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(54) **Catalytic conversion of light-olefinic feedstocks in a fluidized-catalytic-cracking gas plant.**

(57) Olefin-containing streams in the gas plant of a fluid catalytic cracking unit can be catalytically converted to gasoline and/or fuel oil fraction by employing a ZSM-5 type zeolite as the catalyst. Minimum capital investment is required since the separation and recovery facilities of the gas plant may be utilized.

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CATALYTIC CONVERSION OF LIGHT OLEFINIC FEEDSTOCKS IN A FCC GAS PLANT

This invention relates to the catalytic conversion of olefinic feedstocks in a FCC gas plant to gasoline and fuel oil using a ZSM-5 type zeolite catalyst.

The present invention provides a process for producing a gasoline fraction and/or a fuel oil fraction by contacting a feedstock comprising C_2 to C_5 olefins with a crystalline aluminosilicate zeolite having a pore diameter greater than 5 Angstrom Units, a silica-to-alumina ratio of at least 12 and a constraint index of from 1 to 12 under reaction conditions effective to convert the olefins to a gasoline fraction and/or a fuel oil fraction, characterized by employing as the feedstock the discharge stream from the final stage of the wet gas compressor or the overhead from the high pressure receiver in the gas plant of a fluid catalytic cracking unit and passing the effluent from the zeolite-catalyzed conversion through the separation and recovery facilities of the gas plant to recover the gasoline fraction and/or the fuel oil fraction.

Hydrocarbon mixtures containing significant quantities of light olefins are frequently encountered in petrochemical plants and petroleum refineries. Because of the ease with which olefins react, these streams serve as feedstocks in a variety of hydrocarbon conversion processes. Many olefinic conversion processes require that the olefinic feed be provided in a highly purified condition. However, processes which may utilize the olefinic feedstocks without the need for further separation and purification are highly desirable.

Although the main purpose of catalytic cracking is to convert gas oil to compounds of lower molecular weight in the gasoline and middle distillate boiling ranges, significant quantities of C_1-C_4 hydrocarbons are also produced. These light hydrocarbon gases are rich in olefins which heretofore have made them prime candidates for conversion to gasoline blending stocks by means of polymerization and/or alkylation. Fractionation of the effluent from the fluid catalytic cracking reactor has been employed to effect an initial separation of this stream. The gaseous overhead from the main fractionator is collected and processed in the FCC gas plant. Here the gases are compressed, contacted with a naphtha stream, scrubbed, where necessary, with an amine solution to remove sulfur and then fractionated to provide, for example, light olefins and isobutane for alkylation, light olefins for polymerization, n-butane for gasoline blending and propane for LPG. Light gases are recovered for use as fuel.

Since alkylation units were more costly to build and operate than polymerization units, olefin polymerization was initially favored as the route for providing blending stocks. Increased gasoline demand and rising octane requirements soon favored the use of alkylation because it provided gasoline blending stocks at a higher yield and with a higher octane rating than the comparable polymerized product. However, catalytic alkylation can present some safety and disposal problems. In addition, feedstock purification is often required to prevent catalyst contamination. Further, sometimes there is insufficient isobutane available in a refinery to permit all the olefins from the FCC to be catalytically alkylated.

The broad concept of contacting an olefinic charge stock with the special class of zeolites with which this invention is concerned is known in the art and is the subject of various U.S. patents. Thus, for example, U.S. Patent No. 3,960,978 teaches conversion of olefins to olefinic gasolines. U.S. Patent No. 4,021,502 discloses conversion of olefins over ZSM-12. U.S. patent No. 3,760,024 discloses contacting olefins with ZSM-5 type zeolites. U.S. Patent No. 3,775,501 discloses preparation of aromatics by contacting olefins over ZSM-5 type catalysts. U.S. Patent No. 3,827,968 discloses a two-step aromatization process wherein in the first step an olefin is contacted over a ZSM-5 type zeolite. U.S. Patent No. 4,211,640 discloses a process for contacting a highly olefinic gasoline with a ZSM-5 type zeolite to produce fuel oil and gasoline having enhanced gum stability. U.S. Patent No. 4,227,992 discloses a process for separating ethylene from a mixture of C_2-C_5 olefins by contacting the mixture with a ZSM-5 type zeolite under conditions effective to convert at least 80% of the C_3+ olefins and no more than 20% of the ethylene. However, none of the prior art is directed toward the conversion of olefinic gas streams in a fluid catalytic cracking (FCC) unit gas plant to gasoline and fuel oil.

