 separation steps, the hydrogen required for the hydrogenation reactions is already present in the charge gas. The elimination of the cryogenic separation of the hydrogen results in energy saving, lower capital investments and less complexity in the process. In the alternative, the present invention can be employed for hydrogenating the acetylenes and
30 dienes without significant hydrogenation of olefins.

In the two processing sequences currently practiced, fouling in the fractionation towers bottoms typically occurs due to the presence of

acetylenes and dienes. The bottoms operating temperatures of these towers are limited to minimize the fouling tendencies but often spare equipment must be provided to ensure continuity of plant operation. Hydrogenating the dienes and acetylenes prior to the fractionation towers eliminates the fouling tendencies in the fractionation tower bottoms.

Brief Description of the Drawings

Figure 1 is a flow sheet for a conventional prior art olefin plant.

Figure 2 is a flow sheet for a portion of an olefin plant according to the present invention.

Figure 3 is a flow sheet for the remaining portion of an olefin plant according to the present invention illustrating the downstream processing of the olefin containing vapors.

Figure 4 is a flow sheet similar to the flow sheet of Figure 2 but illustrating an alternate embodiment of the present invention.

Description of the Preferred Embodiments

Referring first to Figure 1 which illustrates a conventional prior art olefin plant such as the first process sequence previously discussed, a charge gas 10 is first compressed at 12 up to a pressure of 2.76 to 4.14 MPa (400 to 600 psia). The majority of the compressed gas then undergoes cryogenic treatment at 14 to separate hydrogen followed by separation of methane at 16. A small portion of the C_3 and heavier material condenses in the compressor train and often bypasses the cryogenic demethanization and deethanization steps going directly to the depropanizer 30 as stream 31. The gas stream 18 is then deethanized at 20 with the C_2 gas stream being hydrogenated at 22 and fractionated at 24 to produce essentially ethylene 26 and ethane 28. The bottoms from the deethanizer 20 are depropanized at 30 with the separated C_3 stream 32 being hydrogenated at 34 and fractionated at 36 to produce essentially propylene 38 and propane 40. Likewise, the bottoms from the depropanizer 30 are debutanized at 42 with the C_4 stream being

6

hydrogenated at 44 and the C₅+ stream being hydrogenated at 46. As can be seen, nearly the entire feed stream is subjected to cryogenic treatment and the separation of hydrogen before any hydrogenations or fractionations are carried out. The separated hydrogen is then used
5 downstream in the hydrogenation units 22, 24, 44 and 46. This scheme with its cryogenic treatment and hydrogen separation has the disadvantages previously discussed.

Figure 2 illustrates the present invention where the charge gas 50 is compressed at 52 but only up to a pressure of 0.69 to 1.72 MPa (100
10 to 250 psia) and preferably to 1.21 MPa (175 psia). The compressed charge gas stream is fed into the feed zone 54 of a catalytic distillation tower 56. This catalytic distillation tower is a device which simultaneously carries out a catalytic reaction and distillation and comprises a stripping section 58 below the feed zone 54 and a rectifying/reaction section 60
15 above the feed zone 54. The stripping section 58 contains any desired distillation internals such as conventional trays 62 illustrated in Figure 2. Reboiler 63 returns heated bottoms to the column.

The rectifying/reaction section 60 of the column 56 has the dual function of reacting (hydrogenating) selected components of the feed and
20 distilling the components. Therefore, this section contains beds of a conventional hydrogenating catalyst 64. The criteria for this rectifying/reaction section is that conditions be created wherein the unsaturated hydrocarbons, with the exception of ethylene and propylene, are hydrogenated and wherein the requisite distillation is accomplished to
25 separate essentially all of the C₄ and lighter material as overhead and essentially all of the C₆ and heavier materials as bottoms. A portion of the C₅ materials, 10 to 90% and typically 70%, exits the column overhead and the remaining portion, typically 30%, exits the column as bottoms. In some cases, all of the C₅ will exit the tower overhead depending upon
30 process, feedstock and byproduct requirements of the individual plants. In order to selectively hydrogenate the C₂ acetylenes, the C₃ acetylenes and dienes and the C₄ and heavier acetylenes, dienes and olefins while

leaving the ethylene and propylene unhydrogenated, the rectifying/reaction section 60 of the column 56 is operated such that there is a substantial concentration gradient of C_4 and C_5 materials relative to C_2 and C_3 materials in the liquid phase where the majority of the hydrogenation reaction occurs. In the preferred embodiment, this is accomplished by the use of a high liquid downflow, for example, by using a high reflux ratio and large intercondensing duties. The column reflux which is produced by overhead condensers 86 and 88 and column intercoolers or intercondensers 80 also removes the high heat of reaction.

