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Chabot

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(54) **EXTENSION OF CATALYST CYCLE
LENGTH IN RESIDUUM
DESULFURIZATION PROCESSES**

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(76) Inventor: **Julie Chabot**, Novato, CA (US)

Correspondence Address:
Penny L. Prater
Chevron Corporation
P.O. Box 6006
San Ramon, CA 94583-0806 (US)

(57) **ABSTRACT**

Solvent injection in amounts no greater than 2 wt % can favorably alter the way heavy metals, such as vanadium, are normally deposited in catalyst particles. Heavy metals may be stored on the catalyst in a more compact form, saving catalyst pore volume. Consequently catalyst cycle length is improved, since capacity for deposition is increased.

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Related U.S. Application Data

(63) Non-provisional of provisional application No. 60/230,646, filed on Sep. 7, 2000.

The instant invention has also been demonstrated to control the rate of catalyst fouling by deposition of coke, or micro-carbon residue (MCR). In the past, attempts to increase catalyst activity led to increased rates of catalyst fouling and shorter catalyst life. In the instant invention the rate of deposition of microcarbon residue is decreased, resulting in slower fouling of pores and increased cycle length.

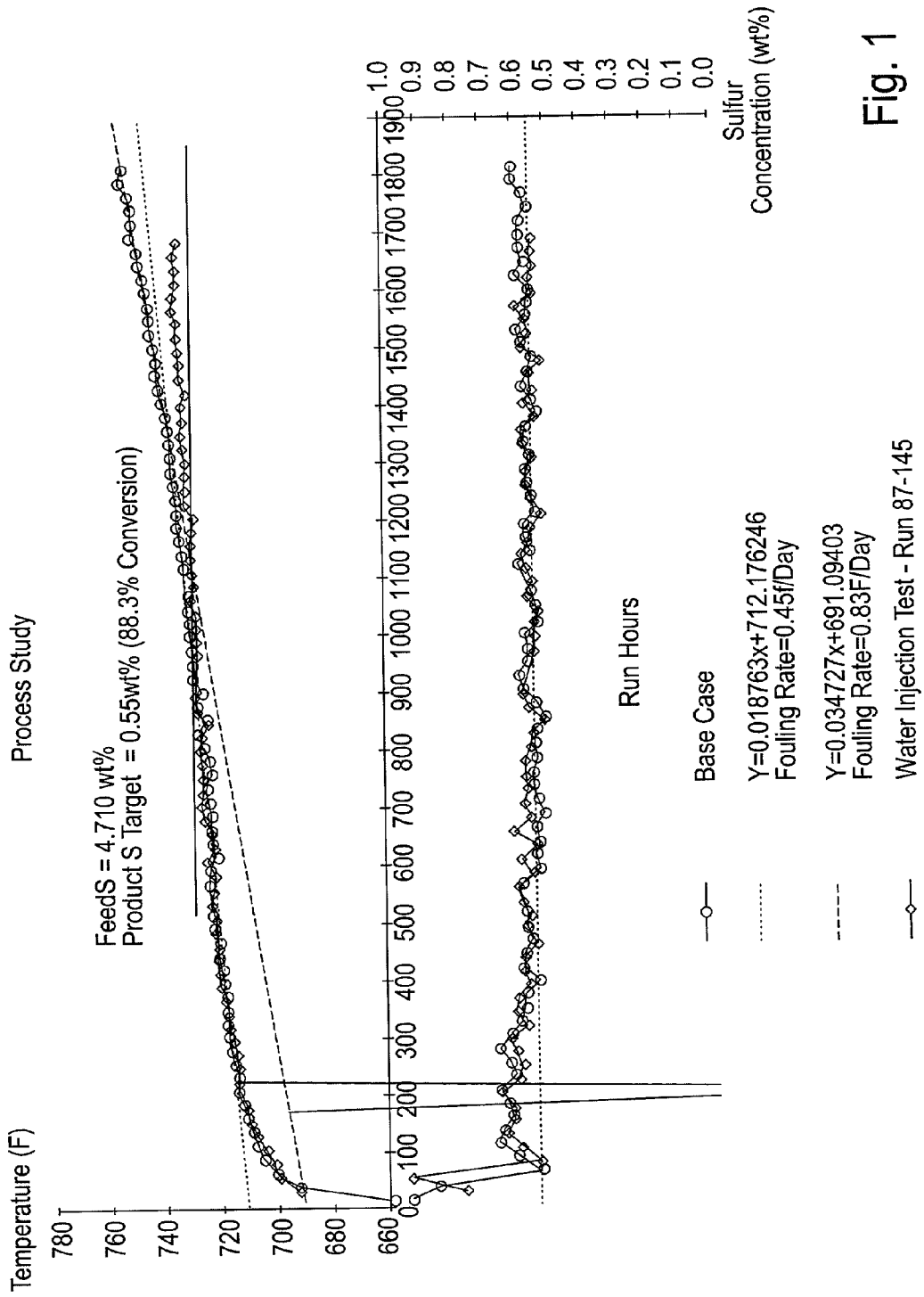


Fig. 1

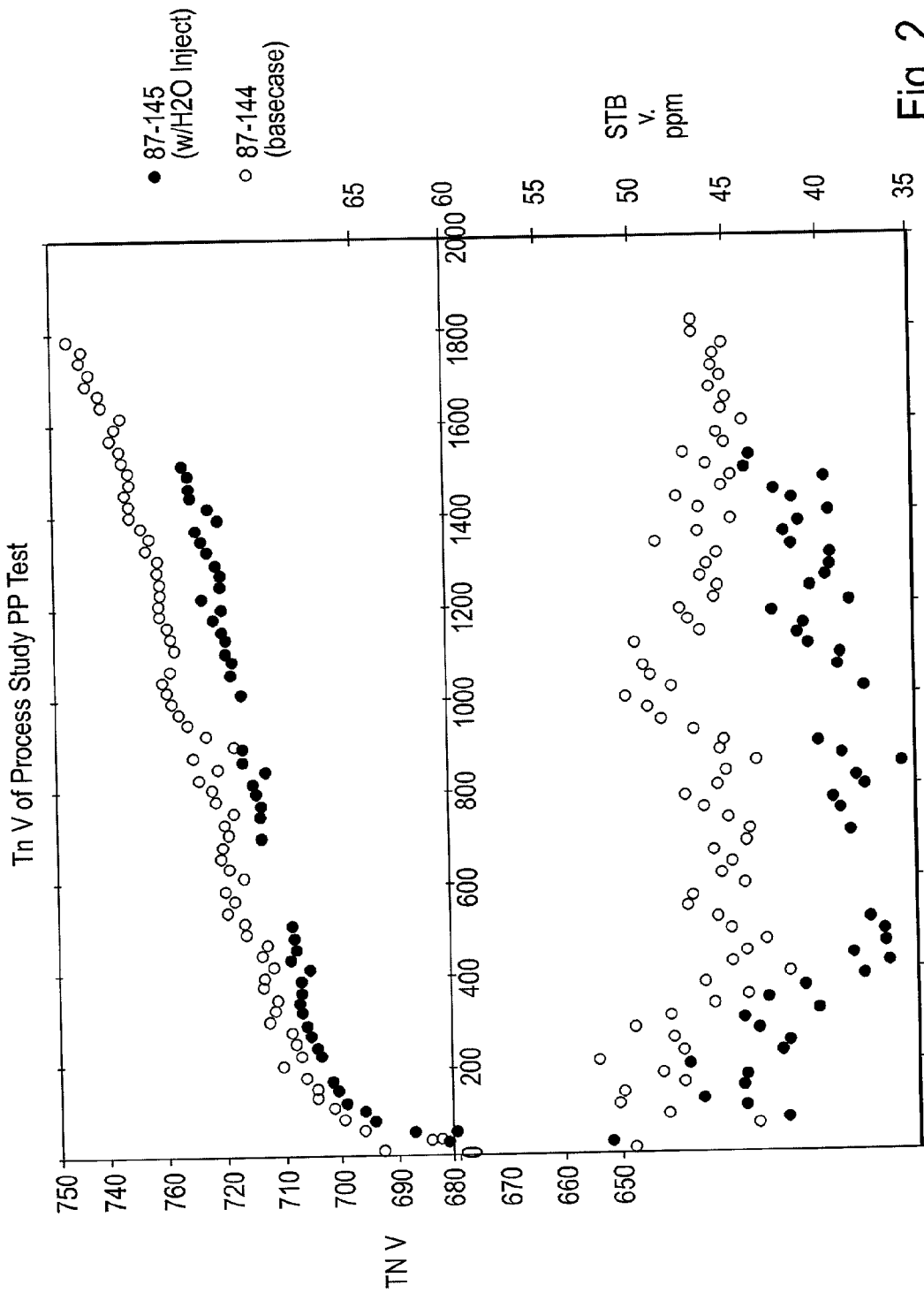


Fig. 2

EXTENSION OF CATALYST CYCLE LENGTH IN RESIDUUM DESULFURIZATION PROCESSES

