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(54) **Residual oil fluid catalytic cracking process**

(57) A process for converting higher molecular weight hydrocarbons to lower molecular weight hydrocarbons, which process includes the steps of (a) introducing a hydrocarbon feedstock selected from the group consisting of gas oils, residual oils and combinations thereof into a first cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the feedstocks into lower molecular weight products, (b) withdrawing from the first reactor a product stream containing a light fraction composed of a distillate and lighter hydrocarbons and a heavy fraction composed of hydrocarbons boiling above the boiling

point of the distillate hydrocarbons and containing aromatic hydrocarbons; (c) separating the lighter product fraction and the heavy product fraction, (d) introducing at least a portion of the resulting separated heavy product fraction into a hydrotreating reactor to contact therein a hydrotreating catalyst under conditions effective to saturate or partially saturate the aromatic hydrocarbons in the heavy fraction so as to produce a hydrotreated product, and (e) introducing at least a portion of the hydrotreated product into a cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the hydrotreated product into lower molecular weight products.

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Description

FIELD OF THE INVENTION

[0001] This invention relates to an improved fluid catalytic cracking (FCC) process for processing gas oils, residual oils, and low hydrogen content hydrocarbons to obtain high conversion to transportation fuel products, and more particularly to such a process wherein a portion of the FCC product not converted to transportation fuels on a first pass through the FCC process system is hydrotreated in a hydrotreater to saturate at least a portion of the aromatic hydrocarbons thereon, and all or a portion of the hydrotreated FCC product portion is passed to an FCC process system and converted to transportation fuels.

BACKGROUND OF THE INVENTION

[0002] The major objective in refining crude petroleum oil has always been to produce the maximum quantities of the highest value added products and to minimize the production of low value products. Except for specialty products with limited markets, the highest value added products of crude oil refining with the largest market have been transportation fuels, such as gasoline, jet fuel and diesel fuels and Number 2 home heating oil. Historically the lower value products have been associated with the hydrocarbon species boiling above Number 2 home heating oil, which includes gas oils (portion boiling between about 650°F- 1000°F (343°C-538°C) and residual oils (defined as the portion of the crude oil boiling above about 1000°F+ (538°C+). The gas oil portion of the crude oil is of less value because it requires more processing for conversion to transportation fuels by processes, such as, FCC and the more expensive hydrocracking process.

[0003] The residual oil is of even lower value because it is in this portion of the crude oil where catalyst poisons are concentrated, plus this portion of the crude oil has more multi-ring aromatic hydrocarbons that do not readily convert to transportation fuels in the FCC process. Historically, the refining industry has striven to find a cost effective method for conversion of the residual oil portion of the crude oil to the higher value products and has had success by employing non-catalytic processes such as visbreaking, coking (delayed and fluid), and solvent deasphalting. However, these process are not as selective to high value transportation fuel products as the catalytic FCC process and require extensive, costly treating to convert the material yielded from these processes into acceptable products.

[0004] Since most of the oil refineries in the world use the well known, low capital requirement fluid catalytic cracking (FCC) process as the major process for the upgrading of gas oils to transportation fuels, it is only natural that the FCC process should be considered for use in the processing of residual oils. Indeed, this has been

the case for the last ten to fifteen years. Until recently, the major obstacle to the processing of residual oil in catalytic processes, such as the FCC or hydrotreating type processes, has been the concentration in residual oils of "catalyst poisons", such as metals, nitrogen, sulfur, and asphaltenes (coke precursors), which are present in all residual oils at different levels, depending on the crude oil processed. These "catalyst poisons" accelerate the deactivation of catalyst and increase the catalyst and operating costs, so that these residual oil processing methods have only been made economical, in most cases, by limiting the amount of residual oil in the feed. However, the technology available for economically processing residual oil feeds containing high concentrations of catalyst poisons in the FCC process is improving so that the major remaining obstacle to such processing of residual oils is their convertibility to transportation fuels. That is, with the limit on catalyst poisons in the FCC feed increasing, more residual oil can be processed in an FCC unit. However, residual oil because of its lower hydrogen content and higher concentration of aromatic hydrocarbons tends to have a lower yield of transportation fuels and a higher yield of the lower value 650°F+ (343°C+) products (commonly referred to as FCC heavy cycle oil [HCO] or slurry oil). Therefore, as the conversion in the FCC unit to transportation fuels decreases, the economics of the FCC process suffer and the amount of low hydrogen/high aromatic content FCC feed that can be economically processed in the FCC unit (FCCU) is reduced.

