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**(54) A COMBINATION PROCESS FOR MANUFACTURING ETHYLENE, ETHYLBENZENE AND  
STYRENE**

EIN KOMBINATIONSVORFAHREN ZUR HERSTELLUNG VON ETHYLEN, ETHYLBENZOL UND  
STYROL

PROCEDE COMBINE DESTINE A LA FABRICATION D'ETHYLENE, D'ETHYLBENZENE ET DE  
STYRENE

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(72) Inventor: **Netzer, David  
Los Angeles, CA 90069 (US)**

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(74) Representative: **Schüssler, Andrea, Dr. et al  
Kanzlei Huber & Schüssler  
Truderinger Strasse 246  
81825 München (DE)**

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(73) Proprietor: **Netzer, David  
Los Angeles, CA 90069 (US)**

(56) References cited:  
**US-A- 4 022 847                   US-A- 4 107 224  
US-A- 4 720 293                   US-A- 5 463 154**

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**Description**

## FIELD OF INVENTION

5 **[0001]** The present invention is directed to a process of the production of ethylene for use in the production ethylbenzene and styrene.

## BACKGROUND OF THE INVENTION

10 **[0002]** Conventional ethylene production consists of the following key process operation:

(a) Thermal cracking, in presence of dilution steam, of C<sub>2</sub>+ hydrocarbon at 15-25 psig (**1.034-1.72 Bar-g**) and 1,500-1,600°F (**815°C -870°C**) to form cracked gas containing ethylene in an amount of 25-40 wt % (and up to 80 wt% for net ethane feed), and other by products such as propylene, acetylene, hydrogen, methane and C<sub>3</sub>+ products. The thermal section includes cracked gas cooling, steam generation and C<sub>3</sub>+ hydrocarbon condensation. Traces of CO, CO<sub>2</sub> and H<sub>2</sub>S are formed in the cracking.

(b) Cracked gas compression to 400-600 psig (**27.6- 41.4 Bar-g**), traces of CO<sub>2</sub> and H<sub>2</sub>S removal, drying, and bulk C<sub>4</sub>+ product recovery by condensation at 100°F, (**38°C**) using cooling water.

(c) Acetylene conversion to ethylene via selective hydrogenation, chill down and cryogenic recovery of ethylene by fractionation at below -30°F. (**-34.4°C**)

(d) Recovery of propylene, propane and C<sub>4</sub>+ hydrocarbons by warm distillation at above 80°F. (**26.6°C**)

(e) Cascade refrigeration of ethylene and propylene refrigerants, to support the above, down to a temperature of below -100°F. (**-73.2°C**)

(f) Methane refrigeration and or expander to reach refrigeration below -180°F. (**-117.7°C**)

(g) In case of Naphtha feed, residual liquid products from cracking such as pyrolysis fuel oil and pyrolysis gasoline, which are rich in aromatics, are selectively hydrotreated for di-olefin and olefin saturation.

**[0003]** Efficient cryogenic recovery of the ethylene is a key element in design of ethylene plants. The motive power for compression and refrigeration, and consequently the capital cost escalates rapidly as the rate of ethylene recovery increases. For example, the typical ethylene recovery of 99.7-99.9% requires much higher investment and 50% more refrigeration energy in the demethanizer as compared with 95% rate of ethylene recovery. Thus, reduction of the marginal refrigeration required for ethylene recovery by using 95% or lower recovery could substantially improve the overall economics of the ethylene plant, if a down stream outlet, other than fuel gas, is found for the 5 % more of the unrecovered gaseous ethylene. Normally the unrecovered ethylene 0.1-0.3% is routed with the methane to the fuel gas system. However, the value of ethylene as fuel is only 15-20 % of its equivalent value as downstream product. The ethylene product is commonly used as a feedstock to many downstream processing including ethylbenzene. Production of ethylbenzene from pure ethylene against dilute ethylene feed, although somewhat advantageous from a stand point of the ethylbenzene plant alone, is not an absolute requirement and its relative cost impact is rather marginal as compared with the estimated saving in the ethylene plant.

**[0004]** In recent years, processes for producing ethylbenzene from dilute ethylene feed streams have been developed by Badger, a subsidiary of Raytheon, ABB Lummus Global/CDTech, Sinopec and others. The key driving forces behind these new developments are the objectives of using offgases from fluid catalytic crackings (FCC) in petroleum refining. These offgases are at 150-250 psig (**10.34-17.24 Bar-g**) and typically contain 8-18 vol% of ethylene, 3-9 vol%, of propylene and 12-20% hydrogen.

**[0005]** Limited integration of ethylbenzene and ethylene production was experienced in a number of locations including El Paso Products (Now Huntsman Chemical) in Odessa, Texas, where rich ethylene rich stream at 40 psig (**2.76 Bar-g**) is compressed to 550 psig (**37.93 Bar-g**) and feeds an ethylbenzene plant.

**[0006]** This invention combines the known technologies as developed for producing ethylbenzene from refinery FCC offgases, and for producing ethylene by conventional cracking of hydrocarbon feeds.

**[0007]** We are aware of United States Patent US 4 022 847 (McClure) in which a process and catalyst for the conversion of hydrocarbons is disclosed. The catalyst is an unsupported solid perfluorinated polymer containing pendent sulfonic acid groups. The processes include alkylation of isoparaffins, isomerization of normal alkanes, disproportionation of toluene, and the alkylation of benzene.

**[0008]** We are also aware of United States Patent US 4 107 224 (Dwyer) which discloses a process for the manufacture of ethyl benzene in which benzene and dilute ethylene are reacted in vapor phase over solid porous catalyst such as zeolite ZSM-5 in a series of reaction zones with intermediate injection of cold reactants and diluent to control temperature.

**[0009]** Further, we are aware of United States Patent US 4 720 293 (Rowles et al) which relates to a process for the

recovery of ethylene from a feed gas containing ethane, methane and other light gases, e.g. cracked gas or refinery off-gases, wherein ethylene is condensed in two stages, preferably rectified, and fed to an integrated demethanizer column. Refrigeration for the process is provided by an integrated combination of work expansion of rejected light gases, by vaporization of separated ethane at low partial pressure but high total pressure, and by a mixed refrigerant system. The process results in the separation and purification of ethylene from the feed gas stream while significantly reducing the energy consumption to do so.

**[0010]** Still further, we are aware of United States Patent US 5 463 154 which describes a method for acetylene hydrogenation which involves adding a member selected from the group consisting of arsine and phosphine to moderate the activity of acetylene hydrogenation catalyst while maintaining acceptable catalyst activity and avoiding the risk of product quality contamination by the acetylene converter moderator. The acetylene hydrogenation process involves adding arsine at a concentration level within the range of about 1 wppb-3 wppb to the gas, such as ethylene, containing acetylene to prevent temperature runaway during the exothermic acetylene hydrogenation reaction. By controlling the presence of arsine levels to such a relatively low level, temperature runaway during the highly exothermic acetylene hydrogenation reaction is prevented while maintaining acceptable catalyst activity levels for purposes of the acetylene hydrogenation reaction.