This invention relates to an improvement in the process for producing a gasoline fraction and/or a fuel oil fraction by contacting a feedstock comprising C_2 to C_5 olefins with a crystalline aluminosilicate zeolite having a pore diameter greater than 5 Angstrom Units, a silica-to-alumina ratio of at least 12 and a constraint index of from 1 to 12 under reaction conditions effective to convert the olefins to a gasoline fraction and/or a fuel oil fraction, the improvement comprising employing as the feedstock the discharge stream from the final stage of the wet gas compressor or the overhead from the high pressure receiver in the gas plant of a fluid catalytic cracking unit and passing the effluent from the zeolite catalyzed conversion through the separation and recovery facilities of the gas plant to recover the gasoline fraction and/or the fuel oil fraction.

In general, the catalysts used in accordance with this invention are crystalline zeolites having a silica/alumina ratio greater than 12 and a Constraint Index (C.I.) of from 1 to 12. The zeolites are generally termed ZSM-5 type zeolites. These zeolites and their use as conversion catalysts for olefins are described in the U.S. patents referred to above, particularly U.S. Patent Nos. 3,760,024, 3,960,978, 4,021,502, 4,211,640 and 4,227,992.

The preferred class of zeolites defined herein are ZSM-5 type zeolites as exemplified by ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-38, with ZSM-5 being particularly preferred.

ZSM-5 is described in U.S. Patent No. 3,702,886, ZSM-11 in U.S. Patent No. 3,709,979, ZSM-12 in U.S. Patent No. 3,832,449, ZSM-35 in U.S. Patent No. 4,016,245 and ZSM-38 in U.S. Patent No. 4,046,859.

By utilizing the olefinic feedstreams of a FCC gas plant as feedstocks in the present invention, the need for separate processes for the polymerization or alkylation of the olefins in this stream is obviated or reduced. The concept of utilizing a ZSM-5 type zeolite catalyzed conversion instead of the prior art processes for providing C_5+ gasoline and/or fuel oil blending stocks has many advantages. Since the ZSM-5 type zeolites can tolerate the poisoning effects of the impurities normally found in raw FCC product streams, extreme purification procedures often encountered in polymerization and alkylation do not have to be employed. Also, locating the process of this invention in the FCC gas plant reduces the capital investment and operating costs required for a conversion process of this nature since no new product recovery facilities have to be provided. The effluent from the catalytic conversion can continue through the gas plant which has the facilities required to separate the gasoline fraction and/or fuel oil fraction as blending stocks from the lighter materials which are recovered as LPG and fuel gas. The only new equipment which must be provided to practice the olefin conversion in accordance with this invention is a catalytic reactor, feed/effluent heat exchangers and a preheat furnace.

Although there are a number of streams in the gas plant of a FCC unit which contain light olefins which might be usefully employed in this invention, two of them are preferred. The discharge stream from the final stage of the wet gas compressor and the overhead from the high pressure receiver are these preferred streams. The multi-stage wet gas compressor in the gas plant is required to increase the pressure of the gaseous overhead from the FCC main fractionator so that it may be effectively processed in the gas plant. The discharge from the final stage is usually from 1308 to 1653 kPa (175 to 225 psig) and 149 to 177°C (300 to 350°F). Where the sulfur content of the FCC light gases is significant, an amine scrubber, employing mono-, di- or triethanol amine or mixtures thereof, may be located between the stages of the wet gas compressor or immediately upstream of the conversion facilities which are the subject of this invention to reduce the sulfur content to acceptable levels. Where the levels of ammonia are significant, a water wash stage might also be incorporated to reduce ammonia content and to remove traces of entrained amine solution.

The overhead from the high pressure receiver associated with the wet gas compressor is the other preferred feedstock for the present process. This gaseous stream does not have the same composition as the discharge from the compressor since other streams, such as the liquid from the interstage receiver and the rich liquid from the primary absorber, as well as the stripper overhead, discharge into this vessel. The gas stream passing from the high pressure receiver is usually at from 1136 to 1480 kPa (150 to 200 psig) and from 32 to 43°C (90 to 110°F).