As shown in Figure 2, the catalyst is separated into a series of discrete beds 66, 68 and 70. Although three beds are shown, this is only by way of example and could be any number of beds depending on the dynamics of any particular plant. These catalyst beds are retained between the screens or perforated plates 72. Located between the catalyst beds are liquid collecting trays 74 which include vapor flow ports or chimneys 76. The liquid descending from a catalyst bed collects on the respective tray and drains into the sumps 78. The liquid is withdrawn from the sumps 78 as side streams through the intercondenser 80 and is then reinjected back into the column over the next lower catalyst bed through the distribution headers 82. This permits a portion of the heat of reaction to be removed in the intercondensers. By arranging the intercondensers in this fashion, the cooling medium can be cooling water while the cooling medium in the overhead condensers may need to be partly by use of mechanical refrigeration. Hence, the use of the intercondensers can significantly reduce the portion of the heat of reaction which needs to be removed by mechanical refrigeration.

The overhead 84 from the column is cooled in the overhead condenser 86 with cooling water and in the condenser 88 with refrigeration and the resulting vapor and liquid separated at 90. The processing of the collected vapor in line 94 will be discussed hereinafter. The resulting liquid from separator 90 is pumped through line 96 back into the column as reflux. A number of trays are provided to fractionate out ethylene and

propylene from the liquid phase preventing these from entering the catalyst beds in high concentrations relative to the C₄ and C₅ material.

In the present invention, it is imperative to limit the loss of ethylene and propylene in the hydrogenation reaction because these are the principal products of an ethylene or olefin plant. However, under conventional conditions which would permit the hydrogenation of the C₄ and heavier olefins, ethylene and propylene losses by hydrogenation would be unacceptably high. That is the primary reason why one of the currently practiced prior art process sequences described earlier only hydrogenates the C₂ acetylenes and a portion of the C₃ acetylenes and dienes upstream of the chilling and condensing step.

The hydrogenation in the column 56 occurs mostly in the liquid phase. The extent of the reaction is dependent upon the relative reactivity of the various components and the concentration of these components in the liquid phase at any particular point in the column. The C₂ and C₃ acetylenes and dienes are far more reactive than ethylene and propylene so that they react first and rapidly. However, the relative reactivities of ethylene, propylene and the C₄ and heavier olefins, dienes and acetylenes are much closer. In order to react a significant quantity of the C₄ and heavier olefins, dienes and acetylenes without any significant loss of ethylene and propylene, the concentration of the ethylene and propylene in the liquid phase must be minimized and the concentration and temperature profiles from top to bottom must be controlled. Since the hydrogenation occurs in a fractionation tower, this control can be accomplished by adjusting the overhead (external) reflux produced by the overhead condensers 86 and 88 and the side stream reflux from the intercondensers 80.

The feed 54 to the column at the previously mentioned pressure of 1.25 MPa (0.69 to 1.72 MPa) is in the temperature range of 25 to 120°C and preferably 70 - 90°C. At the feed point, the concentration of the hydrogen is the highest, the temperature (in the rectifying/reaction section) is the highest and the concentration of ethylene and propylene in the liquid

phase is the lowest. At this point, the concentration of C₄ and C₅ components in the liquid phase relative to the concentration of propylene is maintained in the range of 10 to 80 and preferably about 25 while the concentration of C₄ and C₅ in the liquid phase relative to ethylene is maintained in the range of 30 to 100 and preferably about 80. This low concentration of C₂ and C₃ in the rectifying/reaction section is achieved by a high liquid downflow ratio. This high liquid downflow ratio can be achieved by a high overhead reflux ratio and/or by the reflux created by the intercondensers 80. As will be explained later with respect to Figure 4, this high liquid downflow ratio can also be provided by the recycle and cooling of heavies from the bottom of the column. More specifically, the liquid downflow ratio provided by the overhead reflux 96, the intercoolers 80 and the recycle of heavies (160 in Figure 4) is equivalent to the liquid downflow that would be provided by an overhead reflux ratio in the range of about 0.2 to 10 without intercondensers and heavies recycle. This compares to a reflux ratio of less than 0.2 for a conventional column operated to achieve a similar overhead product specification. At the top of the rectifying/reaction section 60, where the temperature is 38 to 80°C and preferably 60°C and where the concentration of hydrogen is low because most of it has reacted, the ratio of C₄ and C₅ components to C₂ and C₃ components is similarly high. The overhead reflux ratio and intercondenser temperatures are adjusted to maintain these operating parameters. With the hydrogenation of the C₂ acetylenes, the C₃ acetylenes and dienes and the C₄ acetylenes, dienes and olefins, and a major portion of the C₅ and C₆ acetylenes, dienes and olefins, 50 to 90% of the hydrogen contained in the cracked feed gas is reacted.

