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(54) **MULTI-STAGE COUNTERCURRENT
HYDROTREATING PROCESS**

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(57) **ABSTRACT**

A multi-stage process for removing heteroatoms, particularly organic sulfur and nitrogen components, from liquid petroleum and chemical streams. The feedstream flows countercurrent to the flow of a hydrogen-containing treat gas and is reacted with a first catalyst which is relatively tolerant to sulfur and nitrogen, such as a CoMo supported catalyst. When the level of organic sulfur in the feedstream is less than about 3,000 wppm and the level of organic nitrogen is less than about 1,000 wppm, the feedstream is reacted with said counter flowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and a Group VIA metal selected from Mo, W, or both, on a refractory support. The reaction vessel preferably contains vapor and optionally liquid by-pass means in one or more of the catalyst beds.

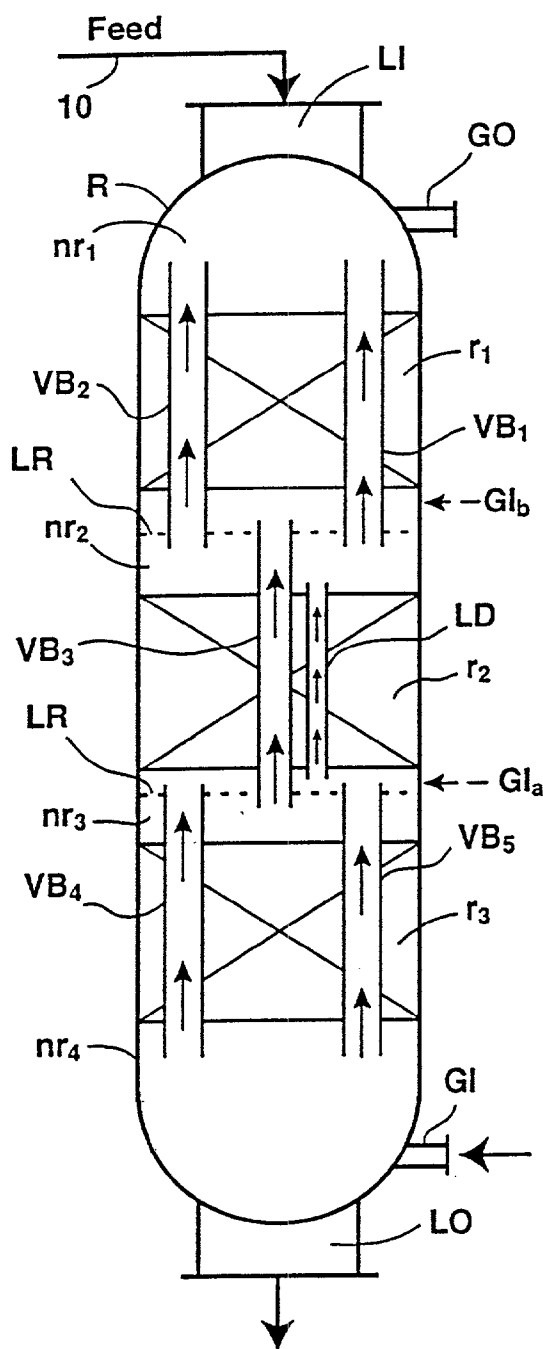


FIG. 1

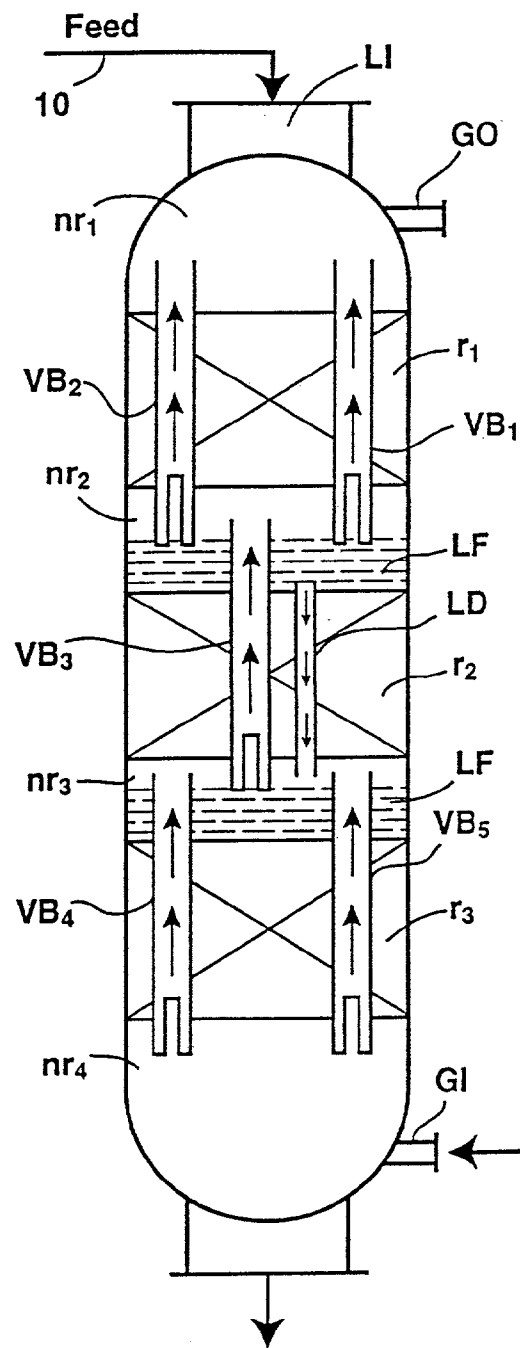


FIG. 2

MULTI-STAGE COUNTERCURRENT HYDROTREATING PROCESS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This is a continuation-in-part of U.S. Ser. No. 08/702,334 filed Aug. 23, 1996.

FIELD OF THE INVENTION

[0002] The present invention relates to a countercurrent process for removing heteroatoms, particularly organic sulfur and nitrogen components, from liquid petroleum and chemical streams. The feedstream flows countercurrent to the flow of a hydrogen-containing treat gas and is reacted with a first catalyst which is relatively tolerant to sulfur and nitrogen, such as a CoMo supported catalyst. When the level of organic sulfur in the feedstream is less than about 3,000 wppm and the level of organic nitrogen is less than about 1,000 wppm, the feedstream is reacted with said counter flowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and a Group VIA metal selected from Mo, W, or both, on a refractory support. The reaction vessel preferably contains vapor and optionally liquid by-pass means in one or more of the catalyst beds.

BACKGROUND OF THE INVENTION

[0003] There is a continuing need in the petroleum refining and chemical industries for improved catalyst and process technology. One type of process technology, which is often referred to as hydrotreating, involves the use of certain catalysts, typically those containing both Group VIA and Group VIII metals, for the removal of heteroatoms, such as sulfur, nitrogen, and sometimes oxygen. More