[0005] Over the last 50 years, as the FCC process and catalyst have been improved, the limits on the amount of "catalyst poisons" has been increased to about 7-8 w% Ramsbottom carbon and about 30 ppm of metals (Ni+V) in the feed, which equates to a fresh catalyst addition rate of about 1 #/bbl (0.45 kg/0. 16 m³) of feed to maintain about 11,000 ppm of metals (Ni+V) on the equilibrium catalyst circulating in the FCCU. Recent commercial improvements in the FCC process, such as the those described in my U. S. patent no. 4,985,136 "ULTRA-Short Contact Time Fluidized Catalytic Cracking Process" (commercially referred to as the Milli-Second Catalytic Cracking [MSCC] Process) have been developed that allow for the processing of residual oils with unlimited Ramsbottom carbon, nitrogen and a much higher metals content. While strides have been made in reducing the cost associated with processing feedstocks with high levels of catalyst poisons in the FCC process units, this is not the case with fixed bed processes, such as hydrotreating or hydrocracking. It should be noted that one of the advantages of using the invention described herein is in using the FCC process as a feed preparation unit for these fixed bed processes. That is, using the FCC process to convert residual oil and/or other low hydrogen content (more aromatic) feedstocks to transportation fuels will greatly reduce the quantity of feedstock that needs to be processed in a hydrotreating type process and will essentially eliminate

the majority of hydrotreating catalyst poisons. As disclosed, this improved processing scheme will, when compared to hydrotreating the residual oil and/or other low hydrogen content FCC hydrocarbon feedstock, reduce the required hydrotreater capacity, increase the hydrotreater catalyst life, reduce the hydrotreater operating and capital costs, and decrease the hydrogen consumption.

[0006] As the sulfur in the FCC feed increases, a refiner's processing costs increase. These increased processing costs are associated with making acceptable low sulfur content products and treating the FCC regenerator flue gas for SO_x (sulphur oxides). With today's fuel standards and environmental regulations becoming more stringent, it is evident that all FCC type units will eventually be required to install regenerator flue gas scrubbing systems for particulate and SO_x control. The refiner will also be required to treat the majority of FCC products for sulfur removal and to install desulfurization and aromatics saturation (cetane improvement) equipment on the FCC distillate product system. In effect, the regulations / specifications on transportation fuels and home heating oil will remove any limit of FCC feed sulfur. Also, it should be noted that the FCCU is a very cost effective sulfur removal process in that it converts about 50% of the feed sulfur to H₂S without hydrogen addition.

[0007] A major objective of the present invention is to allow the FCC process to more economically process hydrocarbon feedstocks with low hydrogen content. Another objective of this invention is to increase the amount of aromatic hydrocarbon feed components that can be economically processed in the FCC process. Still another objective of the invention is to simplify the oil refining process by eliminating the need for operating vacuum units, coking units, visbreaking units, and atmospheric residual oil desulfurization units. This will lower the capital and operating costs associated with upgrading crude oil to higher value transportation feeds. Still another objective is to increase the production of high value transportation fuels from a barrel of crude oil. Other objects of the invention will become apparent from the following description 'and/or practice of the invention.