#### SUMMARY OF THE INVENTION

**[0011]** According to the invention there is provided a process for the simultaneous coproduction of ethylbenzene and ethylene as set out in the appended claims.

**[0012]** More particularly dilute ethylene at concentrations of 3 to 40 vol% and substantially free of propylene is extracted from a cryogenic demethanizer as an overhead gas. The bulk of the dilute ethylene stream comprises methane and hydrogen. The dilute ethylene stream at a typical pressure of 330 to 500 psig (**22.75- 34.48 Bar-g**) and after cold recovery and acetylene removal is the feed, along with common specification benzene, 99.9% wt% purity, or impure benzene, 95 to 98 wt% purity, to an ethylbenzene plant. The ethylbenzene is converted to styrene. If styrene is produced on site along with the ethylbenzene, it normally is produced by thermal dehydrogenation of ethylbenzene. Steam at 30 psig (**2.068 Bar-g**) and 1,500°F (**815°C**) is used as a source of energy and also reduces the partial pressure of ethylbenzene, is directly premixed with ethylbenzene in a typical weight ratio of 1.1 to 1.8. Superheating of steam at 30 (**2.068 Bar-g**) to 40 psig (**2.76 Bar-g**) to 1,500°F (**815°C**) in the cracking furnace of the ethylene plant becomes a second element of this invention. Low pressure saturated steam from the ethylbenzene and styrene plants and extraction steam from turbine drivers of the ethylene plant are superheated at the convection section of the cracker in the ethylene plant. The superheated steam is routed to the styrene plant, eliminating a specially dedicated superheater at the styrene plant.

**[0013]** If naphtha or heavier feeds are used, a pyrolysis gasoline product which is rich in benzene, is used as a source of benzene for the ethylbenzene plant. The benzene and co-boilers, cyclohexane and dimethylpentanes, are used as a feed to the ethylbenzene plant. The saturated C<sub>6</sub> co-boilers are purged from the ethylbenzene plant, ethylation reaction loop.

#### DESCRIPTION OF DRAWINGS

##### **[0014]**

FIG. 1 illustrates the cracking section of the ethylene plant and heat recovery with high pressure steam generation and superheating and includes low pressure steam superheating for a styrene plant which is an element of the invention.

FIG. 2 illustrates the quench oil and quench water pyrolysis gasoline and pyrolysis fuel oil recovery, cracked gas compression, CO<sub>2</sub> and H<sub>2</sub>S removal, cracked gas drying, pyrolysis gasoline hydrotreating, dehexanizer, benzene recovery, toluene conversion to benzene as a feed to the ethylbenzene plant.

FIG. 3 illustrates the dilute ethylene recovery which is the key element of the invention.

FIG. 4 illustrates the ethylene recovery, acetylene reactor and off specification ethylene diversion to the ethylbenzene plant, which is an element of the invention.

FIG. 5 illustrate ethylbenzene and styrene production along with hydrogen recovery.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0015]** For illustration and process consistency, the invention will be described for an ethylene plant when naphtha is the sole feedstock followed by ethylbenzene production and subsequent production of styrene monomer. This enables demonstration of all the elements of the invention. This is reasonable since more than 50% of world ethylene

production capacity originates from naphtha. The principles of this mode will be very similar for all other feedstocks.

**[0016]** The assumed capacity of the ethylene plant for consistency purposes is 1,000,000,000 lb/year, **(453,500 ton per year)** along with co-production of 400,000,000 lb/year **(181,400 ton per year)** of propylene and by products such as hydrogen, pyrolysis gasoline and pyrolysis fuel oil. 8,300 hours per year of operation are assumed. Pyrolysis products such as ethane, propane, C<sub>4</sub> and C<sub>5</sub> are internally recycled and converted to ethylene and propylene. Acetylene is selectively hydrogenated to ethylene, and methylacetylene and propadiene are selectively hydrogenated to propylene.

**[0017]** According to the invention, for illustrative purposes about 15% of the crude ethylene originated in the cracking, is recovered as a dilute ethylene product at a concentration of 10.0 vol.% and serves as a feed for production of 550,000,000 lb/year **(249,400 ton per year)** of ethylbenzene. The ethylbenzene is converted to 500,000,000 lb/year **(226,700 ton per year)** of styrene monomer, along with hydrogen and small amounts of other by products.

**[0018]** The cracking yield is based on of molecular weight of 92, a specific gravity of 0.69, paraffin content of 80 wt % (50% normal, 50% iso), naphthene content of 10 wt % and aromatic content of 10 wt%. The naphtha contains less than 0.1 wt% olefins and traces of sulfur.

**[0019]** With reference now to FIG. 1, Naphtha net feed, 10 33,000 bpsd **(4,921 M<sup>3</sup>/day)** (331,000 lb/hr) **(150.1 ton per hour)** and 65,000 lb/hr **(29.48 ton per hour)** of combined recycles 12 of C<sub>2</sub> H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> gas feed and C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>14</sub> liquids after hydrogenation, are vaporized in vaporizer 14 and mixed with steam in line 16, at a typical weight ratio of 0.5 steam to hydrocarbons feeds.

**[0020]** The steam helps reduce coking in the tubes of the furnaces, and also reduce the partial pressure of the hydrocarbons, thus increasing ethylene yield.

**[0021]** This hydrocarbon steam mixture is further preheated in heater 18 and proceeds, line 20 prior to the cracking section of the pyrolysis furnace 22. The furnace is fired by fuel gas principally CH<sub>4</sub> product 24 as recovered from the down stream process. The source of the CH<sub>4</sub> with reference to FIG. 3, is the cryogenic separation zone (80) in the ethylene plant. However, its final recovery is from the vent gas 121 in the ethylbenzene plant FIG. 5. For the above naphtha net feed and the recycles, the following typical yield, in weight percent per pass, is shown in Table 1.