active catalysts and improved reaction vessel designs are needed to meet this demand. Countercurrent reaction vessels have the potential of meeting some of this demand, but they have not done so to date because of the potential for upset. That is, upflowing treat gas has the potential of causing flooding of the reactor by preventing the feedstream from flowing through one or more catalyst beds. A two stage countercurrent process is disclosed in U.S. Pat. No. 3,147,210 for the hydroprocessing-hydrogenation of high boiling aromatic hydrocarbons. The feedstock is first subjected to catalytic hydroprocessing, preferably in co-current flow with hydrogen, then subjected to hydrogenation over a sulfur-sensitive noble metal hydrogenation catalyst countercurrent to the flow of a hydrogen. U.S. Pat. Nos. 3,767,562 and 3,775,291 disclose a similar process for producing jet fuels, except the jet fuel is first hydrodesulfurized prior to two-stage hydrogenation. U.S. Pat. No. 5,183,556 also discloses a two-stage co-current/countercurrent process for hydrofining - hydrogenating aromatics in a diesel fuel stream.

[0004] While the concept of countercurrent hydroprocessing has been known for some time, countercurrent flow reaction vessels are typically not used in the petroleum industry, primarily because, as previously mentioned, conventional countercurrent reaction vessels are susceptible to upset by catalyst bed flooding. While flooding is undesir-

able, catalyst contacting by the reactant liquid improves as the bed approaches flooding conditions. However, operating close to the point of incipient flooding leaves the process vulnerable to fluctuations in pressure or temperature or in liquid or gas flow rates. This could result in a disturbance large enough to initiate flooding and process unit shutdown, in order to recover stable operation. Such disruptions are highly undesirable in a continuous commercial operation.

[0005] Reaction vessels have been disclosed in co-pending U.S. Patent Applications 08/775,636 and 08/775,638 both filed on Dec. 31, 1996, and both entitled "Countercurrent Reactor", and both of which are incorporated herein by reference. These applications disclose countercurrent reactors which are less susceptible to flooding than conventional countercurrent reaction vessels. This is primarily due to the novel use of vapor passageways, or vapor by-pass means, which act to selectively bypass a fraction of the upward-flowing treat gas so it does not flow through one or more of the catalyst beds.