In general, the process of this invention is carried out at a pressure from 1136 to 1825 kPa (150 to 250 psig), a temperature from 149 to 399°C (300 to 750°F) and a space velocity of from 0.1 to 10 WHSV, based on the C_2 to C_5 olefins.

As has been stated hereinbefore, the broad concept of contacting olefins, alone or in admixture with each other or other hydrocarbons, over the identified catalyst with which this invention is concerned is not per se novel. The key to this invention resides in selecting a C_2 to C_5 olefins-containing gas stream in a FCC gas plant as the feedstock for the desired catalytic conversion and the use of the separation and recovery facilities of the gas plant to process the effluent from the catalytic conversion such that gasoline and/or fuel oil fractions useful in gasoline and fuel oil blending may be produced without the necessity of providing product recovery facilities, thereby minimizing the capital investment and operating costs for the subject process.

The improvements described herein can be illustrated by reference to Figures 1 and 2 which present, respectively, a flowplan of a FCC gas plant and a flowplan of an embodiment of this invention. The dotted squares labeled A and B in Figure 1 indicate the alternate locations for the reactor and attendant equipment depicted in Figure 2.

Referring to Figure 1, the condensed overhead from the FCC main fractionator flows through line 2 into FCC main fractionator overhead accumulator 4 for separation into a gaseous phase and a liquid phase. The gaseous portion of the column overhead flows from accumulator 4 to the FCC gas plant through line 6 to the suction of the first stage of wet gas compressor 8 for the initial increase in pressure. The wet gas discharges from the first stage of the compressor through line 10 to interstage receiver 12 and line 14 and then through the second stage of the wet compressor from which it is discharged through line 16 at about 163°C (325°F) and about 1480 kPa (200 psig). Where the sulfur level of the gaseous stream is above acceptable levels, an ethanolamine scrubber (not shown) may be located in line 10 to reduce the sulfur content to acceptable levels. Alternatively the scrubber may be located upstream of the reactor and equipment depicted in Figure 2, i.e., in lines 16 or 32.

As a first option, the gas stream in line 16 may be employed in the practice of this invention. This stream typically has a composition as shown in Table I. Referring to Figure 2, which may be considered as being located at position A of Figure 1, the olefinic stream in line 16 passes through heat exchanger 102 where it is pre-heated by indirect heat exchange with the reactor effluent, described hereinafter. The partially

TABLE I

USEFUL FEEDSTREAMS

Component, mol. %	2ND STAGE WET GAS COMPRESSOR OUTLET		HIGH PRESSURE RECEIVER OVERHEAD	
	With Amine (1) Scrubber	No Amine Scrubber	With Amine (1) Scrubber	No Amine Scrubber
H_2	11.7	10.7	12.6	11.5
C_1	18.8	17.3	22.3	20.4
N_2	9.1	8.4	9.9	9.2
CO_2	--	1.9	--	2.0
H_2S	--	6.3	0.5	6.6
C_2=	7.3	6.7	12.2	11.2
C_2	9.8	9.0	21.1	19.3
C_3=	11.8	10.8	10.6	9.7
C_3	4.7	4.3	3.5	3.2
iC_4	2.2	2.0	0.7	0.7
C_4=	10.2	9.4	3.0	2.8
nC_4	1.3	1.2	0.4	0.4
Gasoline	11.2	10.3	2.7	2.5
H_2O	1.9	1.7	0.5	0.5
	100.0	100.0	100.0	100.0

(1) Amine absorber located between first and second stage of wet gas compressor.

heated olefin stream then flows through line 104 to preheat furnace 106 where it is heated to the reaction temperature in the range of 149-399°C (300-750°C). The thus heated stream flows through line 108 to reactor 110 which contains a fixed bed 112 of ZSM-5 zeolite catalyst. While passing through the reactor at a space velocity of from 0.1 to 10 WHSV, the C_2 to C_5 olefins in the gaseous mixture are converted to hydrocarbons boiling in the gasoline and fuel oil range. The reaction mixture leaves reactor 110 through line 114 and flows to the shell side of heat exchanger 102 where this effluent stream provides some of the preheat to the olefinic feedstream. Referring to both Figures 1 and 2, the reaction mixture then passes to lines 18, 20 and 22 and enters high pressure receiver 24. Several other streams are also passed into this receiver where they are separated into a liquid phase and a gaseous phase. These include the liquid phase from compressor interstage receiver 12 which flows from receiver 12 through lines 26, 28 and 22 to receiver 24, the rich liquid from the primary absorber, described hereinafter, which passes from the absorber through lines 30, 28 and 22 to the receiver and the overhead from the stripper, also described hereinafter, which passes through lines 31, 20 and 22 to the receiver. The temperature of these combined streams in receiver 24 is about 38°C (100°F).