TABLE 1

Component	Wt%	Destination
Hydrogen	1.05	Product to battery limit.
Methane	15.8	Fuel gas product to cracking furnaces
Acetylene	0.9	Converted to ethylene product
Ethylene	29.6	Main product to battery limits
Ethane	6.2	Recycled and converted to ethylene
Propadiene	0.6	Converted to propylene product
Propylene	14.0	Main product to battery limits
Propane	0.4	Recycled and converted to products.
C <sub>4</sub> Olefins + Paraffins	9.5	Hydrotreated and recycled to cracking
C <sub>5</sub> Olefins + Paraffins	4.5	Hydrotreated and recycled to cracking
Benzene	6.5	Light gasoline product, feed to ethylbenzene.
Toluene	2.3	Light gasoline product to battery limits or as a source of benzene
Xylene + Ethylbenzene	0.4	Heavy gasoline product to battery limits
Balance of Pyrolysis Fuel oil and pyrolysis gasoline (C <sub>6</sub> -C <sub>9</sub> )	8.1	Product to battery limit
H <sub>2</sub> S and CO <sub>2</sub>		Traces waste to battery y limits as sodium salts
CO	Trace	To fuel

**[0022]** The net ethylene make is 5.5 wt% of the naphtha feed in dilute form and 29.0 wt% of the naphtha feed in concentrated pure form. The net propylene recovery is 14.5 wt %.

**[0023]** In the heat recovery section 18 of the Cracker, hot combustion gas from the pyrolysis section undergoes heat recovery providing pre-heating boiler feed water 28 and superheating saturated steam 9 at 1,900 psig **(131 Bar-g)** and 650°F **(343°C)** to 1,800 psig **(124.1 Bar-g)** and 980°F **(526°C)** stream 30. The cracked gas 32 is cooled in transfer line exchangers 34 to 800 to 840°F **(426 - 448°C)** by generating saturated steam at 1,900 psig **(131 Bar-g)** and 650°F **(343°C)**. The overall steam production is typically in balance as a motive power source for the cracked gas compression and refrigeration compression drivers of the ethylene plant.

[0024] Due to the process integration concept of the invention, an additional steam coil 36 is used to convert stream at a pressure of 40 psig (**2.76 Bar-g**) and below 450 °F (**232 °C**) 38 to provide steam at 1,500°F (**815°C**) for the styrene plant 40. For a styrene production rate of 500,000,000 16/year (**226,700 ton per year**), the thermal load of the 40 psig (**2.76 Bar-g**) steam coils is estimated to be 6% of the overall conventional fired duty in the cracking furnace (22).

5 [0025] With reference to FIG. 2 The cracked gas at 800 to 840°F (**426-448°C**) and 10 psig (**0.69 Bar-g**) in line 42 after steam generation is quenched with pyrolysis fuel oil in quench zone 44 using oil recycle and heat absorption by generating saturated steam at 110-130 psig (**7.58-8.96 Bar-g**).

10 [0026] The net product made after stripping of light pyrolysis products is C<sub>9</sub>+, pyrolysis fuel oil. The steam at 110-130 psig (**7.58-8.96 Bar-g**) is ultimately used as a dilution steam for the naphtha and recycle feeds 16. Overhead gas 46 from the quench oil system at 220-250°F (**104-121°C**) proceeds to the quench water system 48, and preheat quench water at 110°F (43.3°C) in 50 (**43.3°C**) to 180°F (**82°C**) in line 52 and recovery of aromatic rich C<sub>6</sub>-C<sub>9</sub> pyrolysis gasoline 54. The 180°F (**82°C**) water 52 serves as a low level heat source to a number of reboiling services in the plant facility. After utilization of the low level heat, water at 110°F (**43.3°C**) is recycled back to the quench water system 48.

15 [0027] Quenched gas is further cooled to 100°F (**38°C**) with 88°F (**31°C**) cooling water (depending on ambient conditions) and the bulk of the water vapors and the C<sub>6</sub>+ products are condensed and separated. The cracked gas at 5.0 psig (**0.345 Bar-g**) proceeds by line 56 to compression. The gas is compressed to 400-600 psig (**27.6-41.4 Bar-g**) in four to five stages. For illustration purposes five stages of compression to 520 psig (**35.86 bar-g**) are assumed. After three stages of compression (58, 60, and 62) to 140 psig (**9.65 Bar-g**), the gas 64 proceeds to caustic scrubber (66) for CO<sub>2</sub> and H<sub>2</sub>S removal and further compressed at 68 and 70 to 520 psig (**35.86 Bar-g**) in line 72 and aftercooled to 100°F (**38°C**). The gas is further cooled in exchanger 74 to 60°F (**15.5°C**) by refrigeration or cold recovery prior to water/hydrocarbon separation. The gas proceeds to molecular sieve dryer 26 as needed for downstream cryogenic product recovery. At this point 99% of the benzene and C<sub>6</sub>, 85% of the C<sub>5</sub> hydrocarbon and 65% of the C<sub>4</sub> hydrocarbons are condensed and separated in lines at 15, 17, 19, 19A and 19B and send to raw pyrolysis gasoline 34.

25 [0028] Water and hydrocarbon liquids, mostly C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> are condensed in the interstage and after stage cooling of the cracked gas compression Fig. 2, stream 15, 17, 19, 19A and also from dryer prechilling (74) and water is separated (not shown). The combined hydrocarbon liquid 19c combines with aromatic rich stream 34 to feed stream 200 to selective olefin and di-olefin saturation unit 202. The hydro treated stream 36 free of sulfur, proceed to dehexanizer (201) where all C<sub>4</sub>, C<sub>5</sub>, and all C<sub>6</sub> except cyclohexane and benzene are separated overhead, at an atmospheric cut point of 167°F (**75°C**). This light saturated liquid 200 A recycles back to cracking section 14, (Fig. 1).

30 [0029] Bottom product from 201 fractionation, proceeds to de-cyclohexanizer 205 where benzene, cyclohexane and dimethylpentanes are separated, at an atmospheric cut point of 183 °F (**84°C**). The overhead product, stream 206 is impure benzene containing typically 2-8 wt% of cyclohexane and dimethylpentanes. This impure benzene is used as a feed for the ethylbenzene 120 (Fig. 5). Toluene rich stream 207, can proceed to battery limits or alternately to toluene fractionation 220. Overhead toluene proceeds to conventional hydro-dealkylation 221 where hydrogen reacts with toluene to form benzene and methane.

35 [0030] With reference to new FIG. 3, 12710 lb-mol/hr (**5,764 kg-mol per hour**) of dry cracked gas at 500 psig (**34.48 Bar-g**) and 60°F (**15.5°C**) in line 78 with the molecular composition shown in Table 2, proceeds to a chill down train for cryogenic product recovery.

