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(54) Improved residual oil fluid catalytic cracking process with catalyst having increased metals tolerance

(57) An improved residual oil fluid catalytic cracking process for reducing catalyst deactivation caused by vanadium and/or sodium deposited on circulating catalyst used in the process from a residual oil feed, which process includes the steps of; contacting a residual oil feed in a fluid catalytic cracking reactor with hot regenerated cracking catalyst under hydrocarbon cracking conditions to convert the residual oil feed into lower molecular weight hydrocarbon product vapors and form a spent catalyst containing carbonaceous deposits including vanadium and/or sodium; separating a majority of the lower molecular weight hydrocarbon product vapors from the spent cracking catalyst to form separated product vapors and separated spent catalyst containing entrained hydrocarbon vapors; processing the separated product vapors into desired product fractions; subjecting the separated spent catalyst to stripping to remove therefrom a majority of the entrained hydrocarbon vapors; contacting the resulting stripped spent catalyst in a regenerator with an oxygen-containing regeneration gas under catalyst regeneration conditions which include a combination of a regeneration temperature and an oxygen level in the regeneration gas which is effective to burn off the spent catalyst a majority of the carbonaceous deposits, while leaving a majority of the vanadium and/or sodium on the catalyst in less than completely oxidized form, and thereby produce a regenerated catalyst having a carbon level reduced from that of the spent catalyst and containing vanadium and/or sodium, a majority of which is in less than the completely oxidized form, and; returning the regenerated catalyst to the reactor.

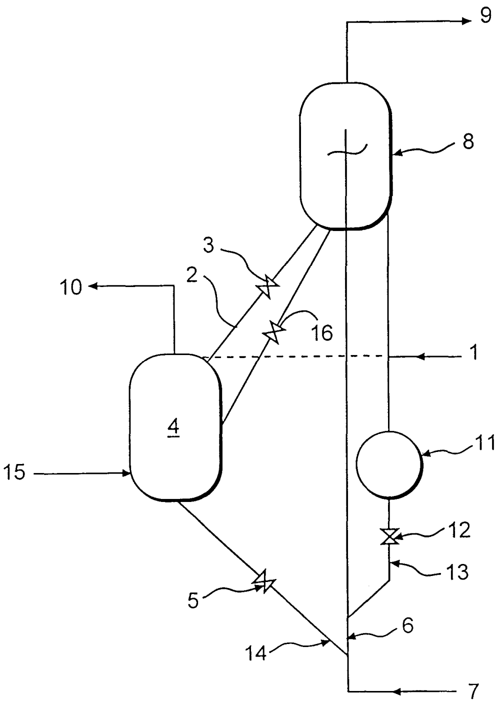

FIG. 1

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Description

FIELD OF THE INVENTION

[0001] This invention relates to an improved fluid catalytic cracking (FCC) process for processing residual oils, in which the FCC unit (FCCU) design and operating conditions enable operating the FCCU with a level of metals on equilibrium catalyst which is increased over and above the current state of the art.

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 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 residual oil, defined as the portion of the crude oil boiling above about 1000°F or 538°C. Heretofore, 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 deasphatting.

[0003] A major obstacle to the processing-of residual oil in catalytic processes, such as the FCC or hydrotreating type processes, has been the concentration on the catalyst 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, reduce catalyst selectivity, and increase the catalyst and other operating costs so that these residual oil processing methods have only been made economical, in most cases, by limiting the proportion of residual oil in the feed relative to other feedstock components containing less catalyst poisons.