The bottoms 98 from the column 56 contain a portion of the C₅ material and essentially all of the C₆ and heavier material. In the preferred embodiment, this bottoms product is sent to a second catalytic distillation hydrogenation column 100 for the production of hydrogenated pyrolysis gasoline. Alternately, the bottoms product can be burned in the plant fuel system or pumped and sent to a conventional fixed pyrolysis gasoline

hydrotreater as previously described under prior art. Also, in the preferred embodiment shown in Figure 2, the total net overhead 94 from the column 56, containing a portion of the C₅ material and essentially all of the C₄ and lighter material, is first compressed at 102 and sent to a hydrogen recovery membrane devices 104. Such membrane devices are commercially available for the separation of hydrogen. The intent of the membrane is to recover most of the hydrogen remaining in the overhead stream 94. The resulting hydrogen stream 106 is then fed to the pyrolysis gasoline hydrogenation column 100 along with the bottoms from the column 56. The compression step may or may not be required depending on the specific composition of the cracked gas, hydrogen membrane selection, and operating condition of column 56. Alternately, a conventional fixed bed pyrolysis gasoline hydrotreater could be used without a membrane separator. In this case, the hydrogen now significantly reduced in stream 94 by the hydrogenation reactions occurring in column 56 would be cryogenically recovered as previously discussed.

Pyrolysis gasoline is a complex mixture of hydrocarbons ranging from C₅ compounds through materials with a boiling point of about 200° C. The raw feed to the pyrolysis gasoline column 100 is highly unstable due to its high content of diolefins. Therefore, in the production of the pyrolysis gasoline, the feed is hydrogenated in the column 100. The column 100 is similar to the column 56 in that it has a typical bottom stripping section 108, a reboiler 110 and an upper rectifying/reaction section 112 containing the hydrogenation catalyst. It includes an overhead condenser 114 and separator 116 from which reflux 118 is returned to the column. The column may or may not include intercoolers or intercondensers similar to the intercondensers for column 56. In this column 100, the feed of the remaining C₅ acetylenes, dienes and olefins and all of the C₆ and heavier acetylenes, dienes and olefins is hydrogenated. This column operates between 0.21 and 0.86 MPa and preferably 0.34 MPa. The C₆ and lighter materials in the feed enter the catalyst bed where the acetylenes, dienes and olefins are hydrogenated. The C₉ and heavier material exits from the

bottoms of column 100. The heat of reaction is removed by the reflux stream 118.

5 The reflux stream 118 also serves to control the selectivity of the hydrogenation reaction. There is a small amount of ethylene in stream 106 and, as has been pointed out, this ethylene is a valuable product and its hydrogenation should be avoided. By the proper control of the column reflux 118, ethylene concentration in the liquid phase in the column can be minimized. This is a technique which is preferable to upgrading the membrane separation process to essentially exclude ethylene from 10 passing through with the hydrogen. The passage of ethylene could be minimized by decreasing the pressure differential across the membrane and/or by increasing the membrane surface area. However, adding membrane surface area is a capital intensive cost and increasing the pressure differential is both energy and capital intensive. The ability to 15 selectively hydrogenate in the column 100 permits a lower capital cost, less energy intensive process. The overhead vapor 120 from the column containing primarily C_4 and lighter material is recycled to the feed for the process. The net overhead product condensed liquid is removed at 122 as pyrolysis gasoline.

20 Figure 3 illustrates the processing of the overhead stream 94 after it passes through the hydrogen separation step at 104 and emerges as stream 124. Alternately, this system can be used to process the stream 94 directly in the event that the membrane separation and pyrolysis gasoline portions of the process described above were not used. In that 25 event, additional provisions would be made for cryogenic hydrogen separation.

The vapor stream 124 is chilled at 128 as required to liquify the C_2 and heavier components. The methane overhead 130 is then separated in the demethanizer tower 132 from the C_2 and heavier bottoms 134. 30 These bottoms 134 are then separated in the deethanizer tower 136 to produce a C_2 overhead 138 and a C_3 and heavier bottoms 140. The C_2 overhead 138, which may first go through a drying step (not shown), is

then separated in tower 142 into ethane bottoms 144 and ethylene overhead 146. The bottoms 140 from the deethanizer 136 is then separated in tower 148 into a C₄ and heavier bottoms 150 and a C₃ overhead 152. This overhead 152, which may also then be dried, is fed to the tower 154 for the separation of propane 156 and propylene 158.

Figure 4 illustrates an alternate preferred embodiment of the present invention which incorporates recycles from the stripping section 58 of the column 56. In this embodiment, a recycle stream 160 from the stripping section 58 is recycled either to the column overhead 84 through line 161 and/or to the catalytic zone of the rectifying/reaction section 60 through line 163. Recycle via line 163 to the catalyst zone only is usually preferable. For example, this recycle may be a portion 162 of the bottoms 98 and/or a portion 164 from within the stripping section. This recycle 160 serves to recycle the heavies, C₅ +, to the overhead or to the catalytic zone of the column. This increases the amount of dienes and acetylenes and perhaps some olefins which will be hydrogenated, thereby increasing the consumption of hydrogen. Also, it provides another control variable to increase the overhead temperature of the tower and/or of the catalyst bed. Increasing the overhead temperature of the tower is desirable since it will decrease or eliminate the refrigeration requirements for generating the reflux. Increasing the temperature of the catalyst bed provides another variable to control the reaction rate of the catalytic reaction beds. Although this embodiment achieves distillation internally in the column, it is not classic distillation since there is now some heavies in the overhead. In that case, some further distillation would be provided downstream to make the final desired separations. The purpose of this embodiment is to improve the control of the reactions taking place in the tower 56 even though that also sacrifices some of the separation by distillation. When the catalytic distillation column is operated with a recycle of heavies to the overhead, the heavy stream is preferably cooled at 165. This cooling effect can be considerable, especially if a high recycle rate of these heavies is utilized. This reduces the reflux ratio of the catalytic distillation