TABLE 2

Component	Mol%
Hydrogen	16.9
Methane	31.8
Acetylene	0.85
Ethylene	33.0
Ethane	5.65
CO	0.25
Propadiene/ Methyl Acetylene	0.35
Propylene	8.90
Propane	0.45
C <sub>4</sub> olefins	1.40
Butanes	0.15
C <sub>5</sub> +	0.25

40  
45  
50  
55 [0031] In an alternate design (not shown) cracked gas after the 4 stages of compression, at 270 psig (**18.62 Bar-g**), will go through H<sub>2</sub>O/CO<sub>2</sub> removal, molecular sieve drying and than a chill down for C<sub>2</sub>/C<sub>3</sub> separation in a front end

deethanizer. The C<sub>2</sub> and lighter fractions are warmed up undergo acetylene hydrogenation to form ethylene and the C<sub>3</sub> and heavier hydrocarbon liquids proceed to propylene and C<sub>4</sub>+ recovery. The acetylene free light gas at 260 psig (**17.93 Bar-g**) is further compressed through the 5th stage to 520 psig (**35.86 Bar-g**). In yet another alternate design (not shown) the front end separation of the C<sub>2</sub> and lighter hydrocarbons will be carried out at 500 psig (**34.48 Bar-g**) using double fractionation system.

**[0032]** In the primary design, as well as alternate designs, the dry cracked gas at 500 psig (**34.48 Bar-g**) and 60°F (**15.5°C**) in line 78 is chilled down to -200°F (**-129°C**) using propylene and ethylene refrigeration, followed by an expander or methane refrigeration (not shown). At this point essentially all the ethylene (99.9%) is condensed in several stages along with the bulk of the methane, and hydrogen rich gas (75% H<sub>2</sub>) is separated from the crude ethylene liquids which are fed to a demethanizer 80, operating at 300 to 500 prig (**20.68-34.48 Bar-g**) and, for this illustration, preferably 460 psig (**31.7 Bar-g**). In a conventional design, the overhead product of the demethanizer overhead is essentially methane, some residual hydrogen with very minimal quantity, say 100 vol. ppm, of ethylene. The bottom product is essentially ethylene, ethane, propylene and C<sub>3</sub>+ hydrocarbons. Methane content is under 100 ppm and hydrogen content is essentially nil. In a conventional design, the ethylene in the overhead of the demethanizer at 48 represents a net ethylene product loss to the fuel gas system, thus a good economical design should minimize its content by appropriate reflux of liquid methane stream 47 at typically -145°F (62.8°C). The cold for the reflux is provided by ethylene refrigeration at -150°F (**-101°C**) which corresponds to slightly above its atmospheric pressure. Typically 99.8% of the ethylene, and essentially 100% of the ethane and acetylene from the charge gas are recovered as a bottom product for further processing and separation. The same is essentially true for the alternate designs except that essentially no C<sub>3</sub>+ and acetylene are present in the bottom of the demethanizer.

**[0033]** In the conventional design stream 48 the CH<sub>4</sub>/H<sub>2</sub> overhead from the demethanizer at 460 psig (31.7 Bar-g) is typically expanding to fuel gas pressure of 50 psig (**3.45 Bar-g**) in a turbo-expander, (not shown) generating motive power as well as refrigeration (needed for the low temperature ethylene condensation and hydrogen separation). The cold is recovered from the H<sub>2</sub>/CH<sub>4</sub> rich gas prior to diversion to the fuel system for subsequent combustion in the cracking furnaces.

**[0034]** In the instant invention all hydrogen separation occurs in the demethanizer, unless the invention is applied toward revamp of an existing plant. The bottom liquid product 54 of the demethanizer 80 at 50°F (**10°C**) proceeds is let down to deethanizer 100 operating at 280 psig (**19.3 Bar-g**). The ethylene, acetylene and ethane are separated as overhead product 102 and propylene and C<sub>3</sub>+ hydrocarbons as bottom products 39. The overhead product 102 with 1.9 wt % acetylene is reheated to 130°F (**54.4°C**) and to passed acetylene hydrogenator 104 with outside hydrogen source 106. The acetylene free, C<sub>2</sub> vapor is condensed by preheating the feed in exchange 108 and proceeds to ethylene fractionator 112 at 240 psig (**16.55 Bar-g**), or lower pressure depending on final disposition of the ethylene product, and the refrigeration system. The above acetylene removal step is not required for the alternate designs, since acetylene is converted upstream of the demethanizer.

**[0035]** The overhead product 114 from the ethylene fractionator 112 is off specification ethylene product. The side draw 79 typically drawn 8-10 trays below the top in the ethylene fractionator. Residual methane originated from the demethanizer and excess hydrogen from the acetylene converter, are vented (if necessary) from the overhead as offspecification ethylene 114.

**[0036]** The offspecification ethylene is suitable as a feed to the ethylbenzene plant. The amount of flow after cold recovery in 116 is small. The ethylene is mixed in an ejector 94 with the bulk of the dilute ethylene feed 53 containing 10% ethylene and 5 ppm acetylene and propylene, and send to ethylbenzene plant 120. The bottom product 122, essentially ethane is re-vaporize via cold recovery and sent to the cracking section 14. In the alternate design (not shown), demethanizer bottom proceeds directly to the ethylene fractionator 112. The C<sub>3</sub>+ hydrocarbon product undergoes separation of C<sub>3</sub> and C<sub>4</sub>+ hydrocarbon (not shown). The C<sub>3</sub> product is undergoes hydrogenation of the methyl acetylene and propadiene and proceeds to propylene fractionation (not shown). The overhead product is propylene, the bottom product is propane which is recycled to the cracking section 14.

**[0037]** In the invention the demethanizer is operating in a "sloppy cut" mode, for ethylene and also separate all the hydrogen at the overhead. For illustrative purposes the demethanizer overhead rather than operating with full ethylene recovery at the bottom and essentially no ethylene at the top, has 10 mol% or more ethylene in the overhead and typical propylene content of below 5 ppm by volume. The methane specification for the bottom will be 100 to 2,000 mol-ppm. By allowing ethylene to escape from the top, at 10 mol% concentration, about 15% of the ethylene, 2% of the ethane, and 8% of the acetylene feeds to the demethanizer, will go overhead. The overhead product gas 6,890 lb-mol/hr (**3,125 kg-mol/hr**) at -115°F (**-81.5°C**) and 450 psig (**31.0 Bar-g**) will have the molecular composition shown in Table 3:

TABLE 3

Component	Lb-mol/hr(kg-mol/hr)		Mol %
Hydrogen	2147	<b>973.6</b>	31.1
CO	31	<b>14.0</b>	0.44
Methane	4041	<b>1832</b>	58.6
Acetylene	9	<b>4.1</b>	0.13
Ethylene	650	295	9.5
Ethane	13	<b>5.9</b>	0.19
Propylene	0.03	<b>0.015</b>	5 ppm

**[0038]** With the reference to FIG. 3, the gas is preheated via cold recovery 122 and 124 to 92°F (33.3°C) and further preheated in exchanger 86 to 130°F (54.4°C) prior to acetylene reactor 88. The acetylene free gas 52 proceeds to activated carbon beds 90 for removal of C<sub>6</sub>-C<sub>8</sub> trace formed in acetylene reactor 88. For the alternate case, these steps are not required. As further optimization, not shown, side reboiler and side condensers can be used for increasing refrigeration economy. Dilute ethylene can be made as a side draw product.