[0004] Since most of the oil refineries in the world use the well known fluid catalytic cracking (FCC) process as the major process for the upgrading of heavy gas oils to transportation fuels, it is only natural that the FCC process should be considered for use in the processing of heavier residual oils. However, processing of residual oil in FCCU's has been retarded by environmental considerations which require the installation of SOx (sulfur oxides) control on FCC regenerator flue gas and the catalyst replacement rates required to control the metals levels on the circulating equilibrium catalyst (ECAT) at acceptable levels. Because of the increased capital costs, without any economic benefit, required for treating the FCC regenerator flue gas and the increase operating costs associated with the higher fresh catalyst replacement rates required to control the ECAT metals level when processing increased quantities of residual oil, many refiners elected to install feed hydrotreating as the preferred method of flue gas SOx control. Hydrotreating of the FCC gas oil feed results in increased yield benefits, so there was an economic incentive for using this approach. However, hydrotreating of the FCC feed limited the feed to gas oil, since the introduction of residual oil into the hydrotreater feed would also increase the hydrotreating catalyst costs, and, typically, was not economical. Another force which retarded the introduction of residual oil into the FCC feed was that many FCCU's were "grandfathered". Operators of these units have been reluctant to consider residual oil processing in their FCCU's because of the increased capital required to modify the FCCU. Ironically, the new environmental regulations on fuels and regenerator flue gas emissions will more than likely require all FCCU to treat the flue gas for particulate as well as SOx and to treat the FCC transportation fuel products to reduce the sulfur and improve the distillate cetane index. This will require the installation of flue gas treating processes, such as wet scrubber's for particulate and SOx control, and the installation of hydrotreating and aromatic saturation processes for treating the FCCU transportation fuel products.

[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. Feeds with up to about 7-8 wt.% Ramsbottom carbon are being processed. Also, economics (catalyst costs) have limited FCC feedstock to about 30 ppm of metals (Ni+V) in the feed. This equates to a fresh catalyst addition rate of about 1#/bbl. (0.45 kg/0.16 m^3) of feed to maintain about 11,000 ppm of metals (Ni+V) on the equilibrium catalyst (ECAT) circulating in the FCCU. This level of Ni+V appears to be achievable with today's state of the art. Recent commercial improvements in the FCC process, such as 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, which allow for the processing of residual oils with nearly unlimited Ramsbottom carbon, nitrogen and nickel levels. The only limit on FCC feed sulfur content has to do with the costs associated with making acceptable products and treating the FCC regenerator flue gas. With today's fuel standards and environmental regulations, it is evident that all FCC type units will eventually be required to install regenerator flue gas scrubbing for particulate and SOx control. They also will be required to treat the majority of FCC products for sulfur, and to install desulfurization and aromatics saturation (cetane improvement) equipment on the FCC distillate product section. In effect, the regulations will remove any limit of FCC feed sulfur content. 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 H_2S without hydrogen addition.

[0006] However, even with these improvements in the FCC process, the amount of residual oil that a refiner has been able to economically convert in the FCC process has been limited by the cost of replacement catalyst required as a result of catalyst deactivation, which results from the metals, especially vanadium and sodium, contained in the residual oil feedstock. The buildup of other catalyst poisons on the catalyst, such as the coke precursors, nitrogen and sulfur, can be effectively controlled by using catalyst coolers to negate the effect of coke formation from the asphaltene compounds, using the MSCC process to overcome the problems associated with riser coking and vaporization in a riser type FCC, using regenerator flue gas and product treating to negate the environmental effects of feed sulfur, and using the MSCC process to negate the effects of feed nitrogen and nickel.