column at equal liquid downflow rates. The reflux rate is further reduced if side cooling is utilized. The net effect of all of these cooling steps is to significantly decrease the reflux ratio. This can reduce refrigeration requirements as some of the cooling required to condense reflux may be provided at higher condensing temperatures. This can be another benefit of recycling heavies from the bottom section to the upper section of the column especially recycling to the vapor outlet 84 since that will raise the overhead temperature and reduce the refrigeration requirements.

When the catalytic distillation column is operated with bottoms recycle, the overhead reflux ratio is in the range of 0.05 to 0.4 and preferably, 0.1 to 0.2 when the bottoms recycle is directed to the top of the catalyst bed through line 163. When the bottoms recycle is directed to the overhead of the column through line 161, the reflux ratio is 0.2 to 10. But even with this lower overhead reflux ratio, a high liquid downflow ratio is maintained in the catalyst beds by the intercondensers and heavies recycle and cooling. The heavies recycle does not conform to what would be considered "classical" distillation since the recycle results in the loss of some of the net separation benefits of the distillation. However, this loss is outweighed by the benefit of minimizing ethylene and propylene concentrations in the liquid in the catalyst zone by the use of high liquid downflow rates and by the benefits of raising the temperature in the catalyst bed.

The ability of the present invention to remove 85 to almost 100%, typically 90%, of the hydrogen contained in the charge gas prior to chilling and condensation steps lowers the energy consumption and reduces capital costs. By using the hydrogen contained in the charge gas as the source of hydrogen for the various hydrogenation reactions, the need for the separate cryogenic separation of hydrogen is eliminated. By the proper control of the concentration profiles in the catalytic distillation hydrogenation column, the C₄ and heavier olefins can be hydrogenated without any significant hydrogenation of either ethylene or propylene.

Therefore, the hydrogenation reactions are combined into one or two reactor systems.

1. A method of processing a thermally cracked feedstream containing the hydrogen, ethylene, propylene, and other C₂, C₃, C₄, C₅, C₆ and heavier unsaturated hydrocarbons produced in said thermal cracking to separate said ethylene and propylene from at least some of said other unsaturated hydrocarbons and to hydrogenate at least some of said other unsaturated hydrocarbons with said hydrogen contained in said feedstream without the prior separation of said hydrogen therefrom and without significantly hydrogenating said ethylene and propylene comprising the steps of:

- 10 a. introducing said feedstream into the feed zone of a distillation reaction column containing a distillation stripping zone below said feed zone and a combination distillation rectifying and catalytic reaction zone above said feed zone;
- 15 b. concurrently:
- (i) contacting said feedstream in said distillation reaction column with a vertically oriented bed of hydrogenation catalyst in said combination distillation rectifying and catalytic reaction zone;
- 20 (ii) maintaining a high ratio of the total of C₄ and C₅ hydrocarbons to the total of the C₂ and C₃ hydrocarbons at the bottom of said vertical oriented bed of hydrogenation catalyst, said high ratio being selected whereby said ethylene and propylene remain essentially un-
- 25 hydrogenated and at least some of said other unsaturated hydrocarbons are
- 30 hydrogenated;

- (iii) fractionating the resulting mixture of hydrogenated and un-hydrogenated products;
- 5 c. withdrawing an overhead stream containing essentially all of said C₂, C₃ and C₄ hydrocarbons and a portion of said C₅ hydrocarbons and a bottoms stream containing essentially all of said C₆ and heavier hydrocarbons and a portion of said C₅ hydrocarbons; and
- 10 d. processing said overhead stream to recover ethylene and propylene.

2. A method of processing as recited in claim 1, wherein said feedstream includes C₉ and heavier material and, said step (d) of processing said overhead stream comprises the steps of:

- 15 a. separating hydrogen from said overhead stream;
- b. feeding said separated hydrogen and said bottoms stream from said distillation reaction column to a pyrolysis gasoline distillation reaction column containing a hydrogenation catalyst;
- 20 c. reacting said separated hydrogen with said bottoms stream in said pyrolysis gasoline distillation reaction column to produce a hydrogenated liquid overhead of pyrolysis gasoline and a bottoms of C₉ and heavier material.