[0006] While the use of vapor by-pass means, typically tubes, has made the use of countercurrent reactors more commercially feasible, there is still a need in the art for improved catalyst staging in such vessels.

SUMMARY OF THE INVENTION

[0007] In accordance with the present invention, there is provided a multi-stage process for removing sulfur and nitrogen containing components from petroleum and chemical feedstreams containing at least one of said components, in the presence of a hydrogen-containing treat gas flowing countercurrent to the flow of said feedstream, the process which comprises:

[0008] reacting said feedstock in a first reaction stage with said hydrogen-containing treat gas in the presence of a catalyst comprised of Co and Mo on a refractory support until the reacted feedstock contains less than about 3,000 wppm sulfur and less than about 1,000 wppm nitrogen;

[0009] reacting said treated feedstock in a second stage with counterflowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and a Group VIA metal selected from one or both of Mo and W, on a refractory support.

[0010] In one embodiment of the present invention the reaction vessel contains a third reaction stage downstream of said second reaction stage, which third reaction stage contains a noble metal supported catalyst.

[0011] In another preferred embodiment of the present invention the third reaction stage is an aromatics hydrogenation stage.

[0012] In still another embodiment of the present invention the feedstock is reacted in the presence of the Ni/Group VIA metal catalyst only when its sulfur level reaches less than about 1,500 wppm and its nitrogen level reaches less than about 750 wppm.

[0013] In yet another embodiment of the present invention at least some of the vapor passageways are external to the reaction vessel.

BRIEF DESCRIPTION OF THE FIGURES

[0014] **FIG. 1** hereof is a reaction vessel of the present invention showing three reaction zones, each of which contains vapor passageways so that upflowing vapor can bypass a reaction zone, and one liquid drain means.

[0015] **FIG. 2** is a representation of how the reaction vessel of **FIG. 1** will respond to a flooding situation while actions are taken to return bed hydrodynamics to normalcy.

DETAILED DESCRIPTION OF THE INVENTION

[0016] In conventional countercurrent processing, the vertically upflowing treat gas has the potential of hindering the downwardly flowing liquid feedstream to such a degree to cause reactor flooding. That is, by not allowing liquid to drain through the catalyst bed(s) in the reactor. At low liquid and gas velocities the hindrance from the slowly moving gas is not enough to cause flooding and the liquid in the reaction vessel is able to pass through the catalyst bed or beds. However, if either the upflowing gas rate or the downflowing liquid rate is high enough, liquid cannot drain through the catalyst bed. As the liquid holdup in a catalyst bed increases, liquid accumulates above the top surface of the bed. The upflowing gas rate at which flooding occurs in a given catalyst bed will depend on such things as the flow rate and the physical properties of the downflowing liquid. Similarly, the downflowing liquid flow rate at which flooding occurs in a given bed similarly depends on the rate and properties of upflowing gas.

[0017] The reaction vessels used in the practice of the present invention are less susceptible to flooding than conventional countercurrent reaction vessels because of vapor passageways which act to selectively bypass a fraction of the upward-moving treat gas so that it does not flow through one or more of the catalyst beds. The fraction of upflowing treat gas that bypasses a catalyst bed will increase as vapor pressure drop increases through a catalyst bed. Thus, the vapor passageways provide a self-adjusting regulation of upward-flowing vapor, thereby extending the hydrodynamic operating window of the reaction vessel. Further extension of this range can be provided by including one or more external vapor passageways having flow control means. Such a system provides a means by which catalyst bed pressure drop, and therefore catalyst contacting efficiency, can be controlled. Preferably, when both internal and external vapor passageways are provided, the external vapor passageways can be controlled with a control means, preferably a valve for so-called "trim" bypassing. The valve of course can be automatically operated so that it opens and closes to the appropriate degree in response to a signal transmitted relating to pressure drop changes in the catalyst bed(s). That is, the trim bypass will be used to keep the reaction vessel operating as close to flooding as desirable.

The remaining treat gas stream, which does not bypass a particular catalyst bed or beds, will pass upward through the catalyst bed(s) and take part in the desired hydrotreating reaction, carry away light or vaporized reaction products, and strip catalyst poisons such as hydrogen sulfide, water and/or ammonia, etc.