[0007] In the operation of an FCCU the process economics are highly dependent upon the replacement rate of the circulating catalyst (equilibrium catalyst) with fresh catalyst including additives, such as ZSM-5 and other zeolitic materials used for specific purposes in the FCCU. Equilibrium catalyst (ECAT) is FCC catalyst which has been circulated in the FCCU between the reactor and regenerator over a number of cycles. The amount of fresh catalyst addition required. or the catalyst replacement rate, is determined by the catalyst loss rate and the replacement rate necessary to maintain the desired equilibrium catalyst activity and selectivity to produce the optimum yield structure. In the case of operations wherein a feedstock containing residual oil is employed, it is also necessary to add sufficient replacement catalyst to maintain the metals level on the circulating catalyst at a level below which the yield structure is still economically viable. In many cases, low metal equilibrium catalyst with good activity is added along with fresh catalyst to maintain the proper catalyst activity at the lowest cost. With today's feed and product prices, most operators are limited to FCC catalyst operating costs of less than \$ 1.00 per barrel (0.16 m^3) of feed processed in the FCCU. At an average fresh catalyst price, including shipping and disposal of equilibrium catalyst, of \$2000.00 per ton (907 kg), this equates to about 1#/bbl (0.45 kg/0.16 m^3). As discussed above, this addition rate would equate to about 11,000 ppm of metals on equilibrium catalyst with 30 ppm of Ni+V in the feed. In today's state of the art, the industry generally accepts that 11,000 ppm Ni + V on equilibrium catalyst is about the maximum for maintaining the desired catalyst activity and selectivity.

[0008] The method of FCC catalyst deactivation by vanadium is not completely understood. However, it is believed that steam (water vapor formed by burning of the hydrogen in the coke, entrained stripping steam, and water vapor in the combustion air) will react with V_20_5 to form volatile vanadic acid, $VO(OH)_3$. This is the primary mechanism of particle to particle transfer of vanadium species. In the pentoxide or vanadic acid form, vanadium has an affinity for zeolite crystals. While the exact mechanism of destruction of zeolite crystals is a subject for debate, the vanadium-clearly causes an irreversible loss of zeolite crystallinity and surface area. Catalyst activity is reduced, and selectivity for gasoline and light olefins is diminished. This catalyst deactivation mechanism requires that the vanadium be fully oxidized, i.e., in the pentoxide form (not in the di-, tri-, or tetra-oxide form). Therefore, some oxidation of the vanadium can take place without resulting in such catalyst deactivating. It is believed that the mechanism for catalyst deactivation by sodium is similar to that for vanadium.

[0009] The present process is contrary to the philosophies employed by the major users of FCC technology. That is, the current FCC design philosophy used in several FCC processes is the so-called two stage regenerator, which regenerates the catalyst in two stages, with the second stage having a high temperature, typically greater than 1 300°F (704°C), and an oxidizing atmosphere. In another process the spent catalyst is distributed across the top of the regenerator bed so that the lower part of the fluidized bed where the combustion air is injected into the bed contacts the hottest catalyst with the highest oxygen concentration. All of the above are contrary to the principles of the present invention and do not permit satisfactory operation of an FCCU on a residual oil feedstock.

[0010] A primary objective of this invention is an FCC process enabling economical processing of residual oil feeds having greater than 30 ppm of metals (Ni+V) in the feed. Another objective is to reduce the detrimental effect of vanadium on catalyst activity. Another objective is to reduce the detrimental effect of sodium on catalyst activity. Still another objective of the invention is to reduce the FCC fresh catalyst replacement rate required to compensate for the catalyst deactivation effect caused by vanadium and sodium, which will reduce fresh catalyst costs, transportation costs, equilibrium catalyst disposal costs, and unit catalyst losses. Other objects of the invention will become apparent from the following description and/or practice of the invention.

SUMMARY OF THE PRESENT INVENTION

[0011] The above objectives and other advantages of the present invention may be achieved by an improved residual oil fluid catalytic cracking process for reducing catalyst deactivation caused by vanadium and/or sodium deposited on circulating catalyst used in the process from a residual oil feed, which process includes the steps of; contacting a residual oil feed in a fluid catalytic cracking reactor with hot regenerated cracking catalyst under hydrocarbon cracking conditions to convert the residual oil feed into lower molecular weight hydrocarbon product vapors and form a spent catalyst containing carbonaceous deposits including vanadium and/or sodium; separating a majority of the lower molecular weight hydrocarbon product vapors from the spent cracking catalyst to form separated product vapors and separated spent catalyst containing entrained hydrocarbon vapors; processing the separated product vapors into desired product fractions; subjecting the separated spent catalyst to stripping to remove therefrom a majority of the entrained hydrocarbon vapors; contacting the resulting stripped spent catalyst in a regenerator with an oxygen-containing regeneration gas under catalyst regeneration conditions which include a combination of a regeneration temperature and an oxygen level in the regeneration gas which is effective to burn off the spent catalyst a majority of the carbonaceous deposits, while leaving a majority of the vanadium and/or sodium on the catalyst in less than completely oxidized form, and thereby produce a regenerated catalyst having a carbon level reduced from that of the spent catalyst and containing vanadium and/or sodium, a majority of which is in less than the completely oxidized form, and; returning the regenerated catalyst to the reactor.