**[0039]** Propylene and acetylene free gas at 415 psig (28.62 Bar-g) in line 53 combines with off specification ethylene from ethylene fractionator in ejector 94 and the combined gas 118 proceeds as feed to the ethylation reactor section 120 of the ethylbenzene plant.

**[0040]** For process control purposes, liquid ethylene product provides up to 10% of the feed to the ethylbenzene plant.

**[0041]** Liquids, mostly C<sub>4</sub>, C<sub>5</sub>, and C<sub>6</sub> as condensed in the gas compression inter and after coolers FIG. 2. 19C combines with 34 to a C<sub>4</sub>-C<sub>8</sub> raw pyrolysis gasoline 200. The raw pyrolysis gasoline is undergoing selective di-olefins and olefins saturation qt. 201. Hydrotreated liquid 36 and C<sub>6</sub> boilers below benzene (170°F) (76.6°C) are separated at 202, and sent at 203 for cracking at 14. C<sub>6</sub>+ stream at 204, is sent to dehexanizer 205 where benzene and cyclohexane are separated. 206 lb from heavy C<sub>6</sub> and C<sub>7</sub> = 207. The benzene cyclohexane, 206 containing over 90 wt% benzene is used as impure benzene feed to the ethylbenzene plant 120.

**[0042]** In the ethylbenzene plant 120, ethylene reacts with benzene feed 206 and stoichiometric excess of benzene. The exothermic reaction forms ethylbenzene and poly ethylated benzene (PEB). In a separate trans alkylation reactor 126 the polyethylated benzene reacts with benzene to form ethylbenzene. After series of products fractionation and purifications (128-130), the final products are: (1) Ethylbenzene with purity above 99.5%; (2) Vent gas 132 depleted of 95-99% of the ethylene feed and containing 34.5 mol% of hydrogen; and (3) A small amount, 0.5-2.0% of the benzene remains converted to polyethylated product commonly referred to as flux oil (134) The flux oil is routed to pyrolysis fuel oil. The cyclohexane and dimethylpentanes are close boilers to benzene and purged 208 from the benzene recycle loop with 75 wt% benzene. The purge will go to battery limits or to conventional extraction of benzene 212 and benzene 211 will recycle to the feed. The cyclohexane residue 210 will go to battery limits. Additional benzene can be made by separation of toluene. FIG. 2,220 and conversion of toluene to benzene by hydrodelakylation 221 which is a conventional and known process. After toluene conversion, the benzene, will be used as make up 60% of the requirement for the ethylbenzene production. Without toluene conversion, the benzene will provide about 40% of the requirement. As an alternative, cyclohexane rich purge 213 will go to benzene hydrogenation for cyclohexane production 214.

**[0043]** If high benzene conversion yield is desired, the cyclohexane rich purge 208 can be ethylated in a purge reactor (not shown). The benzene reacts with ethylene to form ethylbenzene and polyethylated benzene. The reaction products will go through a fractionation (not shown). Benzene cyclohexane and other co-boilers will be separated at an atmospheric cut point of 183 °F (84°C). Ethylbenzene and polyethylated benzene will be recycled to the trans alkylation reaction 126 (Fig. 5).

**[0044]** As another alternative (not shown) cyclohexane can be selectively oxidized to cyclohexanol. The cyclohexanol will be separated by fractionation to be recovered as valuable product.

## Claims

1. A process for the simultaneous coproduction of ethylbenzene from dilute ethylene along with purified ethylene as a key product which comprises:

- (a) forming in one or more hydrocarbon cracking zones a fluid mixture comprising hydrogen, carbon monoxide, methane, ethylene, and ethane;
- (b) fractionating said fluid mixture in a demethanization zone to form (1) a dilute ethylene fluid mixture com-

prising hydrogen, carbon monoxide, methane, and ethylene, in which ethylene is present in an amount ranging from 3 to 40 mol% and (2) bottoms comprising ethylene and ethane;  
 (c) reheating the dilute ethylene fluid mixture;  
 (d) feeding the dilute ethylene fluid mixture to an ethylbenzene production zone, wherein the dilute ethylene fluid mixture fed to the ethylbenzene production zone contains no more than 200 mol-ppm of propylene;  
 (e) providing a benzene stream comprising benzene;  
 (f) introducing the benzene stream to the ethylbenzene production zone;  
 (g) reacting the ethylene in the dilute ethylene fluid mixture with the benzene to form ethylbenzene in the ethylbenzene production zone; and  
 h) further purifying the bottoms for ethylene product recovery.

2. A process as claimed in claim 1, further comprising further processing the bottoms for propylene product recovery.
3. A process as claimed in claim 1, wherein the fractionation of the fluid mixture in the demethanization zone forms a dilute ethylene vapor mixture comprising no more than 200 mol-ppm of propylene.
4. A process as claimed in claim 1, wherein the dilute ethylene fluid mixture further comprises acetylene and wherein the acetylene is hydrogenated to ethylene prior to being fed to the ethylbenzene production zone.
5. A process as claimed in claim 1, in which the dilute ethylene fluid mixture contains from 8 to 25 mol percent ethylene.
6. A process according to any of the above claims, further comprising converting the ethylbenzene to styrene.
7. A process as claimed in claim 6, further comprising producing steam in the ethylbenzene production zone, superheating the steam at (10 to 70 psig) 0.69-4.83 Bar-g in the cracking zone, and feeding the steam to a styrene production zone as a source of thermal energy during conversion of ethylbenzene to styrene.