[0018] The vapor passageways of the reaction vessels used in the practice of the present invention provide an extended operating range and an opportunity to operate close to the flooding point of the reaction vessel. This enables a more stable, more efficient reaction vessel operating regime. Further, the reaction vessel can safely and continuously operate while responding to normal process fluctuations in temperature and in liquid and vapor flow rate. The range of total flow rates that can be tolerated is thereby extended. Operating close to the flooding point results in very efficient contacting because the catalyst particles are well irrigated by the downflowing liquid. In the absence of vapor passageways, a conventional countercurrent reaction vessel would need to operate at lower efficiency in order to remain operable. The higher vapor flow rate capacity of the reaction vessels used in the practice of the present invention provides flexibility to use higher quench gas rates and/or treat gas rates, enabling a wider breadth of application for reactions involving high hydrogen consumption and heat release, such as aromatics saturation. Furthermore, the higher gas handling capacity enables the use of countercurrent reaction processing for reactions involving evolution of vapor phase products which might otherwise result in flooding due to excessive vapor generated during reaction, e.g., hydrocracking.

[0019] When flooding does occur, the reaction vessels used in the practice of the present invention are also more easily recovered and brought back to normal operation. During flooding, the liquid holdup in a catalyst bed increases and liquid may begin to accumulate above the top surface of the catalyst bed. This liquid must be drained to recover the reactor from a flooded state. The vapor passageways reduce gas flow rate through the catalyst bed(s), thus allowing the liquid to more easily drain through the catalyst bed(s). The liquid drain means of the present invention also helps recover the reaction vessel from flooding. Unless otherwise stated herein, the terms "downstream" and "upstream" are with respect to the flow of liquid which will flow downward.

[0020] The reaction vessels used in the practice of the present invention can be better understood by a description of an example reaction vessel, which is shown in **FIGS. 1 and 2** hereof. Miscellaneous reaction vessel internals, such as flow distributor means, thermocouples, heat transfer devices etc. are not shown in the figures for simplicity. **FIG. 1** shows reaction vessel R which contains liquid inlet LI for receiving a feedstock to be treated, and a liquid outlet LO for removing liquid reaction product. There is also provided treat gas inlet GI and gas outlet GO. The reaction vessel contains three vertically disposed reaction zones, r_1 , r_2 , and r_3 . Each reaction zone is immediately preceded and immediately followed by a non-reaction zone, nr_1 , nr_2 , nr_3 , and nr_4 . The non-reaction zone may be a void, or empty section,

in the reaction vessel. That is, a section which does not contain catalyst. Liquid distribution means LR (which is not shown in FIG. 2 for simplicity) can be situated above each reaction zone in order to more evenly distribute downflowing liquid to the next downstream reaction zone. Each reaction zone is comprised of a bed of catalyst suitable for the desired reaction.

[0021] Hydrotreating catalysts which are relatively tolerant to sulfur and nitrogen will be used in the first catalyst stage. By "tolerant to sulfur and nitrogen" we mean catalysts that are not as easily poisoned by sulfur and nitrogen as is a NiMo catalyst. Such sulfur/nitrogen tolerant catalysts will typically be those containing at least one Group VIII metal, preferably Fe or Co, more preferably Co; and at least one Group VIA metal, preferably Mo and W, more preferably Mo, on a high surface area support material, preferably alumina. The Groups referred to herein are from the Period Table of the Elements, Sargent-Welch Scientific Co., 1980, Catalog No. S-18806. The Group VIII metal is typically present in the an amount ranging from about 2 to 20 wt. %, preferably from about 4 to 12%. The Group VIA metal will typically be present in an amount ranging from about 5 to 50 wt. %, preferably from about 10 to 40 wt. %, and more preferably from about 20 to 30 wt. %. All metals weight percents are on support. By "on support" we mean that the percents are based on the weight of the support. For example, if the support were to weigh 100 g. then 20 wt. % Group VIII metal would mean that 20 g. of Group VIII metal was on the support. It is within the scope of the present invention that more than one type of sulfur/nitrogen hydrotreating catalyst be used in this first reaction stage. For example, two or more different hydrotreating catalysts can be blended together and used in a mixed catalyst bed. Further, two or more hydrotreating catalysts can be extruded together so that they are composited in the same extrudate. Also, two or more hydrotreating catalysts can be used in separate catalyst beds, preferably fixed beds, wherein each catalyst bed will represent a catalyst zone within the same single catalyst stage. That is, each catalyst stage can contain more than one catalyst zones. Typical hydrotreating temperatures will range from about 100° C. to about 400° C. at pressures from about 50 psig to about 2,000 psig. Liquid hourly space velocities are from about 0.2 to 10 volumes of liquid per volume of catalyst per hour. Typical treat gas rates are from about 200 to about 3,000 SCF hydrogen-rich gas per barrel of feedstock.