The streams entering high pressure receiver 24 are separated therein into a gaseous phase and a liquid phase. The gaseous phase passes through lines 32 and 34 to primary absorber 36. Dotted square B represents an alternate location for the Figure 2 flowplan and this embodiment will be described hereinafter. For purposes of the present description where the Figure 2 flowplan is located at dotted square A, the gaseous phase from high pressure receiver 24 passes directly to primary absorber 36 where a C_5+ liquid stream passing in countercurrent flow to the gas absorbs heavy hydrocarbons from the gas stream. The C_5+ liquids employed include the liquid phase from FCC main column overhead accumulator 4 and a portion of the final liquid product from the gas plant. These streams are passed to primary absorber 36 through lines 38 and 40, respectively. The rich liquid from absorber 36 flows from the column through lines 30, 28 and 22 and enters high pressure receiver 24, as described above.

The unabsorbed gases pass from the top of absorber 36 through line 42 where they are combined with coker gas supplied through line 44. The combined gaseous stream passes through line 46 into sponge absorber 48 where they are contacted in countercurrent fashion with sponge oil which is a stripped heavy naphtha or light fuel oil boiling in the 177-260°C (350-500°F) range. In this absorber, the C_3+ gases are absorbed by the sponge oil which passes from sponge absorber 48 through line 50 and discharges into FCC main column (not shown) by means of line 2. The unabsorbed C_2- gases pass from the absorber through line 52 and are eventually burned as fuel gas.

Returning to the liquid phase in high pressure receiver 24, which contains the gasoline and/or fuel oil fractions obtained by the ZSM-5 catalytic conversion of the light olefin gases, this liquid passes from the receiver through line 54 to stripper 56 where steam is employed to remove the light gases from this stream. The steam and the light gases pass from the top of the stripper through line 31 and eventually discharge into high pressure receiver 24 from which the useful light gases are recovered.

The stripped C_3+ liquid passes from stripper 56 through line 58 to debutanizer 60 where a C_4- fraction is separated and passes from the column as the overhead through line 62 where it is recovered as LPG product. The gasoline and/or fuel oil fraction is removed from debutanizer 60 as the bottoms fraction through line 64. A portion of this fraction is recycled through line 40 to the primary absorber as a portion of the absorbing liquid as described above. The remaining portion of the C_5+ bottoms is recovered as product through line 66 and is employed as blending stock for gasoline and/or fuel oil following futher fractionation, as required.

As described above, this invention may optionally be practiced employing the overhead from high presure receiver 24 as the feed for the conversion to gasoline and/or fuel oil. Typically, this stream has a composition as shown in Table I. In this embodiment, the flowplan of Figure 2 is located at position B of Figure 1 with the feed passing through line 32 and the reaction mixture continuing on to the separation equipment of the gas plant through line 34. Obviously, when practicing this embodiment the discharge from the wet gas compressor flows directly from line 16 to line 18. In other regards this embodiment is practiced in substantially the same manner as the embodiment described above where the Figure 2 flowplan is located at position A of Figure 1.

By practicing the invention as described herein whereby the olefinic feedstreams in the FCC gas plant are catalytically converted in the presence of a ZSM-5 type zeolite to gasoline and/or fuel oil fractions and the existing facilities are employed to separate and recover these fractions, the capital investment and operating costs required for this conversion are minimized.