[0001] This application claims priority from U.S. Provisional Application Serial No. 60/230,646, filed Sep. 7, 2000.

FIELD OF INVENTION

[0002] This invention is concerned with a process for the extension of catalyst cycle length when employed in residuum hydrodesulfurization processes.

BACKGROUND OF THE INVENTION

[0003] Catalyst poisoning has long been a problem in hydrodesulfurization of residuum and heavy oils. These feeds often contain organometallic compounds, such as nickel and vanadium. These metallic impurities are thought to deposit on the surface and in the pores of the hydrodesulfurization catalyst. Catalyst poisoning has been known to decrease catalyst activity, particularly if dissolved metals such as nickel and vanadium are present in amounts greater than 10 to 20 ppm.

[0004] U.S. Pat. No. 5,215,955 (Threlkel) attempted to solve the problem of fouling by the use of a catalyst having a minimum number of macropores. Less than 2% of the pore volume of the catalyst of Threlkel may possess a diameter greater than 1000Å. This catalyst contains Group VIB and Group VIII metals on a support comprising alumina. At least 80% of the pore volume comprises pores having a diameter between 110 and 190Å. In addition to increased activity, this catalyst was known to have increased life and increased metals capacity. This solution did limit residuum processing to the use of specific catalysts, however.

[0005] Other approaches have been used over the years to enhance catalyst effectiveness in hydrodesulfurization processes, among them "solvent injection." Though the concept of "solvent injection" into residuum hydroprocessing units is not new, and has actually been practiced commercially for many years in a number of units, its impact on catalyst performance has actually been very poorly understood. The most common solvent has always been water. If used in large amounts, however, solvent injection could create deleterious side effects.

[0006] U.S. Pat. No. 4,013,637 (Eberly, Jr.) discloses a hydrodesulfurization process in which water is employed. The effectiveness of the process is improved by injecting 1-32 volume percent in the gas phase of the reaction zone. The feed however, contains substantially no metals. The intent of the instant invention employs water to enhance catalyst life when feeds containing heavy metals are being desulfurized.

[0007] GB 1468160 and GB 1505886 are commonly owned and disclose processes for catalytic hydrodesulfurization in the presence of water vapor of oils containing vanadium and nickel, without catalyst replenishment. These inventions possess specific requirements concerning water vapor partial pressure and the ratio between average pore diameter and average particle diameter for the catalyst or catalyst combination employed. Another commonly owned patent, GB 1525508, also discloses catalytic desulfurization employing water, or another solvent, such as a lower alcohol or other water precursor.