#### Patentansprüche

1. Ein Verfahren für die gleichzeitige Herstellung von Ethylbenzol aus verdünntem Ethylen zusammen mit gereinigtem Ethylen als Hauptprodukt, das folgendes umfasst:
  - a) die Bildung eines Fluidgemischs, das Wasserstoff, Kohlenmonoxid, Methan, Ethylen und Ethan enthält, in einer oder mehrerer Kohlenwasserstoffspaltzonen;
  - b) die Fraktionierung des Fluidgemischs in einer Demethanisierungszone, um (1) ein verdünntes Ethylenfluidgemisch, das Wasserstoff, Kohlenmonoxid, Methan und Ethylen enthält, in der Ethylen in einer Menge von 3 - 40 mol% enthalten ist und (2) einen Sumpf, der Ethylen und Ethan enthält, herzustellen;
  - c) Rückerhitzen des verdünnten Ethylenfluidgemischs
  - d) Einspeisen des verdünnten Ethylenfluidgemischs in die Ethylbenzolproduktionszone, wobei das in die Ethylbenzolproduktionszone eingespeiste, verdünnte Ethylenfluidgemisch nicht mehr als 200 mol-ppm an Propylen enthält;
  - e) Bereitstellen eines Benzolstroms, welcher Benzol enthält;
  - f) Einleiten des Benzolstroms in die Ethylbenzolproduktionszone;
  - g) Umsetzen von Ethylen aus dem verdünnten Ethylenfluidgemisch mit Benzol zu Ethylbenzol in der Ethylbenzolproduktionszone;
  - h) weiteres Reinigen des Sumpfes zur Ethylenproduktgewinnung.
2. Ein Verfahren nach Anspruch 1, das zusätzlich die weitere Aufarbeitung des Sumpfes zur Propylengewinnung umfasst
3. Ein Verfahren nach Anspruch 1, bei dem die Fraktionierung des Fluidgemischs in der Demethanisierungszone ein verdünntes, gasförmiges Ethylengemisch, das nicht mehr als 200 mol-ppm an Propylen enthält, bildet.
4. Ein Verfahren nach Anspruch 1, bei dem das verdünnte Ethylenfluidgemisch ausserdem Acetylen enthält, wobei das Acetylen zu Ethylen hydriert wird bevor es der Ethylbenzolproduktionszone zugeführt wird.
5. Ein Verfahren nach Anspruch 1, bei dem das verdünnte Ethylenfluidgemisch 8 bis 25 mol % Ethylen enthält.



6. Ein Verfahren gemäß einem der oben genannten Ansprüche, das zusätzlich die Umwandlung von Ethylbenzol zu Styrol umfasst.
7. Ein Verfahren nach Anspruch 6, das weiter umfaßt: Herstellen von Dampf in der Ethylbenzolproduktionszone, Überhitzen des Dampfes bei (10 bis 70 psig) 0,69-4,83 Bar-g in der Spaltzone, und Zuführen des Dampfes in die Styrolproduktionszone als Wärmeenergiequelle während der Umwandlung von Ethylbenzol in Styrol.

**Revendications**

1. Un procédé pour la co-production simultanée d'éthylbenzène à partir d'éthylène dilué, avec d'éthylène purifié en tant que produit-clé comprenant :
- a. la production dans une ou plusieurs zones de craquage d'hydrocarbures d'un mélange fluide comprenant d'hydrogène, monoxyde de carbone, méthane, éthylène et éthane ;
  - b. le fractionnement du dit mélange fluide dans une zone de déméthanisation pour produire (1) un mélange fluide d'éthylène dilué comprenant hydrogène, monoxyde de carbone, méthane et éthylène, dans lequel la concentration en éthylène est comprise entre 3 et 40% mole ; et (2) un fond de fractionnement comprenant éthylène et éthane ;
  - c. le réchauffage du mélange fluide d'éthylène dilué ;
  - d. l'alimentation du mélange fluide d'éthylène dilué vers une zone de production d'éthyl-benzène, où le propylène dans le mélange fluide d'éthylène dilué qui est alimenté vers la zone de production d'éthyl-benzène n'excède pas 200 ppm mole ;
  - e. l'approvisionnement d'un flux de benzène contenant du benzène ;
  - f. l'introduction du flux benzène vers la zone de production d'éthyl-benzène ;
  - g. la réaction de l'éthylène inclus dans le mélange fluide d'éthylène dilué avec le benzène pour produire de l'éthyl-benzène dans la zone de production d'éthyl-benzène ;
  - h. la purification du fond de fractionnement pour récupérer de l'éthylène.
2. Un procédé tel que revendiqué dans la revendication 1, incluant le traitement supplémentaire du fond de fractionnement pour récupération du propylène.
3. Un procédé tel que revendiqué dans la revendication 1, où le fractionnement du mélange fluide dans la zone de déméthanisation produit un mélange de vapeur d'éthylène dilué ne contenant pas plus de 200 ppm mole de propylène.
4. Un procédé tel que revendiqué dans la revendication 1, où le flux d'éthylène dilué comprend additionally de l'acétylène et où l'acétylène est hydrogéné en éthylène avant alimentation vers la zone de production d'éthyl-benzène.
5. Un procédé selon la revendication 1, où le mélange fluide d'éthylène dilué contient entre 8% et 25% mole éthylène.
6. Un procédé selon n'importe laquelle des revendications ci-dessus, comprenant additionally la conversion d'éthyl-benzène en styrène.
7. Un procédé tel que revendiqué dans la revendication 6, comprenant additionally la production de vapeur d'eau dans la zone de production d'éthyl-benzène, la surchauffe de la vapeur d'eau à (10 - 70 psig) 0.69 - 4.83 Bar-g dans la zone de craquage, et l'alimentation de la vapeur d'eau vers la zone de production de styrène comme source d'énergie thermique lors de la conversion d'éthyl-benzène en styrène.