25 3. A method of processing as recited in claim 2, wherein said step of separating hydrogen comprises the step of separating hydrogen from said overhead stream through a hydrogen separation membrane.

4. A method of processing as recited in claim 1, wherein said step of maintaining a high ratio includes the step of withdrawing at least one portion of descending liquid as a side stream at a selected point from said bed of hydrogenation catalyst, cooling said side stream and
5 injecting said cooled side stream back into said bed of hydrogenation catalyst.

5. A method of processing as recited in claim 4, wherein said side stream is injected back into said bed at a point below said selected point.

10 6. A method of processing as recited in claim 1, wherein said hydrogenation reactions occur essentially in the liquid phase in said distillation reaction column.

7. A method of processing a thermally cracked feedstream containing hydrogen, ethylene, propylene, and other C₂, C₃, C₄ and
15 heavier unsaturated hydrocarbons, to hydrogenate at least some of said unsaturated hydrocarbons with said hydrogen contained in said feedstream without hydrogenating said ethylene and propylene comprising the steps of:

20 a. introducing said feedstream into the feed zone of a distillation reaction column containing a distillation stripping zone below said feed zone and a combination distillation rectifying and catalytic reaction zone above said feed zone;

b. concurrently
25 (i) contacting said feedstream in said distillation reaction column with a vertically oriented bed of hydrogenation

- catalyst in said combination distillation rectifying and catalytic reaction zone;
- 5 (ii) maintaining hydrogenation conditions within said bed of hydrogenation catalyst including a high ratio of the C₄ and heavier hydrocarbons to the C₂ and C₃ hydrocarbons said high ratio being selected whereby said ethylene and propylene remain essentially un-
- 10 hydrogenated and essentially all of said other C₂, C₃, and C₄ and heavier unsaturated hydrocarbons are hydrogenated;
- 15 (iii) fractionating the resulting mixture of hydrogenated and un-hydrogenated products;
- 20 (iv) recycling heavy materials from said stripping zone to a location in said column above said catalytic reaction zone to assist in maintaining said high ratio and to increase the temperature in said catalytic reaction zones and to provide additional unsaturates to be hydrogenated;
- 25 c. withdrawing an overhead stream containing essentially all of the said C₂, C₃, and C₄ hydrocarbons and a portion of the heavier hydrocarbons and a bottoms stream containing the remaining portion of the heavier hydrocarbons;
- 30 and

d. processing said overhead stream to recover ethylene and propylene.

5 8. A method of processing as recited in claim 7 wherein said step of recycling heavy materials includes the step of cooling said heavy materials prior to introduction into said column.

10 9. A method of processing as recited in claim 8 wherein said step of maintaining a high ratio includes the step of withdrawing at least one portion of descending liquid as a side stream at a selected point from said bed of hydrogenation catalyst, cooling said side stream and injecting said cooled side stream back into said bed of hydrogenation catalyst.

15 10. A method of processing as recited in claim 9 wherein said step of maintaining a high ratio further includes the step of maintaining a high reflux ratio back to said combination distillation rectifying and catalytic reaction zone.

11. A method of processing as recited in claim 10 wherein said reflux ratio is in the range of 0.05 to 0.4.

12. A method of processing as recited in claim 10 wherein said reflux ratio is in the range of 0.1 to 0.2.

20 13. A method of processing as recited in claim 7 wherein said step of recycling heavy materials to a location in said column above said catalytic reaction zone comprises recycling into said withdrawn overhead stream.

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14. A method of processing as recited in claim 13 wherein said step of maintaining a high ratio further includes the step of maintaining a high reflux ratio back to said combination distillation rectifying and catalytic reaction zone.

5 15. A method of processing as recited in claim 14 wherein said reflux ratio is in the range of 0.5 to 1.5.