CLAIMS

1. Process for producing a gasoline fraction and/or a fuel oil fraction by contacting a feedstock comprising C_2 to C_5 olefins with a crystalline aluminosilicate zeolite having a pore diameter greater than 5 Angstrom Units, a silica-to-alumina ratio of at least 12 and a constraint index of from 1 to 12 under reaction conditions effective to convert the olefins to a gasoline fraction and/or a fuel oil fraction, characterized by employing as the feedstock the discharge stream from the final stage of the wet gas compressor or the overhead from the high pressure receiver in the gas plant of a fluid catalytic cracking unit and passing the effluent from the zeolite-catalyzed conversion through the separation and recovery facilities of the gas plant to recover the gasoline fraction and/or the fuel oil fraction.

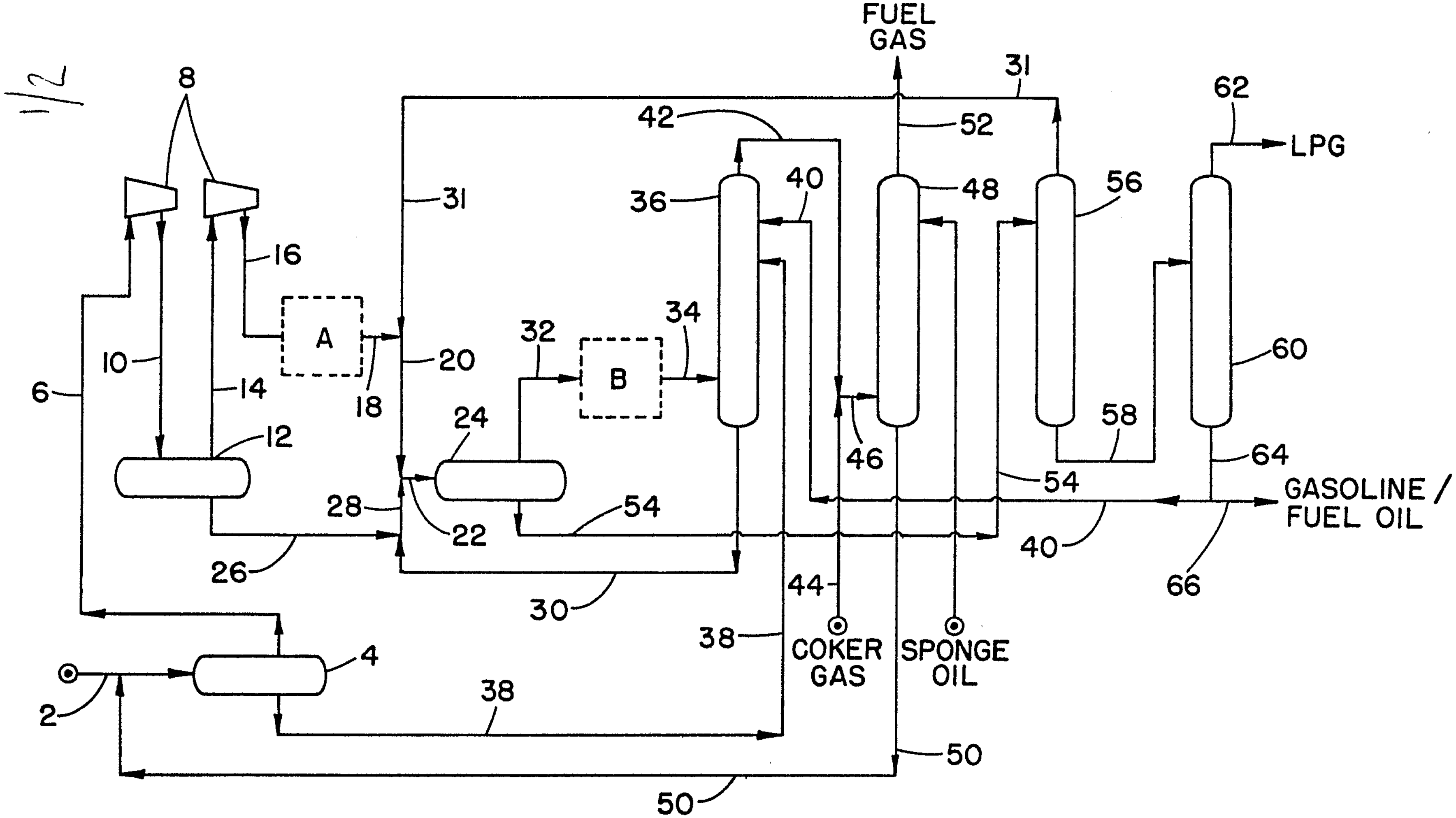
2. The process of Claim 1 wherein the feedstock is passed through an amine absorber under conditions to effectively reduce the CO_2 and H_2S contents of the feedstock or a water scrubber under conditions to effectively reduce the NH_3 and amine contents of the feedstock or combinations of the amine absorber and water scrubber prior to contacting the feedstock with the zeolite.