[0012] In one embodiment, the present invention employs an FCC process design which incorporates a regenerator design and method of operation that maintains a less than complete oxidation atmosphere and/or reducing atmosphere in the regenerator and/or a regenerator temperature below 1300°F (704°C). A less than complete oxidation atmosphere is defined as process conditions in the regenerator that results in at least 0.08 wt. % carbon on regenerated catalyst. That is, when processing residual oil feedstocks containing vanadium and/or sodium, it has been determined that the catalyst deactivation caused by vanadium and sodium can be substantially prevented by maintaining a less than complete oxidation atmosphere and/or a reducing atmosphere in the regenerator. This will retard the formation of vanadic acid and vanadium pentoxide and low melting point sodium compounds, and therefore, as discussed above, reduce the adverse effects of vanadium and sodium on catalyst activity.

[0013] It has also been determined that by maintaining the regenerator temperature below 1300°F (704°C), and more preferably below 1250°F (677°C), that one can also reduce, even when utilizing an excess of oxygen for regeneration, the effect of vanadium and sodium on catalyst activity. While the FCCU can be designed to operate the regenerator in a reducing atmosphere and/or at a temperature less than 1300°F (704°C) to minimize the catalyst deactivation by vanadium and sodium, combining both these processing conditions will result in the least catalys deactivation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] 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

[0015] The feedstock employed in the present process contains residual oil, which may be in admixture with other lower-boiling hydrocarbons such as one or more gas oils or the like. The proportion of residual oil in the feed may vary, depending upon the nature of the feedstock components. Typically, the residual oil feed will contain from about 5 to 90 vol. % residual oil, with the remainder being one or more gas oils, for example, a vacuum gas oil, atmospheric gas oil, recycle, or the like.

[0016] As used herein, the term residual oil refers to a crude oil fraction boiling above about 1000°F (538°C). Among the above-mentioned catalyst poisons, the residual oil will contain vanadium, sodium, or both.

[0017] It is recognized that a "residual oil" may contain sodium and vanadium in the metallic form and/or in the form of any various inorganic or organometallic compounds of these metals. When said sodium and vanadium are deposited on the circulating catalyst such deposits may be in the form of a metal or one or more compounds thereof, e.g., sulfur compound or organometallic compound. Thus, as used herein the term "vanadium used sodium deposits" refers any of various types of vanadium- and sodium- containing deposits formed on the catalyst as metals or as compounds thereof.

[0018] In a preferred method of practicing the invention a residual oil feed supplied via line 1 is mixed with regenerated catalyst supplied via line 2 in a reactor 4 of an FCC type reaction system. The design and operation of FCC reaction systems are well known, and need not be described in detail herein. Any type of FCC reaction system can be employed. However, the aforementioned MSCC system is preferred because of the reasons stated above. The flow of regenerated catalyst in line 2 from regenerator vessel 8 is regulated by regenerated catalyst slide valve 3 to control the outlet temperature of product vapors exiting the reactor 4 via line 10. After the residual oil feed is mixed with hot regenerated catalyst to vaporize and convert the feedstock into hydrocarbon products having molecular weights lower than that of the feedstock, the resultant reactor vapors flowing in line 10 are separated from the now spent catalyst. The reactor vapors, essentially free of catalyst, exit reactor 4 via line 10 and are further processed into desired product fractions in downstream equipment by means which are well known. The separated spent catalyst and entrained hydrocarbon vapors flow downward through reactor 4 into stripper section 15, where, in a preferred method, it is mixed with hot regenerated catalyst regulated by slide valve 16 to control the stripper temperature at a higher temperature than that of the reactor vapors in line 10. The now elevated temperature mixture of spent and regenerated catalyst is subjected to steam stripping in stripper 15 to remove as much hydrocarbon as possible before exiting reactor 4 through spent catalyst slide valve 5, which controls the catalyst level in the reactor stripper 15.