FIG. 1

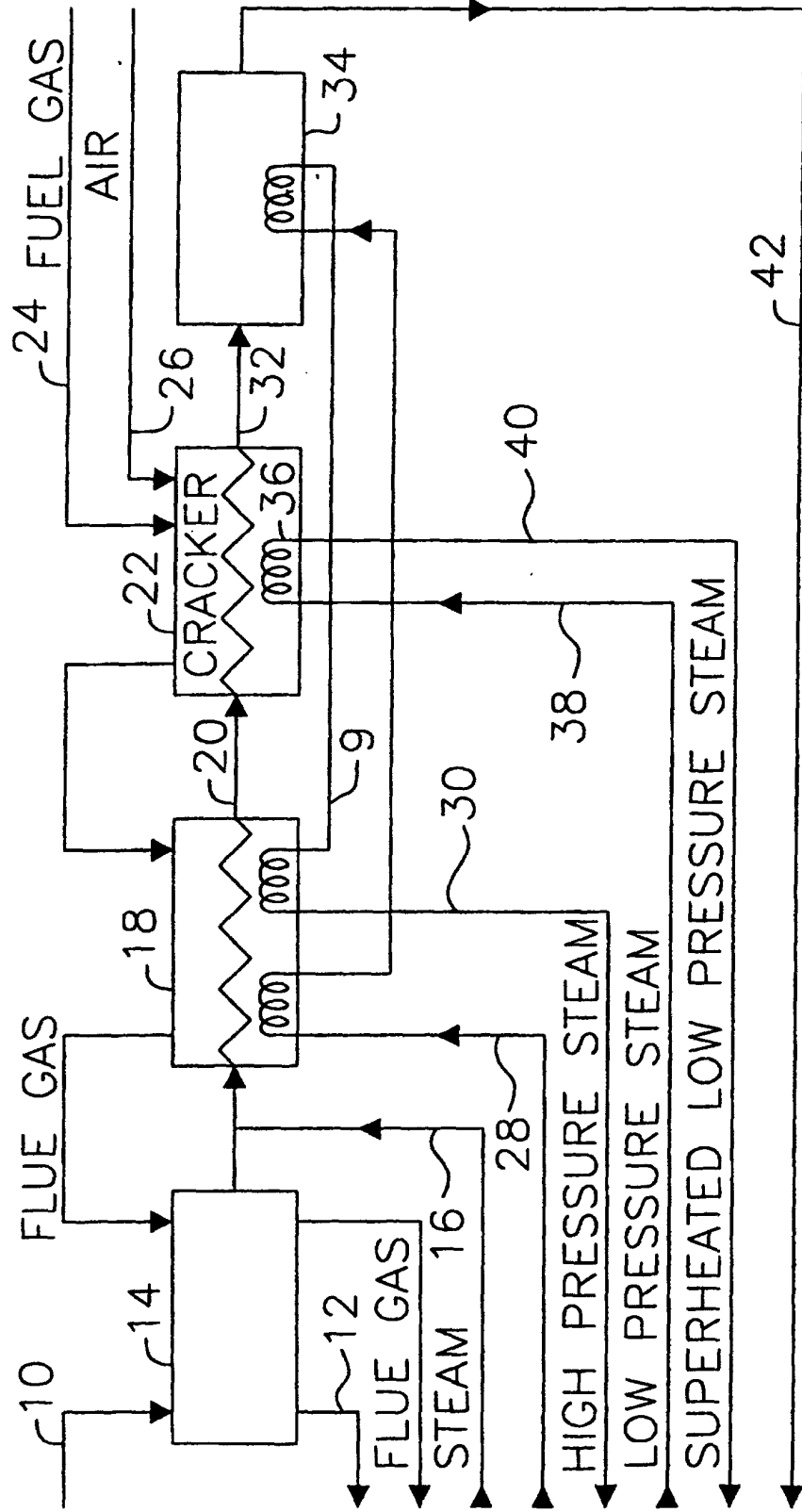
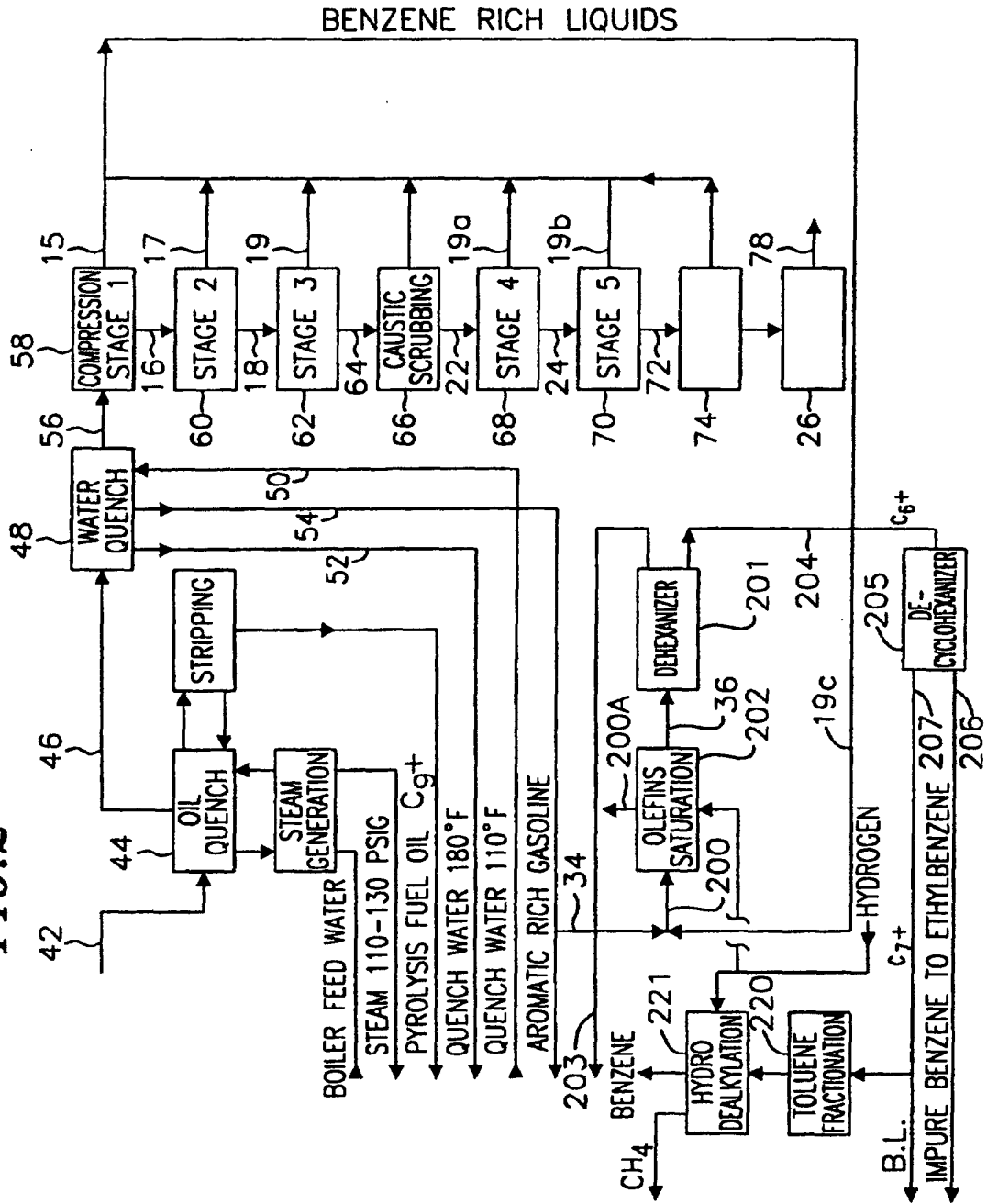
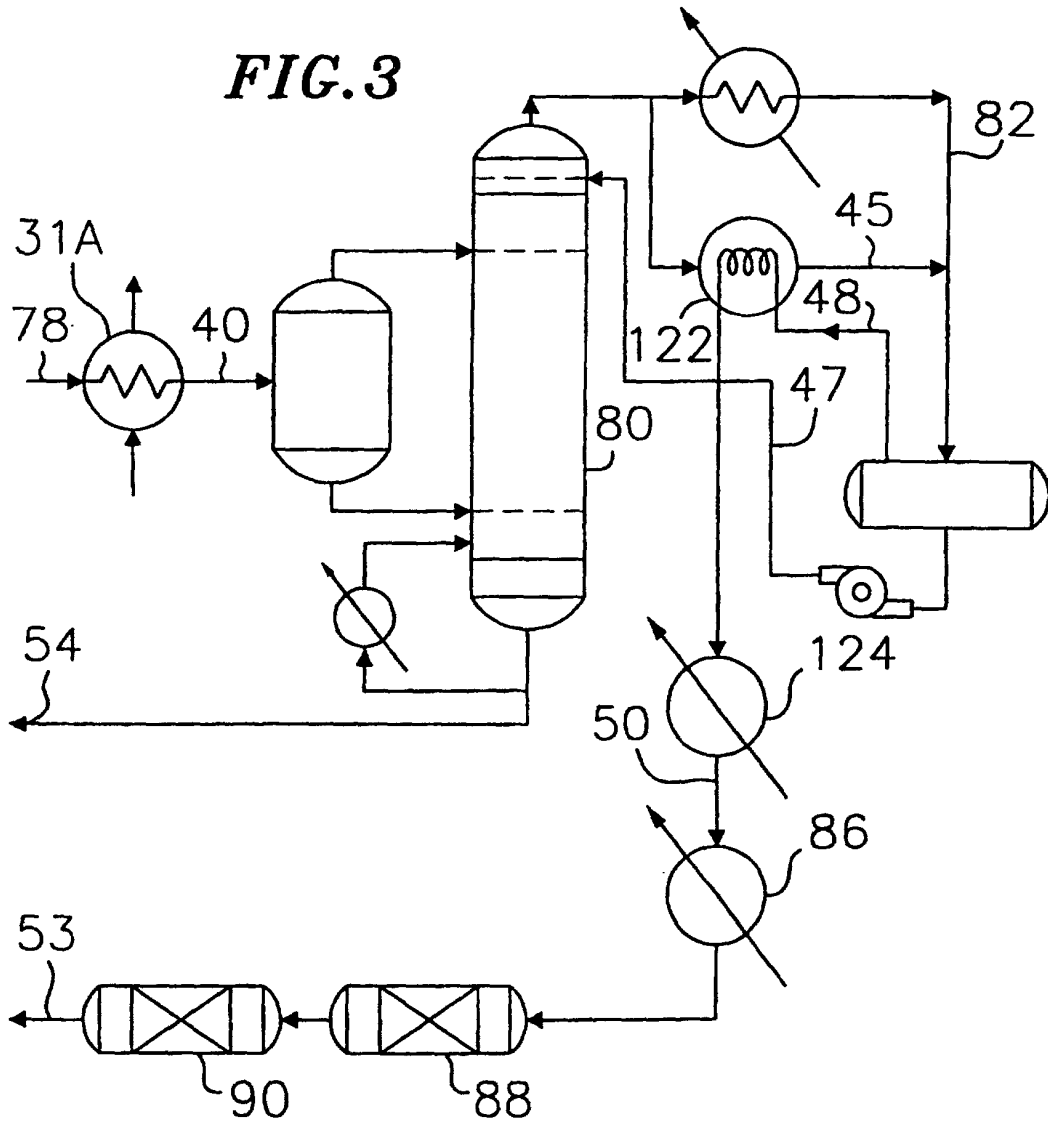