3. The process of Claim 1 or 2 wherein the zeolite is ZSM-5, ZSM-11, ZSM-12, ZSM-35 or mixtures thereof.

4. The process of Claim 3 wherein the zeolite is ZSM-5.

5. The process of any one of Claims 1 to 4 wherein the source of the feedstock is a fluid catalytic cracking unit.

6. The process of any one of Claims 1 to 4 wherein the source of the feedstock is a coker.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FUEL GAS
31
62
LPG
42
52
40
36
48
56
31
16
A
10
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34
60
32
B
6
14
18
24
58
12
46
64
54
28
22
54
GASOLINE / FUEL OIL
26
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44
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38
COKER GAS
SPONGE OIL
4
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FIG. I

2/2

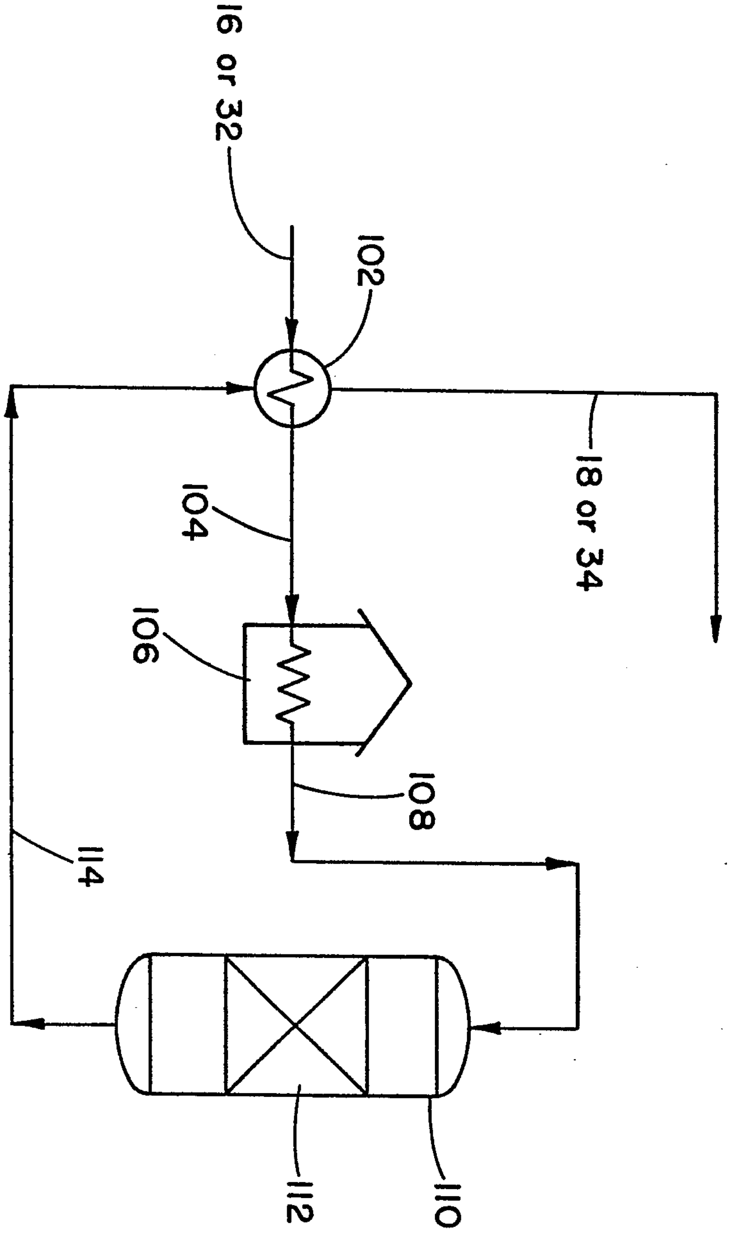

FIG.2