[0019] In the reactor 4 vapors of the residual oil feedstock intimately contact the catalyst therein under cracking conditions to produce lower molecular weight hydrocarbon product vapors, while at the same time there is formed spent catalyst having formed thereon carbonaceous deposits and metal deposits, including vanadium and sodium deposits, which typically are in form of sulfides or other metal-containing compounds.

[0020] Downstream of spent catalyst slide valve 5, the spent catalyst 14 is mixed with an oxygen-containing combustion gas, e.g., air, supplied via line 7 in combustor riser 6, wherein the mixture flows upwardly and into the regenerator vessel 8. The rate of combustion air used to burn the carbon from the spent catalyst is regulated to control the oxygen in regenerator flue gas, which exits the regenerator via line 9, at less than 1 mole%, more preferably less than 0.5 mole%, and still more preferably less than 0. 1 mole%. The lower the temperature of the regenerated catalyst, the higher one can operate the oxygen content of flue gas exiting the regenerator 8 via line 9. As the temperature of the outlet of combustion riser 6 is lowered, the carbon burning rate is decreased so that it is possible to maintain the level of carbon on regenerated catalyst using a less than complete oxidizing atmosphere or a reducing atmosphere, with oxygen exiting combustion riser 6.

[0021] This method, use of a combustor riser, of regeneration is preferred over a conventional fluidized bed regenerator, or a fast fluid regenerator, as it minimizes backmixing and minimizes oxygen partial pressure as the carbon on regenerated catalyst decreases and exposes the metals on the surface of the catalyst to possible oxidation. In the combustor riser, there is employed a high velocity, preferably greater than 10 ft. per second, and a short residence time, preferably less than 20 seconds, and more preferably less than 15 seconds. Use of a high velocity, short time riser regenerator 6 allows for operation at higher regenerated catalyst temperatures without complete regeneration or complete burning of the carbon from the catalyst surface, which will protect the majority of the metals from complete oxidation, compared to other methods of regeneration. This will result in less coke yield and more product yield. If one employs the more common fluidized bed regenerator or fast fluid regenerator, the regenerator temperature must be lowered to reduce the oxidation-potential of the vanadium and sodium. After the combustion air is and spent catalyst are mixed, the combustion of the carbonaceous deposits on the spent catalyst is initiated. As the fluidized mixture flows upwardly in combustion riser 6, the oxygen is consumed as the carbon is burned off the surface. This reduces the oxygen partial pressure which has the effect of limiting the oxidation driving force for burning the carbon or oxidizing the metals. Since the metals are mainly on the surface of the catalyst and the carbon deposited in reactor 4 covers these metals, the metals become exposed and can only be oxidized once they are uncovered and while at high temperature. Using a co-current regeneration system, as described above, minimizes or substantially prevents the oxidation of the metals. However, any type of regenerator, when operated in accordance with these teachings, can be used to reduce the catalyst deactivating effects of sodium and vanadium.