SUMMARY OF THE PRESENT INVENTION

[0008] The above objectives and other advantages of the present invention may be achieved by employing a process for converting higher molecular weight hydrocarbons to lower molecular weight hydrocarbons, which process comprises the steps of (a) introducing a hydrocarbon feedstock selected from the group consisting of gas oils, residual oils and combinations thereof into a first cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the feedstocks into lower molecular weight products, (b) withdrawing from the first reactor a product stream containing a light fraction composed of a distil-

late and lighter hydrocarbons and a heavy fraction composed of hydrocarbons boiling above the boiling point of the distillate hydrocarbons and containing aromatic hydrocarbons, (c) separating the lighter product fraction and the heavy product fraction, (d) introducing at least a portion of the resulting separated heavy product fraction into a hydrotreating reactor to contact therein a hydrotreating catalyst under conditions effective to saturate or partially saturate the aromatic hydrocarbons in the heavy fraction so as to produce a hydrotreated product, and (e) introducing at least a portion of the hydrotreated product into a cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the hydrotreated product into lower molecular weight products.

[0009] The present FCC process system includes hydrotreating all or a portion of the heavy FCC product that boils above the desired distillate product and returning this hydrotreated heavy FCC product to the a FCC reactor system for conversion to transportation fuels. This processing scheme can employ any type of FCC design but the MSCC reactor design is preferred as the MSCC short contact time reactor system reduces the hydrogen transfer. This results in lower HCO and slurry oil specific gravity, which indicates more hydrogen content, and therefore requires less severity in the hydrotreater.

[0010] The feedstock for the primary FCC process can be any gas oil or residual oil or any combination of the two, as the primary FCC process will remove essentially all the metals, asphaltenes, and a majority of the sulfur and nitrogen so that the economics of hydrotreating the heavy FCC product from the primary FCC is superior to hydrotreating the feed. Not only will the primary FCC remove most of the hydrotreating catalyst poisons, the quantity of the feed to the primary FCC is between 20 and twice the amount that would be processed in the hydrotreater. That is, the primary FCCU would be operated to convert at least 50% of the FCC feedstock to transportation fuels and lighter, or as high as 95% of the feedstock to transportation fuels and lighter. This decision would be based on economics, which would be dependent mainly on feedstock type. The FCC unit does not readily convert multi-ring aromatics to transportation fuels, so the FCC heavy product is more concentrated in aromatics than the feedstock. Also, as the conversion in the FCCU is increased the aromatic concentration in the FCC heavy product increases. As the aromatics level of the FCC heavy product increases, the severity (pressure, space velocity) of the hydrotreater will need to be increased. Therefore, there is a trade-off between conversion (amount of hydrotreater feed) and the required severity of the hydrotreater. Typically, the hydrotreater will operate above 600 psi (40.8 atm) and less than 3000 psi (204 atm), at space velocities of 0.1 to 4.0 and could employ several catalyst types (hydrotreating catalyst for sulfur and nitrogen reduction, and aromatic saturation catalyst). Since the FCC heavy product to be hydrotreated contains 3+ ring aromatic structures that

will not readily convert in the FCC process, the objective of hydrotreating the primary FCC heavy product is to saturate at least one of the rings so that when this hydrotreated material is processed in the recycle FCC reactor at least one of the rings will crack off, which will result in increasing the yield of transportation fuel products.

[0011] In one preferred processing scheme, the hydrotreated FCC heavy product is processed in a separate recycle FCC reaction system that operates in parallel with the primary FCC reaction system. These two FCC type reaction systems can share a common catalyst regeneration system. In the preferred processing scheme the two FCC type reaction systems would have separate heavy oil product separation systems and a common distillate and lighter product recovery system. The HCO and slurry oil product from the primary FCC reaction system may be segregated, as the hydrotreater feed, and the HCO and slurry oil from hydrotreated recycle FCC reaction system would be product for producing needle coke, anode grade coke, or other types of products including fuel oil. Of course, the primary FCC process and the hydrotreated recycle FCC process could be a separate standalone FCC units.