[0022] It has been found by the inventors hereof that when the feedstream contains less than about 3,000 wppm, preferably less than about 1,500 wppm, and more preferably less than about 1,000 wppm sulfur; and less than about 1,000 wppm, preferably less than about 750 wppm, and more preferably less than about 500 wppm nitrogen, a catalyst comprised of Ni and one or both of Mo and W will remove unexpectedly more of the remaining sulfur and nitrogen components when compared to other conventional hydrotreating catalyst. Such catalysts include NiMo, NiW, and Ni-Mo-W, on a refractory support. Preferred are NiMo and Ni-Mo-W. Thus, it is critical to the present invention that

the portion of the reaction zone, where the feedstream contains said low levels of sulfur and nitrogen components be subjected to a said Ni-based supported hydrotreating catalyst.

[0023] It is within the scope of the present invention that additional reaction stages can follow the second reaction stage containing the Ni/Group VIA metal catalyst. One such stage can be an aromatics hydrogenation stage containing a noble metal sulfur sensitive hydrogenation catalyst. Non-limiting examples of noble metal catalysts include those based on platinum and/or palladium, which is preferably supported on a suitable support material, typically a refractory oxide material such as alumina, silica, alumina-silica, kieselguhr, diatomaceous earth, magnesia, and zirconia. Zeolitic supports can also be used. Such catalysts are typically susceptible to sulfur and nitrogen poisoning. The aromatic saturation zone is preferably operated at a temperature from about 40° C. to about 400° C., more preferably from about 260° C. to about 350° C., at a pressure from about 100 psig to about 3,000 psig, preferably from about 200 psig to about 1,200 psig, and at a liquid hourly space velocity (LHSV) of from about 0.3 V/V/Hr. to about 2.0 V/V/Hr.

[0024] A hydrocracking reaction stage can also be present downstream of the NiMo reaction stage. If one of the downstream reaction zones is a hydrocracking zone, the catalyst can be any suitable conventional hydrocracking catalyst run at typical hydrocracking conditions. Typical hydrocracking catalysts are described in U.S. Pat. No. 4,921,595 to UOP, which is incorporated herein by reference. Such catalysts are typically comprised of a Group VIII metal hydrogenating component on a zeolite cracking base. The zeolite cracking bases are sometimes referred to in the art as molecular sieves, and are generally composed of silica, alumina, and one or more exchangeable cations such as sodium, magnesium, calcium, rare earth metals, etc. They are further characterized by crystal pores of relatively uniform diameter between about 4 and 12 Angstroms. It is preferred to use zeolites having a relatively high silica/alumina mole ratio greater than about 3, preferably greater than about 6. Suitable zeolites found in nature include mordenite, clinoptilolite, ferrierite, dachiardite, chabazite, erionite, and faujasite. Suitable synthetic zeolites include the Beta, X, Y, and L crystal types, e.g., synthetic faujasite, mordenite, ZSM-5, MCM-22 and the larger pore varieties of the ZSM and MCM series. A particularly preferred zeolite is any member of the faujasite family, see Tracy et al. Proc. of the Royal Soc., 1996, Vol. 452, p813. It is to be understood that these zeolites may include demetallated zeolites which are understood to include significant pore volume in the mesopore range, i.e., 20 to 500 Angstroms. Non-limiting examples of Group VIII metals which may be used on the hydrocracking catalysts include iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, and platinum. Preferred are platinum and palladium, with platinum being more preferred. The amount of Group VIII metal will range from about 0.05 wt. % to 30 wt. %, based on the total weight of the catalyst. If the metal is a Group VIII noble metal, it

is preferred to use about 0.05 to about 2 wt. %. Hydrocracking conditions include temperatures from about 200° to 425° C., preferably from about 220° to 330° C., more preferably from about 245° to 315° C.; pressure of about 200 psig to about 3,000 psig; and liquid hourly space velocity from about 0.5 to 10 V/V/Hr, preferably from about 1 to 5 V/V/Hr.