[0022] The outlet temperature of combustion riser 6 is controlled at less than 1300°F (704°C) and more preferably at less that 1250°F (677°C), to maintain a carbon level on regenerated catalyst, preferably of less than 0.4, preferably 0.3, wt%, but more than 0.08 wt.%. This is accomplished by mixing regenerated catalyst that has been cooled by catalyst cooler 11 with the upwardly flowing spent catalyst and combustion air at a point in combustion riser 6 where the temperature of the resulting mixture is less than 1250°F (677°C) and preferably less than 1200°F (649°C) to minimize the oxidation of metals and carbon burning from the surface of the cooled regenerated catalyst flowing in line 13. The rate of cooled regenerated catalyst is regulated by slide valve 12 to control the regenerated catalyst temperature at less that 1300° F (704°C), and more preferably below 1250°F (677°C). In regenerator vessel 8, the products of combustion (the flue gas in line 9) and the regenerated catalyst plus cooled regenerated catalyst are separated. The regenerator flue gas can be further processed for heat recovery and treated for particulate and SOx control before being exhausted to the atmosphere. The regenerated catalyst is returned to reactor 4 to vaporize and contact the residual oil feed in reactor 4 and recycled through catalyst cooler 11 and slide valve 5 to combustion riser 6 to control the regenerated catalyst temperature.

[0023] Thus, in accordance with the present invention the spent catalyst regeneration conditions in the regenerator, i.e. in the combustor riser 6 and the regenerator vessel 8, are maintained so that they are effective to burn a majority of the carbonaceous deposits from the spent catalyst while leaving a majority of the vanadium and sodium deposits in the non-oxidized or lower oxidation state. Preferably the regenerated catalyst has a carbon level of not more than about 0.4 wt.%, but at least about 0.08 wt.%, and oxidation of the vanadium and sodium deposits is substantially prevented. This can be accomplished by controlling the regenerator temperatures and atmosphere as described herein.

[0024] Having described preferred embodiments of the invention, various modifications thereof falling within the spirit of the invention may become apparent from the description and practice of the invention, and it is to be understood that the scope of the invention shall be determined by the appended claims and their equivalents.

Claims

1. An improved residual oil fluid catalytic cracking process for reducing catalyst deactivation caused by vanadium and/or sodium deposited on circulating catalyst used in the process from a residual oil feed, which process comprises the steps of:

a. contacting a feedstock containing residual oil in a fluid catalytic cracking reactor with hot regenerated cracking catalyst under hydrocarbon cracking conditions to convert the feedstock into hydrocarbon product vapors having a molecular weight lower than that of the feedstock and form a spent catalyst containing carbonaceous deposits and vanadium and/or sodium deposits,
b. separating a majority of the lower molecular weight hydrocarbon product vapors from the spent cracking catalyst to form separated product vapors and separated spent catalyst containing entrained hydrocarbon vapors,
c. processing the separated product vapors into desired product fractions,
d. subjecting the separated spent catalyst to stripping to remove therefrom a majority of the entrained hydrocarbon vapors,
e. contacting the resulting stripped spent catalyst in a regenerator with an oxygen-containing regeneration gas under catalyst regeneration conditions which include a combination of a regeneration temperature and an oxygen level in the regeneration gas which is effective to burn off the spent catalyst a majority of the carbonaceous deposits, while not completely oxidizing the majority-of the vanadium and/or sodium deposits on the catalyst so as to produce a regenerated catalyst having a carbon level reduced from that of the spent catalyst and containing vanadium and/or sodium, a majority of which is not completely oxidized, and
f. and returning the regenerated catalyst to the reactor.

2. The process of claim 1, wherein the stripping is conducted at a temperature greater than the temperature of the product vapors exiting the reactor.

3. The process of claim 1 wherein the regeneration temperature is less than 1300°F.

4. The process of claim 1 wherein the catalyst regeneration temperature is less than 1250°F.

5. The process of claim 1 wherein the regeneration produces a flue gas having an oxygen content is less than 1.0 mole%.

6. The process of claim 1 wherein the regeneration produces a flue gas having an oxygen content of less than 0.5 mole%.

7. The process of claim 1 wherein the regeneration produces a flue gas having an oxygen content less than 0.1 mole%

8. The process of claim 1, wherein the carbon level on the regenerated catalyst is not more than 0.4 wt.%.

9. The process of claim 1, wherein the carbon level on the generated catalyst is not less than 0.08 wt.%.

10. The process of claim 1, wherein the regeneration temperature is less than 1300°F and the regeneration is conducted in a reducing atmosphere.