16. A method of processing as recited in claim 14 wherein said reflux ratio is in the range of 0.2 to 10.

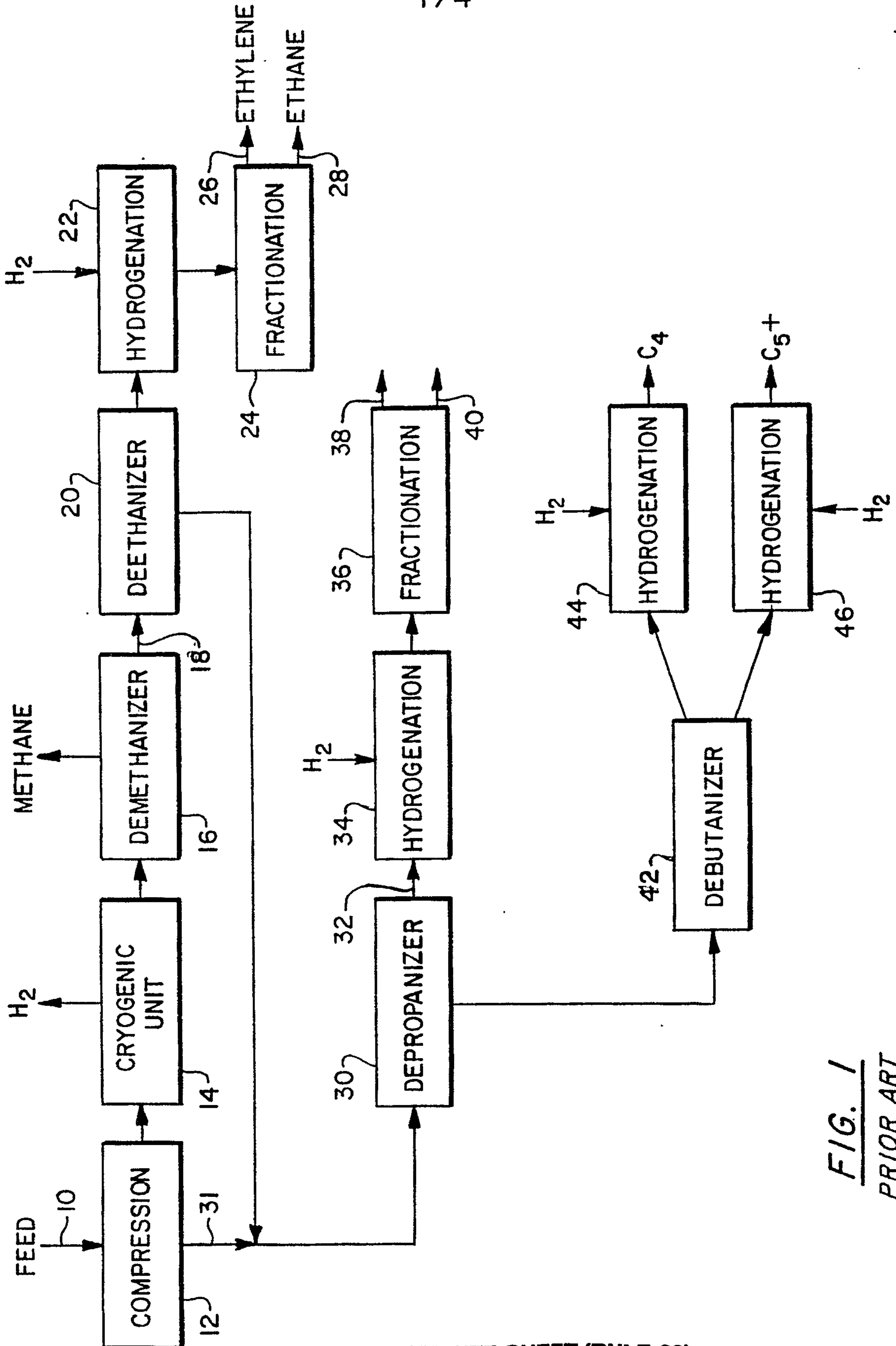


FIG. 1
PRIOR ART

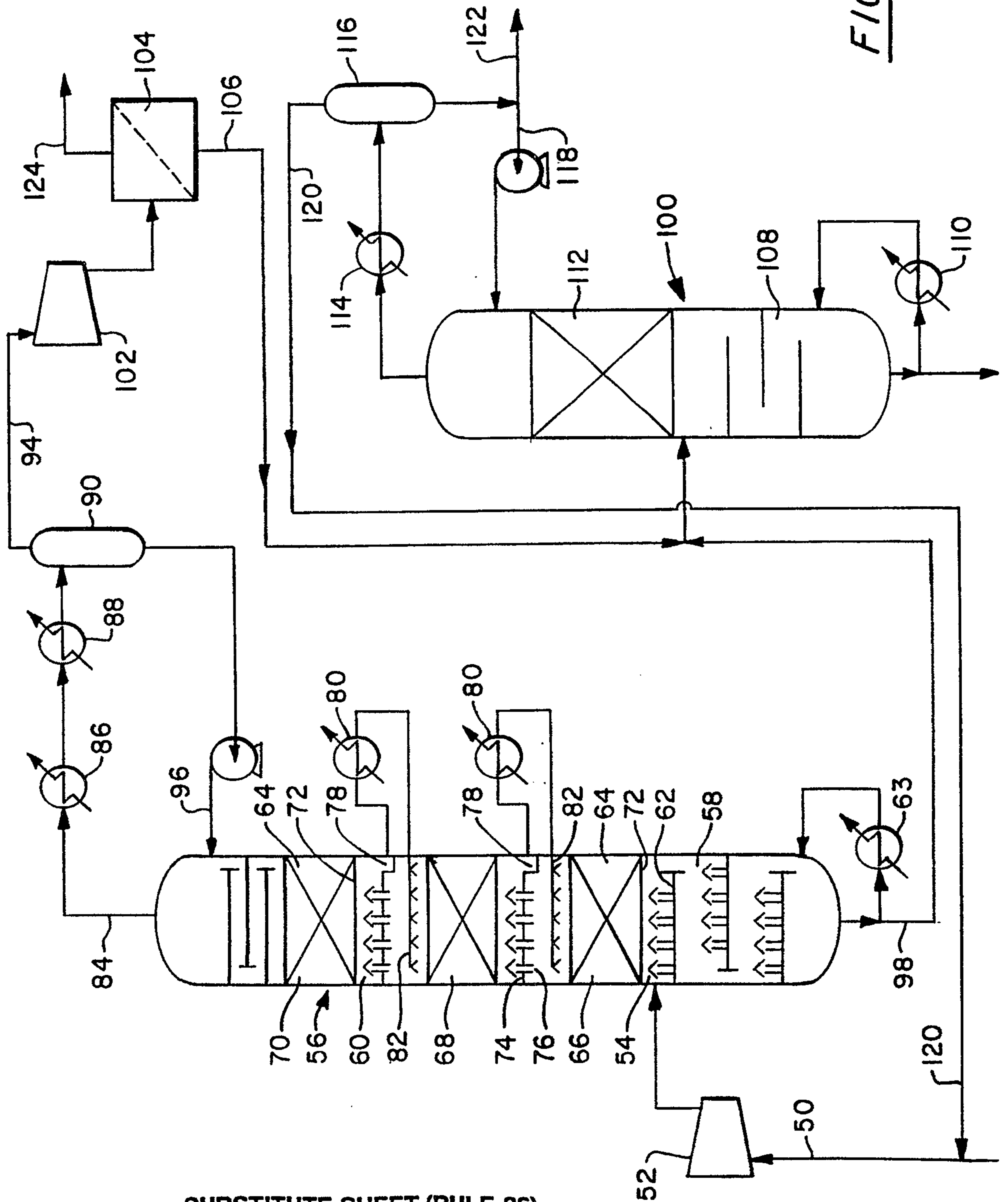