[0008] U.S. Pat. No. 4,052,295 (Prnk) discloses a process for catalytic hydrodesulfurization of vanadium-containing heavy hydrocarbon oils. Heavy hydrocarbon oil containing vanadium is contacted at elevated temperature and pressure with hydrogen and with a catalyst. The catalyst is loaded with nickel and/or cobalt and with about 2.5 to 60 parts by weight of molybdenum and or tungsten on a porous carrier such as alumina. No water vapor is added until the average vanadium content of the catalyst has increased during the contacting by at least 5 parts by weight per 100 parts by weight.

[0009] Prnk states that the use of water vapor can be used effectively toward the end of a desulfurization operation which has been operated in the absence of added water vapor when the temperature has been raised to the maximum allowable level and operation under normal circumstances would have to be terminated.

[0010] Prnk points out problems that arose in its invention with the use of water vapor in hydrodesulfurization of heavy oils containing vanadium or other heavy metals. The use of water vapor, according to Prnk, requires extra energy to evaporate the requisite quantity of water, resulting in a rise of costs associated with desulfurization. Furthermore, Prnk found, in order to ensure that the process be carried out at a constant total pressure, the hydrogen partial pressure must be reduced if the desulfurization is carried out in the presence of water vapor. Reduction of the hydrogen partial pressure generally results in lower catalyst activity. For these reasons water was added at a certain stage in the process, but not initially. In the instant invention it is preferable to add water early in the operational cycle in order to maximize metals deposition. Metals are deposited constantly throughout the cycle if water deposition begins early.

[0011] U.S. Pat. No. 3,501,396 (Gatsis) discloses a process for the desulfurization of petroleum crude oil, which comprises admixing the crude oil with hydrogen and from 2 to 30 wt % water and reacting the resultant mixture in contact with a catalytic composite at desulfurizing conditions. The patent states that utilization of water in these comparatively excessive amounts appears to improve the hydrogen diffusion rate through the liquid phase on the catalyst, being increased as a result of the reduced viscosity and surface tension characteristics of the liquid phase. The difficulty of supplying hydrogen to the active sites of the catalyst is greatly reduced, and catalytic stability and increased. There is no mention in U.S. Pat. No. 3,501,396 of extension of catalyst life. Furthermore, the instant invention obtains its benefits using no more than 2 wt % water.

[0012] U.S. Pat. No. 3,753,894 (Shoemaker et al.), discloses a hydrodesulfurization process for processing a sulfur-containing residuum feed, wherein water is injected between the several catalyst beds of a multi-bed reactor to quench the products of the reaction and simultaneously to suppress deactivation of the catalyst, particularly as occurs during the initial period of a production run. Water may be added in concentrations as high as 50 wt %.

[0013] As these references demonstrate, it was commonly believed that solvent injection induced slight benefits in catalyst activity, particularly concerning sulfur or heavy metals removal and to a lesser degree the removal of microcarbon residue. Conditions, feeds, and catalysts useful in these inventions were specifically limited, however. Often

solvents such as water were used in large amounts. Finding a process in which the optimal amount of solvent could be used would reduce the need for process modifications, simplify downstream processing, decrease operating costs, and lessen hydrogen partial pressure penalties.

SUMMARY OF THE INVENTION

[0014] Catalyst fouling by heavy metals, such as vanadium, may be inhibited by the injection of an effective amount of solvent during the residuum hydrodesulfurization process or just prior to it. Water injection aids in the control of the temperature increase requirement over time. Water injection results in a more uniform deposition of metals such as vanadium within the catalyst pellets, thereby delaying the onset of pore mouth plugging.

[0015] The most preferred solvent is water. The process of the instant invention has been found to operate effectively under a wide variety of conditions and with a wide variety of feeds and catalysts.