BRIEF DESCRIPTION OF THE DRAWING

[0012] The present invention will be more fully understood by reference to the following description thereof read in conjunction with the accompanying drawing which is a schematic flow diagram of a preferred process in accordance with the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0013] In a preferred embodiment of the present invention, a residual oil or low hydrogen content feedstock is charged to a primary FCC reactor system where it is contacted with hot regenerated catalyst to convert the feedstock to lower molecular weight reaction products which are separated from the now spent catalyst containing carbonaceous deposits, which consists of essentially all the feed asphaltenes and metals and catalytic coke plus significant feed sulfur and nitrogen. The spent catalyst is subjected to steam stripping to remove as much of the interstitial and volatile hydrocarbons as possible before it is conveyed to the regenerator system where it is contacted with combustion air to burn off the carbonaceous deposits and elevate the catalyst temperature, so that the now hot regenerated catalyst can be returned to the reactor to complete the cycle and contact more feedstock. The separated primary FCC reactor vapors flow to a main fractionator where these vapors are separated into distillate and lighter fractions for further processing into transportation fuels and fuel gas and a heavy fraction consisting of HCO, which contains no catalyst fines, and slurry, which will contain catalyst fines. These two fractions can be removed from the main frac-

tionator as two separate streams or yielded together from the bottom of the main fractionator as slurry. In either case, the slurry after treatment to remove catalyst fines is processed in a hydrotreater for sulfur and nitrogen removal and for saturation of some of the aromatic rings. This can be accomplished with high pressure using a hydrotreating type catalyst or at lower pressures utilizing a dual catalyst type system consisting of hydrotreating catalyst and aromatics saturation type catalyst. The liquid product from the hydrotreater, which is now lower in sulfur and nitrogen compounds and has a higher hydrogen content, can be returned as recycle to the primary FCC reactor system along with the primary FCC reactor feedstock, but the preferred method is to process this hydrotreated recycle in a separate recycle FCC reactor system containing a separate spent catalyst stripping section and a common regenerator system. Those skilled in the art will realize that any combination of reactors, strippers, and regenerators can be employed, but a separate recycle FCC reactor system is used in this case so that the heavy products from the recycle FCC reactor, which are much more hydrogen deficient than the heavy products from the primary FCC reactor system, are not mixed with the heavy products from the primary FCC reactor. The recycle FCC reactor vapor's flow to a separate main fractionator system, which can be a separate system or a stub column consisting of only the heavy (HCO and slurry) fractionation sections with a common distillate and lighter sections shared with the primary FCC reactor main fractionator, where the HCO and slurry can be yielded as products along with the recycle FCC reactor distillate and lighter materials.

[0014] As shown in the drawing, crude oil, preferably after desalting, is passed through line 1 and processed in crude distillation column 2 to produce, in addition to the typical lighter products, a primary FCC reactor feedstock. As shown in the drawing, the primary FCC reactor feedstock, passed to reactor 4 via line 3, is atmospheric tower bottoms, but this feedstock could also be composed of any hydrocarbon feedstock including heavy crude oil. The primary FCC process may be any type of FCC process, but the preferred process employs a short contact time reactor system, such as that employed in the MSCC Process. The primary FCC process consists of the primary reactor 4 including a spent catalyst stripper, catalyst regenerator 8, regenerated catalyst standpipe 7, spent catalyst standpipe 6 and regenerator flue gas 9. Primary reactor 4 reactor vapors, which exit the reactor via line 5, are separated in main fractionator 16. The heavy products are taken near to bottom; HCO via line 24 and slurry via line 25. In the top of the fractionator 16, distillate product is taken via line 23 as a side draw from the fractionator and the overhead vapors exiting via line 17 flow through cooler 18 into overhead receiver 20, where an overhead unstabilized gasoline in line 22 and a gas stream in line 21 are separated for further processing into the desired products in a gas concen-

tration unit that is not shown.