[0025] Five vapor passageways VB₁, VB₂, VB₃, VB₄, and VB₅ and one liquid drain means LD are shown for the reaction vessels of the Figures, although any number and size of the vapor passageways can be used depending on the portion of the vapor one wishes to bypass the reaction zone(s). For purposes of the present invention, it is desirable that only a portion of the vapor bypasses one or more countercurrent reaction zones. It is preferred that less than about 50 vol. %, more preferably less than about 25 vol. %, and most preferably less than about 10 vol. % of the vapor bypasses any individual countercurrent reaction zone. The liquid drain means serves as a vapor passageway during normal operation but can allow liquid to drain during flooding upsets. It is to be understood that more than one liquid drain means can be used in any one or more reaction zones. The size and number of such liquid drain means will be dependent on such things as the size of the reaction vessel, the packing of the catalyst in the catalyst bed(s) and the flow rate of liquid feedstock through the catalyst bed.

[0026] The reaction vessel of **FIG. 1** is operated by introducing the feedstock to be treated into liquid inlet LI of reaction vessel R. A suitable treat gas, such as a hydrogen-containing gas, is introduced via port GI into the reaction vessel countercurrent to the downward flow of the liquid feedstock. The term "hydrogen-containing treat gas" means a treat gas stream containing at least an effective amount of hydrogen for the intended reaction. The treat gas stream will preferably contain at least about 50 vol. %, more preferably at least about 75 vol. % hydrogen. It is also preferred that the hydrogen-containing treat gas be make-up hydrogen-rich gas, preferably hydrogen. It is to be understood that the treat gas need not be introduced solely at the bottom of the reaction vessel at GI, but may also be introduced into any one or more of the non-reaction zones, for example at GI_a and/or GI_b. Treat gas can also be injected into any one or more of the catalyst beds. An advantage of introducing treat gas at various points in the reaction vessel is to control the temperature within the reaction vessel. For example, cold treat gas can be injected into the reaction vessel at various points to moderate any exothermic heat of reaction. It is also within the scope of this invention that all of the treat gas can be introduced at any one of the aforesaid points as long as at least a portion of it flows countercurrent to the flow of liquid in at least one reaction zone.

[0027] The reaction vessels of the present invention are operated at suitable temperatures and pressures for hydrotreating reactions. The liquid feedstock passes downward through the catalyst bed of reaction zone r₁, where it reacts with the treat gas on the catalyst surface. Any resulting vapor-phase reaction products are swept upwards by the

upward-flowing treat gas. Such vapor-phase reaction products may include relatively low boiling hydrocarbons and heteroatom components, such as H₂S and NH₃. Any unreacted feedstock, as well as liquid reaction product passes downwardly through each successive catalyst bed of each successive reaction zone r₂ and r₃. This Figure shows an optional liquid distribution means LR which can be positioned above each catalyst bed. The ends of the vapor passageways may be situated above or below the liquid distribution means. For example, **FIG. 1** shows the upper end of vapor passageway VB₃ terminating at a point above liquid distribution means LR. The lower end of vapor passageways VB₁ and VB₂ terminate at a point below the liquid redistribution means LR. This arrangement allows selective bypassing of vapors produced in reaction zone r₂ to the reaction vessel gas outlet, while bringing a higher purity hydrogen-containing treat gas into catalyst bed r₁ by selectively bypassing higher-purity hydrogen-containing gas from nr₃ to the inlet of catalyst bed r₁. It is within the scope of this invention that the upper or lower ends of one or more of the vapor passageways terminate at a point within the reaction zone. The reaction vessel may employ any conventional distribution trays, such as sieve trays, bubble cap trays, etc. The liquid effluent exits the reaction vessel via port LO and vapor effluent via port GO. The preferred mode of operation of the reaction vessels of the present invention is to bypass only a portion of the vapor while still maintaining enough vapor upflowing through the catalyst bed(s) to meet the treat gas (hydrogen) demand for that catalyst bed(s) with relatively high kinetic efficiency.

[0028] As previously mentioned, countercurrent reaction vessels are typically susceptible to upset by flooding. That is, the upflowing treat gas can prevent liquid feedstock and liquid effluent from flowing downward through one or more catalyst beds. **FIG. 2** hereof depicts how the reaction vessel of **FIG. 1** would operate during a flooding situation to get the reaction vessel back on-stream without substantial downtime. For example, during a flooding situation in reaction zone r₂, liquid holdup in the bed increases and liquid may begin to accumulate above the top surface of the catalyst bed. One or more liquid drain means LD are provided to allow the liquid to bypass one or more catalyst beds. Prior to flooding, the liquid drain means will act as a vapor passageway. The top of the liquid drain means can be flush with, or any height above the top surface of the catalyst bed. It is preferred that the top of the liquid drain means be substantially flush with the top surface of the catalyst bed. Any liquid that passes through the drain means can be passed to the next downstream bed or it can preferably be recycled to any one or more reaction zones.