[0016] In the past as the references in the Background of the Invention demonstrate, water in relatively large quantities was added in order to increase catalyst activity. Recent findings have shown that the most interesting aspect of solvent injection in specific amounts is not actually its relatively minor impact on catalyst activity, but its significant impact on catalyst cycle length. Solvent injection in amounts no greater than 2 wt %, results in a controlled temperature increase across the reactor, and can favorably alter the way heavy metals, such as vanadium, are normally deposited in catalyst particles. Heavy metals may be stored on the catalyst in a more compact form, saving catalyst pore volume. Consequently catalyst cycle length is improved, since capacity for deposition is increased.

BRIEF DESCRIPTION OF THE FIGURES

[0017] **FIG. 1** demonstrates the effect that the introduction of 2 wt % water 200 hours into the operation cycle has on the temperature increase requirement over time, as compared to an operation cycle with no water injection. The normalized temperature of about 730° F. levels out at approximately 800 hours on stream. The normalized temperature is the temperature that would be required to keep the sulfur concentration at 0.55 wt %. Product sulfur concentration remains constant at 0.55 wt % until the end of the operation cycle without temperature increase.

[0018] **FIG. 2** illustrates the same operational cycles as shown in **FIG. 1**. The concentration of vanadium in the product is lower at lower operating temperatures in the case, in which 2 wt % water was injected, while in the cycle in which no water was added vanadium concentrations in the product were higher. This demonstrates that more vanadium is remaining on the catalyst at the end of the run and is better penetrating the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Solvent injection, as depicted in the instant invention, is useful in most residuum hydroprocessing applications experiencing significant vanadium induced catalyst aging. Benefits are generally most pronounced in applications with very high end of run vanadium loading, severe

processing conditions, and those using catalysts with low surface to volume ratio. This would include catalysts used in onstream catalyst replacement (OCR) processes and other large extrudate catalysts.

[0020] Catalysts with low surface to volume ratio are generally more sensitive to pore mouth plugging, since access to the pellet interior (a significant portion of the overall catalyst volume and surface area) is more restricted. OCR applications combine utilization of large catalyst pellets, severe operating conditions and high vanadium loading. The concept of solvent injection (the preferred solvent is water, although oxygen-containing compounds such as short chain alcohol, either or other water precursors may also be used) is particularly well suited to OCR technology.

[0021] The minimal amount of water (no greater than 2 wt % in the instant invention) necessary to trigger the beneficial chemical reactions is injected into the OCR reactor. Minimizing the injection of excess solvent to the OCR (or to a reactor in any hydrodesulfurization process) is important to avoid significant process modifications, simplify downstream processing, decrease operating costs, lessen hydrogen partial pressure penalties and minimize gas rate to maintain good flow conditions. The OCR process is more completely disclosed in U.S. Pat. No. 5,076,908 (Stangeland et al) which is hereby incorporated by reference. As illustrated in the Examples below, highly effective results are obtained when a solvent such as water is added early in the operating cycle. Solvent may be added at any time during the operating cycle but addition at the beginning of the cycle is preferable. The Examples demonstrate addition of water in the first 200 hours of the operational cycle.

[0022] Feeds suitable for use in the instant invention include "heavy" hydrocarbon liquid streams, and particularly crude oils, petroleum residua, tar sand bitumen, shale oil or liquefied coal or reclaimed oil. Petroleum residua may be crude oil atmospheric distillation column bottoms (reduced crude oil or atmospheric column residuum), or vacuum distillation column bottoms (vacuum residua).

[0023] These feed streams generally contain product contaminants, such as sulfur, and/or nitrogen, metals, including heavy metals such as vanadium and organo-metallic compounds possibly in porphyrin or chelate-type structures. Residua typically contain greater than 10 ppm metals. These contaminants tend to deactivate catalyst particles during contact by the feed stream and hydrogen under hydroprocessing conditions. This invention is particularly effective with residuum feeds, such as the Maya residuum employed in the Examples below.