FIG. 2

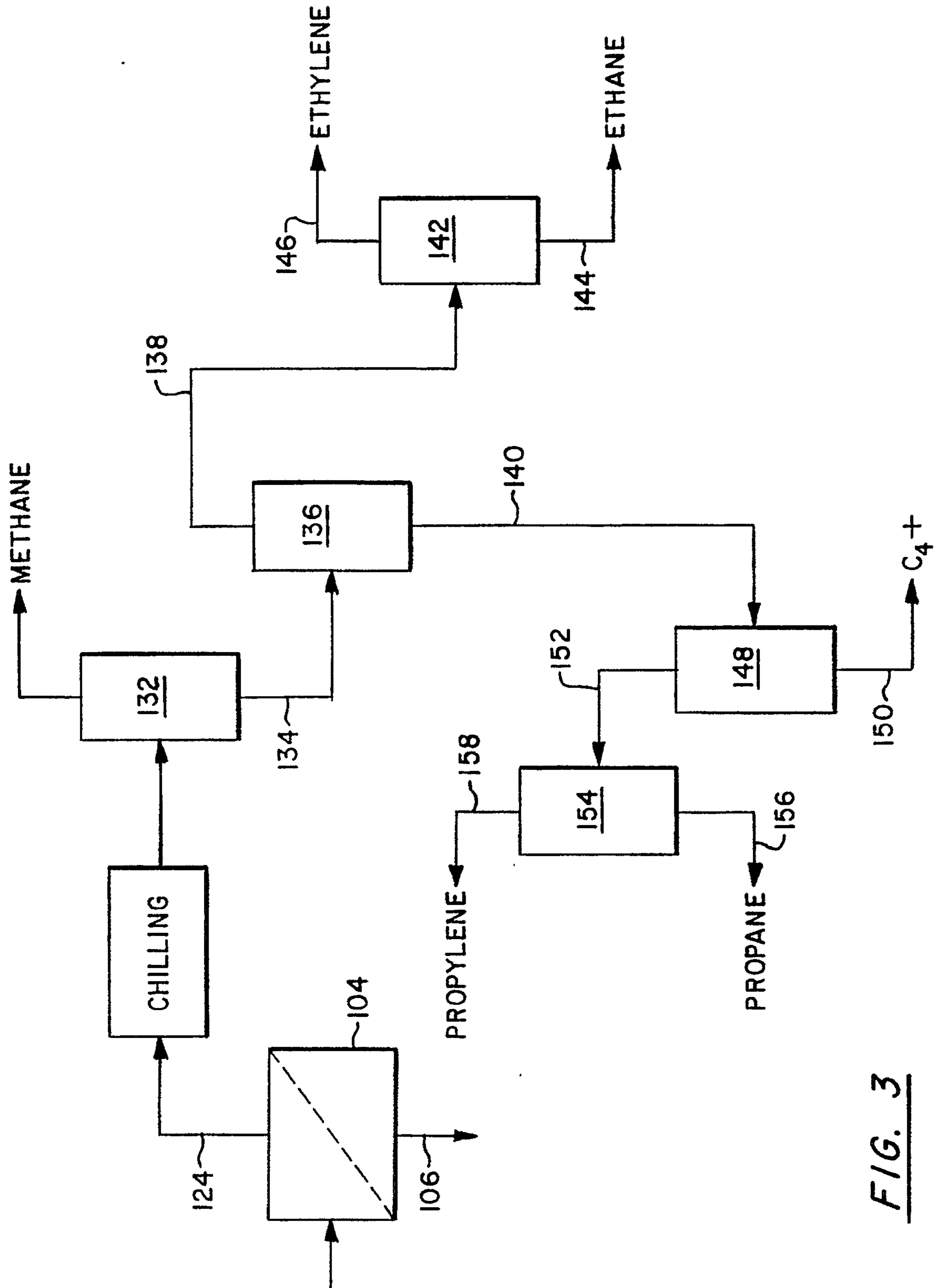


FIG. 3

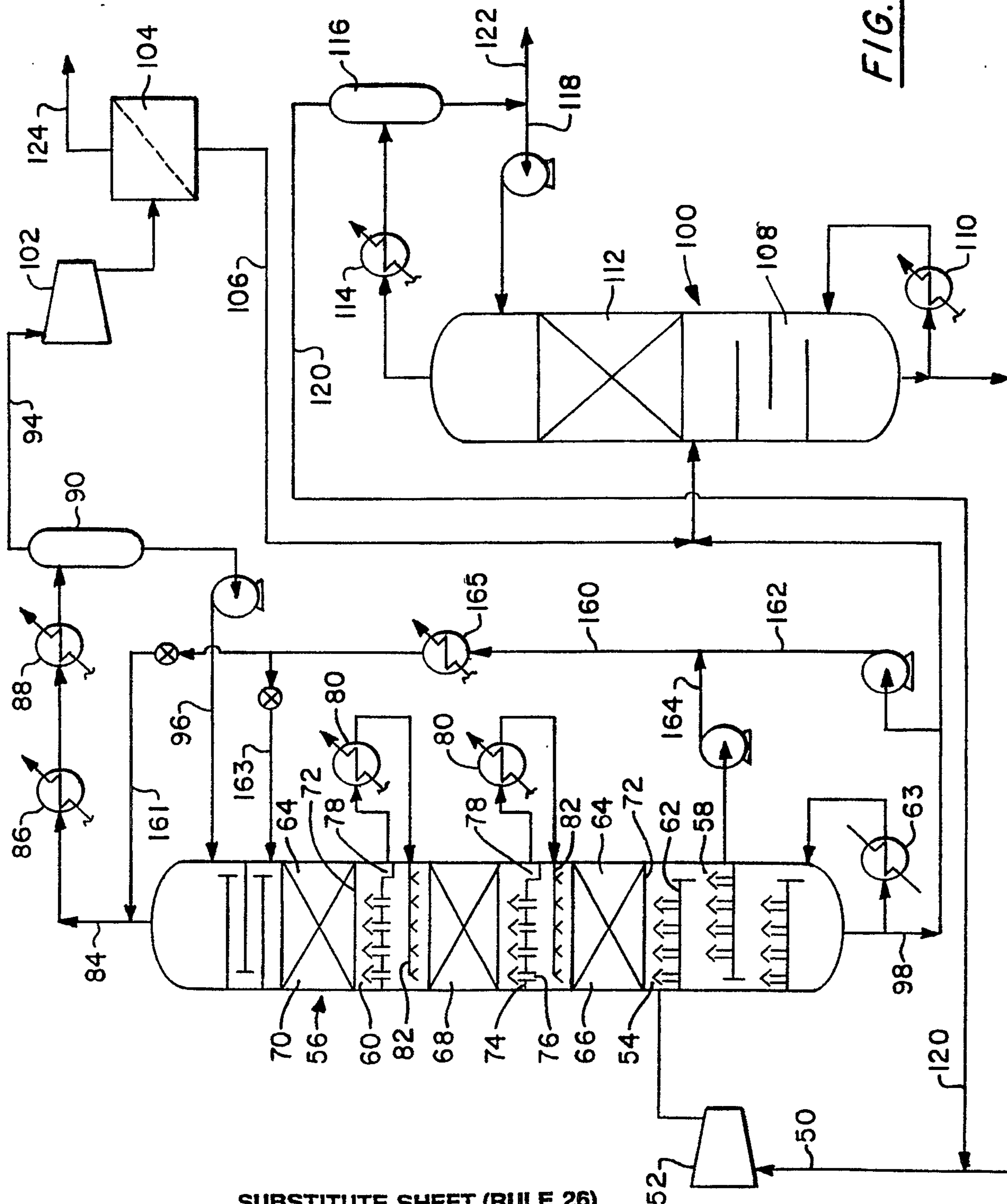


FIG. 4