[0015] Hydrotreater 26 can treat either the HCO from line 24 or slurry from line 25 after treatment for removal of catalyst fines in separator unit 19 to saturate some of the aromatics, while at the same time reducing the sulfur and nitrogen contents of these streams. In the preferred embodiment, there would be no HCO yield, and only slurry after treatment for catalyst fines removal in unit 19 would be processed in the hydrotreater. Typically the hydrotreater would operate above 600 psi (40.8 ATM.) and less than 3000 psi (204 ATM.), at a space velocity of from 0.1 to 4.0 and may employ several catalyst types (hydrotreating catalyst for sulfur and nitrogen, and aromatic saturation catalyst). Since the primary FCC heavy product to be hydrotreated contains 3+ ring aromatic structures that will not convert in the FCC process, the objective of hydrotreating the primary FCC heavy product is to saturate at least one of the aromatic rings, so that when this hydrotreated material withdrawn from the hydrotreater via line 27 is processed in recycle reactor 12 at least one of the rings will crack off, which will result in increasing the yield of transportation fuel products.

[0016] In one preferred embodiment, recycle FCC reactor 12 is connected to the common regenerator 8 by regenerated standpipe 11 and spent standpipe 10. The use of this type of FCC system with a common regenerator results in the need for less catalyst cooling in the regenerator because the recycle material from line 27 acts to remove heat from regenerator 8 as it is processed in recycle reactor 12. Recycle reactor 12 vapors exiting the reactor via line 13 are partially separated in a fractionator into heavy products, HCO taken in line 29 and slurry taken in line 28, which can be further processed or yielded as products, in stub fractionating column 14. Stub column 14 can be a separate column as shown, but in the preferred embodiment this function would be incorporated into main fractionator 16 by installation of a baffle separating the two bottom sections of the fractionator. Vapors exiting stub column 14 via line 15, which are composed of the transportation fuel products from recycle FCC reactor 12, are combined with the vapors from primary reactor 4, which contain its transportation products and separated into products as outlined above.

[0017] Although hydrotreatment of gas oil or similar FCC feedstocks has been heretofore employed, the present invention provides numerous advantages thereover, as noted above. Also, surprisingly, it has been determined that the present process enables a significant improvement in the yield of transportation fuels from a barrel of crude oil, for example, an increase of about 5 volume % or more may be obtained.

[0018] Having described preferred embodiments of the present invention, modifications thereof falling within the spirit of the invention may become apparent to those skilled in the art, and the scope of the invention shall be determined by the appended claims and their equivalents.

Claims

1. A process for converting higher molecular weight hydrocarbons to lower molecular weight hydrocarbons, which process comprises the steps of:
 - (a) introducing a hydrocarbon feedstock selected from the group consisting of gas oils, residual oils and combinations thereof into a first cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the feedstock into lower molecular weight products;
 - (b) withdrawing from the first reactor a product stream containing a light fraction composed of a distillate and lighter hydrocarbons and a heavy fraction composed of hydrocarbons boiling above the boiling point of the distillate hydrocarbons and containing aromatic hydrocarbons;
 - (c) separating the lighter product fraction and the heavy product fraction;
 - (d) introducing at least a portion of the resulting separated heavy product fraction into a hydrotreating reactor to contact therein a hydrotreating catalyst under conditions effective to saturate or partially saturate the aromatic hydrocarbons in the heavy fraction so as to produce a hydrotreated product; and
 - (e) introducing at least a portion of the hydrotreated product into a cracking reactor to contact therein a fluidized cracking catalyst under cracking conditions effective to convert the hydrotreated product into lower molecular weight products.
2. The process of claim 1 wherein the separated heavy fraction contains no entrained catalyst.
3. The process of claim 1, wherein the separated heavy fraction contains entrained catalyst,
4. The process of claim 3, wherein a majority of the entrained catalyst is removed before the hydrotreating step.
5. The process of claim 1, wherein the hydrotreated product from the hydrotreating step is introduced into a second cracking reactor different from the first cracking reactor.
6. The process of claim 5, wherein reactor vapors from the first and second reactors are at least partially separated into product fractions in separate fractionation equipment downstream from each reactor.
7. The process of claim 6, wherein only the heavy fraction from the first cracking reactor is hydrotreated

and passed to said second cracking reactor.