[0029] The vapor and liquid drain passageways may be any suitable structure constructed from a material that can withstand the operating conditions of the reaction vessel. Suitable materials include metals, such as stainless and carbon steels; ceramic materials; as well as high performance composite materials such as carbon fiber materials. Preferred are tubular passageways. The passageways need not be perfectly vertical. That is, they can be inclined or

curved, or even in the form of a spiral. They can also be perforated along the sides. It is to be understood that the passageways can be of any suitable size depending on the amount and rate of vapor one wishes to pass from one non-reaction zone to another. Further, one or more of the passageways, or drain means, can have a flat substantially horizontal member, such as a baffle, above it to prevent liquid from an upstream bed from falling into the passageways. Also, more than one passageway can be extended through at least a portion of any one or more reaction zones. It is preferred that the vapor passageways be extended entirely through the one or more reaction zones. When a plurality is used it is preferred that they be concentrically located about the vertical axis of the reaction vessel. One or more vapor passageways can also be routed external to the reaction zone. For example, a tubular arrangement can be used on the outside of the reaction vessel so that one or more non-reaction zones are in fluid communication with any one or more other non-reaction zones. The vapor passageways may contain a flow control means to control the portion of vapors which is passed from one non-reaction zone to another non-reaction zone. If the vapor passageways are external to the reaction vessel, then it is preferred that the flow control means be simply a flow control valve.

[0030] It is within the scope of the present invention that the vapor passageways bypass two or more catalyst beds, or reaction zones. Further, the vapor passageways need not be hollow structures, such as solid-walled tubes, but they may contain a packing material, such as inert balls. The packing material in the vapor passageways can be of a different size than the catalyst particles in the catalyst beds of the reaction zones. Such packing may help to improve the bypassing characteristics of said tubes. It is preferred that one or more co-current reaction zones be upstream of one or more countercurrent reaction zones. The zones can be in separate vessels or two or more zones can be in the same vessel. It is preferred that all countercurrent zones be in the same vessel.

[0031] Feedstocks suitable for use in the practice of the present invention include those in the naphtha boiling range to heavy feedstocks, such as gas oils and resids. Typically, the boiling range will be from about 50° C. to about 1000° C.. Non-limiting examples of such feeds which can be used in the practice of the present invention include vacuum resid, atmospheric resid, vacuum gas oil (VGO), atmospheric gas oil (AGO), heavy atmospheric gas oil (HAGO), steam cracked gas oil (SCGO), deasphalted oil (DAO), and virgin and cracked distillates and mixtures thereof.

[0032] In the case where the first reaction zone is a co-current hydrotreating reaction zone, the liquid effluent from said hydrotreating reaction zone will be passed to at least one downstream reaction zone where the liquid is passed through a bed of catalyst countercurrent to the flow of upflowing hydrogen-containing treatgas. Depending on the nature of the feedstock and the desired level of upgrading, more than one reaction zone may be needed. For example, the first stage containing the sulfur/nitrogen toler-

ant catalyst can consist of two catalyst zones. The first catalyst zone of the first stage can be a co-current catalyst zone and the second a countercurrent catalyst zone.

[0033] The liquid phase in the reaction vessels of the present invention will typically be comprised of the higher boiling point components of the feed. The vapor phase will typically be a mixture of hydrogen-containing treat gas, heteroatom impurities, and vaporized lower-boiling components of the fresh feed, as well as light products of hydroprocessing reactions. The vapor phase in the catalyst bed of a countercurrent reaction zone will be swept upward with the upflowing hydrogen-containing treat gas and collected, fractionated, or passed along for further processing. If the vapor phase effluent still contains an undesirable level of heteroatoms and/or aromatics, it can be passed to a vapor phase reaction zone containing additional hydrotreating catalyst and subjected to suitable hydrotreating conditions for further removal of heteroatoms. It is to be understood that all reaction zones can either be in the same vessel separated by non-reaction zones, or any can be in separate vessels. The non-reaction zones in the later case, will include the transfer lines leading from one vessel to another.