[0024] The high reactivity of the Maya/Arabian Heavy Atmospheric Residua blend, coupled with high temperatures of operation, usually promotes significant vanadium deposition on the outside of the catalyst pellets. Such deposition tends to block access of the crude to the interior catalytically active portion of the catalyst. In the instant invention, significant vanadium deposition has been found within the catalyst itself. Catalyst life is extended significantly because the pores are not blocked as quickly.

[0025] As further described in U.S. Pat. No. 5,215,955, typical operating conditions for hydrodesulfurization processes include a reaction zone temperature of 600° F. to 900° F., a pressure of 200 to 3,000 psig, and a hydrogen feed rate

of 500 to 15,000 SCF per barrel of oil feed. Generally such hydrodesulfurization is in the presence of a catalyst or combination of catalysts which contain Group VI or VIII metals such as platinum, molybdenum, tungsten, nickel, cobalt, etc. These metals may be loaded onto refractory supports such as alumina, silica, magnesia and so forth. A high surface to volume ratio is preferable for the catalysts employed in this invention.

[0026] Alumina is the preferred catalytic support material although alumina may be combined with silica or magnesia. The support materials are available from a variety of commercial sources, or they may be prepared as disclosed in Tamm'661. The preparation of catalysts suitable for use in the hydroprocessing of residuum is further disclosed in U.S. Pat. No. 5,620,592, U.S. Pat. No. 5,215,955 and U.S. Pat. No. 5,177,047. It is notable that the catalysts disclosed in these patents preferably have few macropores. The catalysts of the OCR process are highly macroporous. The instant invention may thus be employed with catalyst possessing wide variation in pore structure.

[0027] The hydrocarbon hydrodesulfurization catalysts of the present invention contain at least one hydrogenation agent, and preferably contain a combination of two such agents. One or more catalysts may be used in any of the reaction zones. The metals and/or the compounds of the metals, particularly the sulfides and oxides of Group VIB (especially molybdenum and tungsten) and Group VIII (especially cobalt and nickel) of the elements are in general satisfactory catalytic agents. The combinations of cobalt, nickel and molybdenum catalytic agents are preferred. Suitably, the Group VIII metal is present in the catalyst in the range of about 0.1 wt. % to about 5 wt. %, calculated as the metal and based upon the total catalyst weight, and the Group VIB metal is present in an amount within the range of about 4 wt. % to about 20 wt. %, calculated as the metal and based upon the total catalyst weight. The most preferred catalyst contains between about 2% and about 4% nickel and between about 7% and about 9% molybdenum. The catalysts used in the Examples (Table 3) are typical.

[0028] The catalytic agents required for the present catalyst compositions may be incorporated into the calcined carrier by any suitable method, particularly by impregnation procedures ordinarily employed in general in the catalyst preparation art. It has been found that an especially outstanding catalyst is made by a single step impregnation of the alumina using a solution of a cobalt or nickel salt and a heteropolymolybdic acid, for example, phosphomolybdic acid.

EXAMPLES

Example I

[0029] A reactor system, consisting of three reactors connected in series for downflow operation, was loaded with commercially available catalyst comprising Al/Mo/P/Ni (See Table 3). The reactor system was run at 57% MCR conversion based on a target material balance. A similar adiabatic temperature profile was established in each of the reactors. The temperature increase across each reactor was set to 50 - 55° F. with an overall maximum temperature of 780° F. The reactor system total pressure was maintained at 2200 psig with a hydrogen partial pressure of 1800 psia &

a hydrogen flow rate of 5000 scf/bbl. The feed consisted of Arabian Heavy / Maya atmospheric residuum (See Table 1 for Feed 2 physical properties) fed at a liquid hourly space velocity (LHSV) of 0.46 hr⁻¹.

[0030] After 1,508 hrs on-stream in this accelerated aging regime, water was continuously injected at 3 wt % or 3.2 gms/hr into the feed for the remainder of the run ending at 2,806 hrs. The results from this run clearly show a significant improvement of catalyst cycle length and metal loading. The cycle length increased by 27% as compared to the base case reactor system, and the metal loading increased by 28% as compared to the base case reactor system.