FIG. 2



**FIG. 3**



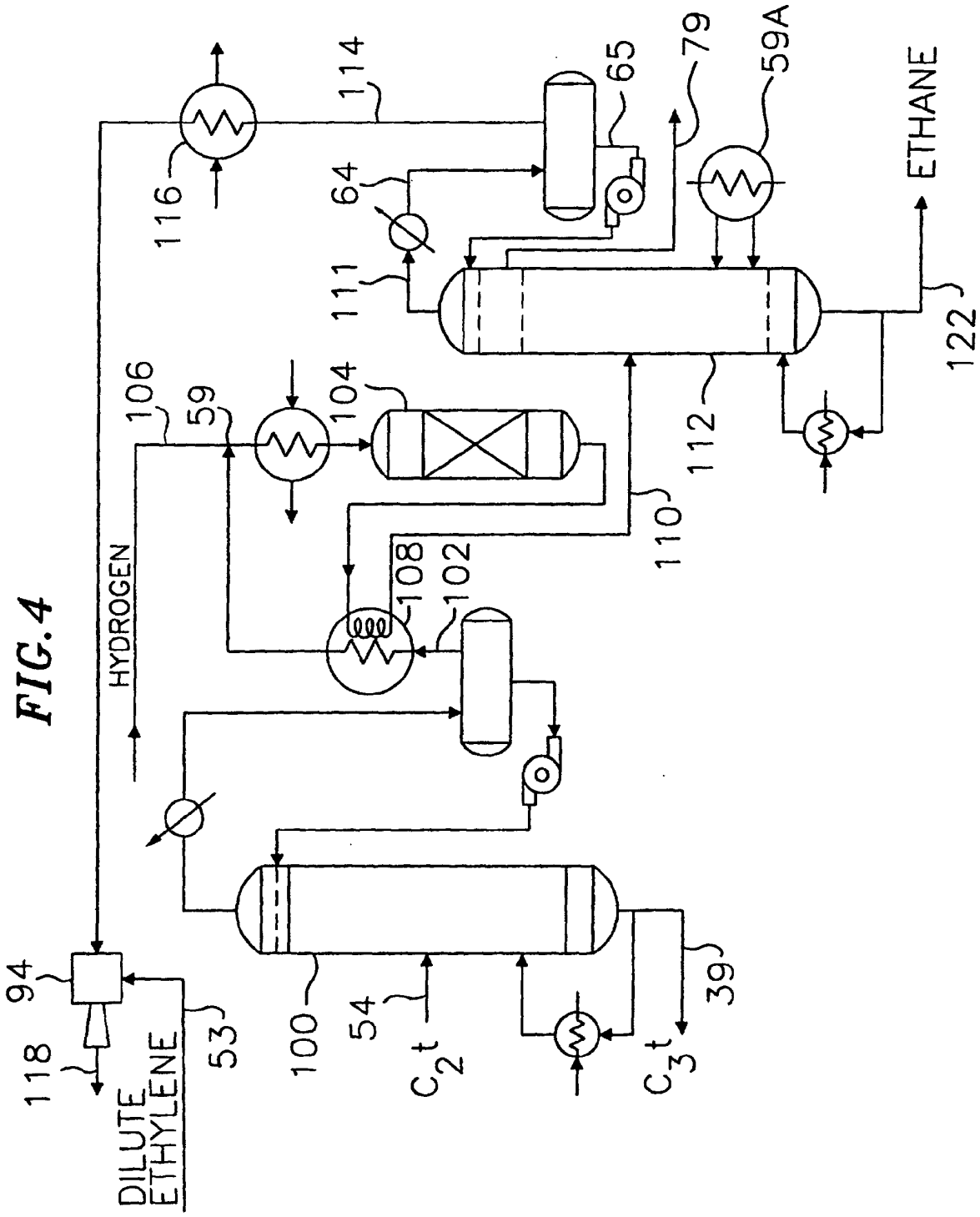


FIG. 5