[0034] In an embodiment of the present invention, the feedstock can be introduced into a first catalyst zone co-current with the flow of hydrogen-containing treat-gas and reacted with a sulfur/nitrogen tolerant catalyst. A vapor phase effluent fraction can then be separated from the liquid phase effluent fraction between reaction zones. That is, in a non-reaction zone. The vapor phase effluent can be passed to additional hydrotreating, or collected, or further fractionated. The liquid phase effluent will then be passed to the next downstream reaction zone, which will preferably be a countercurrent reaction zone. If the sulfur and nitrogen levels are below the 3,000/1,000 wppm levels respectively, this countercurrent zone can in fact be the second reaction stage containing the NiMo catalyst. If the levels of sulfur and nitrogen are still too high, then this countercurrent zone can contain another sulfur/nitrogen tolerant hydrotreating catalyst. In other embodiments of the present invention, vapor phase effluent and/or treat gas can be withdrawn or injected between any reaction zones.

[0035] The countercurrent contacting of liquid from an upstream reaction zone with upflowing treat gas strips dissolved H₂S and NH₃ impurities from the effluent stream, and results in greater hydrogen partial pressure and improved catalyst performance downstream. The resulting final liquid product will contain a substantially lower level of heteroatoms and somewhat more hydrogen content than the original feedstock. This liquid product stream may be sent to downstream hydroprocessing or conversion processes.

What is claimed is:

1. A multi-stage process for removing sulfur and nitrogen containing components from petroleum and chemical feedstreams containing at least one of said components, in the

presence of a hydrogen-containing treat gas flowing countercurrent to the flow of said feedstream, the process which comprises:

reacting said feedstock in a first reaction stage with said hydrogen-containing treat gas in the presence of a hydrotreating catalyst comprised of at least one Group VIII metal and at least one Group VIA metal on a refractory support, at hydrotreating conditions, until the reacted feedstock contains less than about 3,000 wppm sulfur and less than about 1,000 wppm nitrogen;

reacting said treated feedstock from said first reaction stage in a second stage with counterflowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and one or both of a metal selected from Mo and W, on a refractory support.

2. The process of claim 1 wherein the hydrotreating conditions include temperatures ranging from about 100° C. to about 400° C. at pressures from about 50 psig to about 2,000 psig.

3. The process of claim 1 wherein the Group VIII metal is Co and the Group VIA metal is Mo.

4. The process of claim 1 wherein the first reaction zone is operated in a co-current mode wherein the feedstream and the treat gas are both flowing in the same direction.

5. The process of claim 1 wherein both the first and the second reaction stages are operated in countercurrent mode wherein the feedstream and the treat gas flow countercurrent to each other.

6. The process of claim 1 wherein the amount of Group VIII metal is from about 2 wt. % to 20 wt. %, based on the total weight of the catalyst.

7. The process of claim 1 wherein the amount of Group VIA metal is from about 5 to about 50 wt. %, based on the total weight of the catalyst.

8. The process of claim 3 wherein 2 wherein the Group VIII metal is Co and the Group VIA metal is Mo.

9. A multi-stage process for removing sulfur and nitrogen containing components from petroleum and chemical feedstreams containing at least one of said components, in the presence of a hydrogen-containing treat gas flowing countercurrent to the flow of said feedstream, the process which comprises:

reacting said feedstock in a first reaction stage with said hydrogen-containing treat gas in the presence of a hydrotreating catalyst comprised of at least one Group VIII metal and at least one Group VIA metal on a refractory support, at hydrotreating conditions, until the reacted feedstock contains less than about 3,000 wppm sulfur and less than about 1,000 wppm nitrogen;

reacting said treated feedstock from said first reaction stage in a second stage with counterflowing hydrogen-containing treat gas in the presence of a catalyst comprised of Ni and one or both of a metal selected from Mo and W, on a refractory support; and

reacting the treated feedstock from said second reaction stage in a third reaction stage in the presence of a hydrogen-containing treat gas and an aromatics hydrogenation catalyst comprised of a noble metal on a refractory support at hydrogenation conditions.

10. The process of claim 9 wherein the hydrotreating conditions include temperatures ranging from about 100° C. to about 400° C. at pressures from about 50 psig to about 2,000 psig.

11. The process of claim 10 wherein the Group VIII metal is Co and is present in an amount ranging from about 2 wt. % to 20 wt. %, and the Group VIA metal is Mo in an amount ranging from about 5 to 50 wt. %, based on the total weight of the catalyst.

12. The process of claim 11 wherein the first reaction zone is operated in a co-current mode wherein the feedstream and the treat gas are both flowing in the same direction.

13. The process of claim 11 wherein both the first reaction stage is operated in co-current mode and the second and third reaction stages are operated in countercurrent mode wherein the feedstream and the treat gas flow countercurrent to each other.

14. The process of claim 11 wherein the all three stages are operated in countercurrent mode.

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