11. The process of claim 1, wherein the regeneration conditions are effective to substantially prevent complete oxidation of the vanadium and/or sodium deposits on the catalyst during the regeneration.

12. The process of claim 1, wherein the stripped spent catalyst is mixed with an oxygen-containing combustion gas in a combustor riser and transported upwardly in the riser to the regenerator.

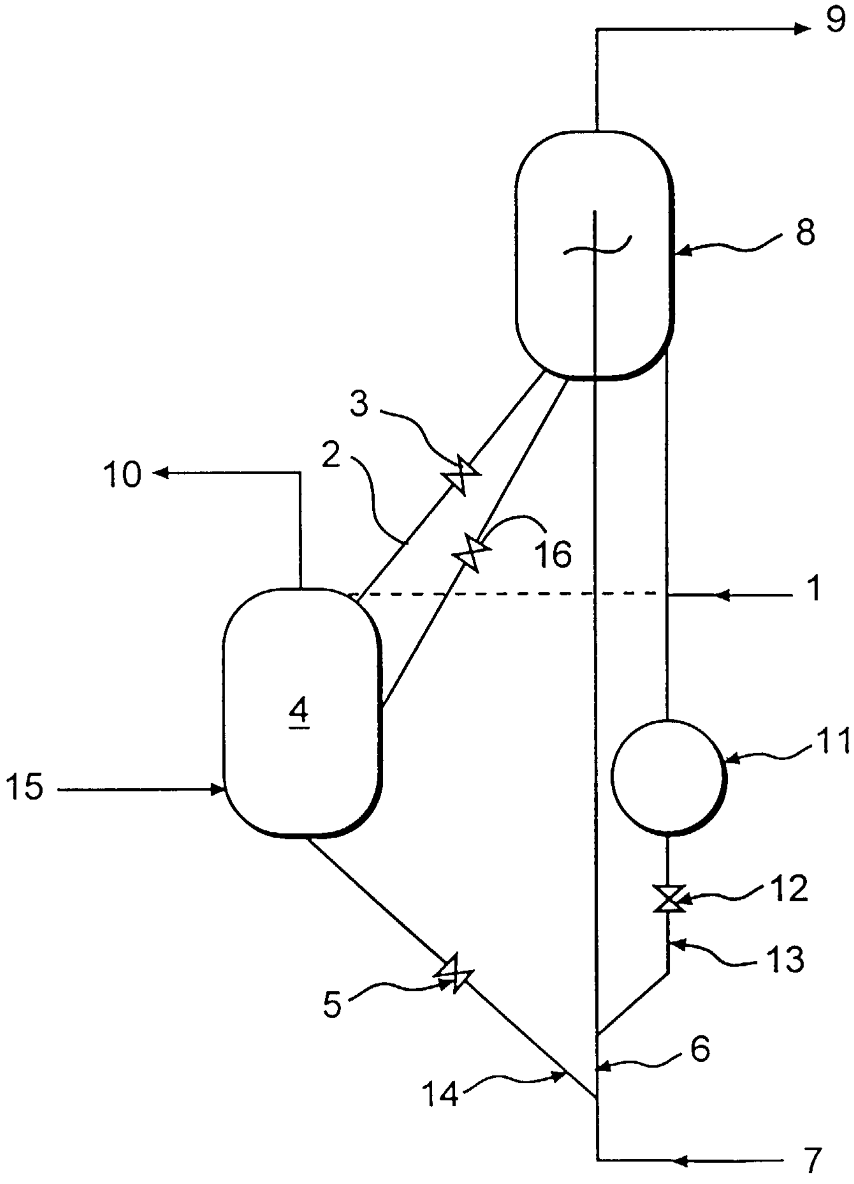

FIG. 1