8. The process of claim 1, wherein the separated heavy fraction is recycled to the first cracking reactor.

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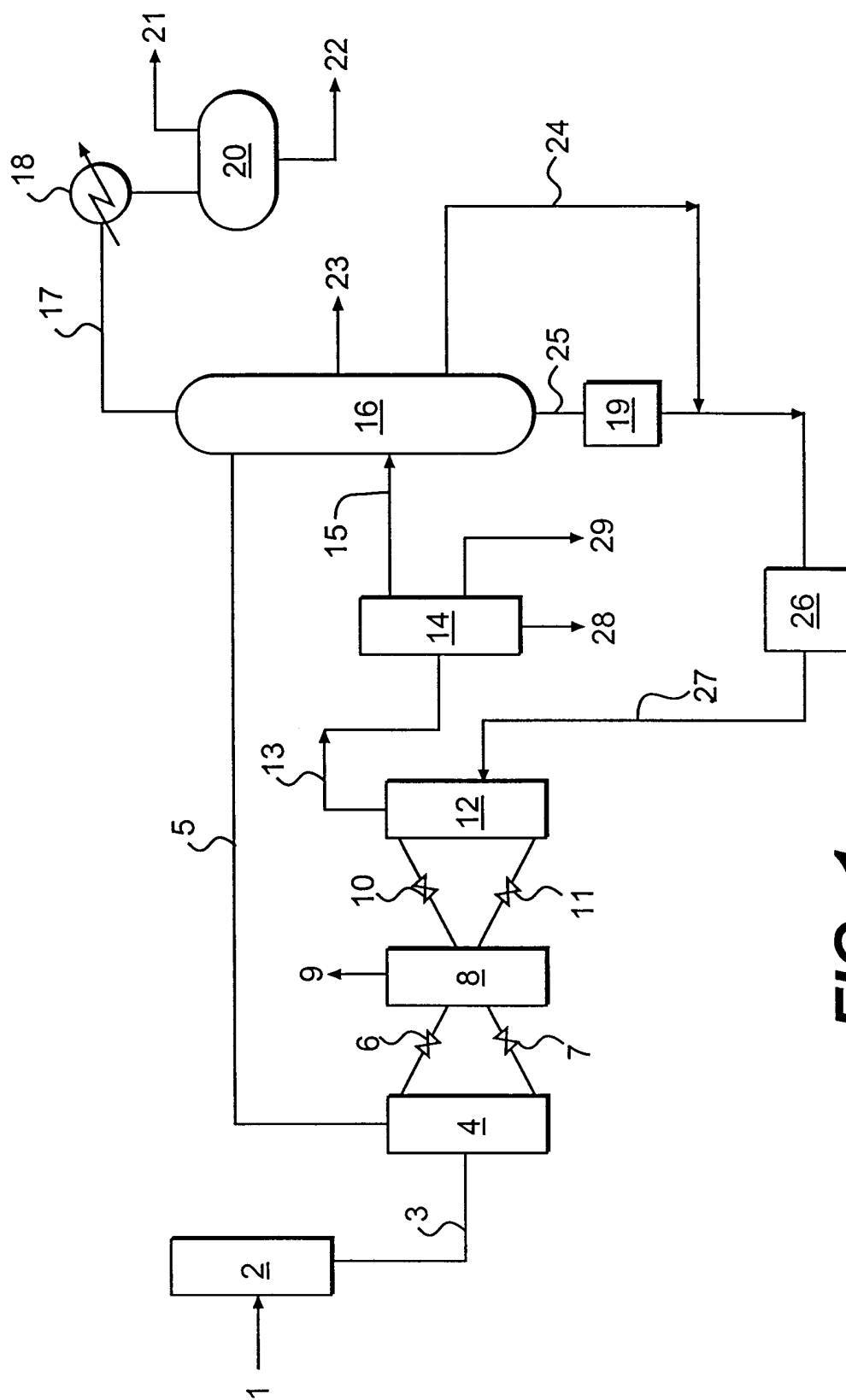


FIG. 1