Example II

[0031] The reactor system and conditions were identical to Example I above except that the LHSV was 0.22 hr⁻¹, and Feed 2 was used. (See Table 1 for feed 1 physical properties).

[0032] In this example, water was continuously injected at 2.0 wt % or 2.2 gms/hr into the feed at the start of the run and ending after 2380 hrs. The cycle length improved by 31% and the metal loading increased by 34% as compared against the base case reactor system.

Example III

[0033] The reactor system was a single stage reactor with the same conditions as Example I except the feed was a different feed (See Table 1 for feed 3 physical properties) and only catalyst 2 (See Table 3) was used for this run.

[0034] In this example, water was continuously injected at 1.5 wt % or 1.7 gms/hr into the feed throughout the 750 hrs of run time. However, despite the short duration of this run and the relatively low catalyst metal loading there was a clear indication that a water-induced catalyst metal capacity and a lower catalyst aging rate was starting to develop as compared to the base case reactor system.

Example IV

[0035] The reactor system was a single stage reactor with the same conditions as Example 1 except the feed was a different feed (See Table 1 for feed 3 physical properties) and only catalyst 2 (See Table 3) was used for this run.

[0036] In this example, water was continuously injected at 1.0% or 1.2 gms/hr into the feed throughout the 750 hrs of run time. Here again, given the short duration of this run, there was an indication that the water injection was starting to improve the metal loading capacity & the aging rate of the catalyst.

TABLE 1

Feed: Arab Heavy/Maya Atmospheric Residuum			
	Feed 1	Feed 2	Feed 3
Sulfur, wt %	4.660	4.620	4.551
Nitrogen, ppm	4087	4024	4260
MCR, wt %	18.9	704.8	284.5
API	7.5	7.4	8.9
Iron, ppm	5.6	8.2	7.3
Nickel, ppm	58.9	59.6	70.2
Vanadium, ppm	264.0	265.0	358.0
IBF (° F.)	684	676	641

[0037]

TABLE 2

Water Injection Wt.	% Run Length Improvement	% Metal Load Improvement
0.75%		
1.5%		
2.0%	+30.8%	+34.0%
3.0%	+26.6%	+28.0%
Estimated values		

[0038]

TABLE 3

Composition	Catalyst 1	Catalyst 2	Catalyst 3
Al ₂ O ₃	79%	86%	80%
MoO ₃	13%	9%	12%
P ₂ O ₅	4%	2%	4%
NiO	4%	3%	4%

What is claimed is:

1. A process for the extension of catalyst cycle length in the hydrodesulfurization of feeds containing heavy metal contaminants, said process occurring in one or more reaction zones, where the feed is contacted with the hydrodesulfurization catalyst, whereby no more than 2 wt % of a solvent is mixed with the feed prior to its entry into the initial reaction zone or is subsequently added to the initial reaction zone or a succeeding reaction zone.

2. The process of claim 1, wherein the solvent is a compound comprising oxygen which is selected from the group consisting of water, alcohol, ether and other water precursors.

3. The process of claim 1, wherein a heavy metal contaminant is nickel, vanadium, or a mixture of the two.

4. The process of claim 1, wherein no more than 1.5 wt % of a solvent is mixed with the feed prior to its entry into the initial reaction zone or is subsequently added to the initial reaction zone or a succeeding reaction zone.

5. The process of claim 4, wherein no more than 0.75 wt % of a solvent is mixed with the feed prior to its entry into the initial reaction zone or is subsequently added to the initial reaction zone or a succeeding reaction zone.

6. The process of claim 1, wherein the solvent is injected during the first 200 hours of the operational cycle.

7. The process of claim 1, wherein the feed is selected from the group consisting of crude oils, petroleum residua, tar sand bitumen, shale oil, or liquefied coal or reclaimed oil.

8. The process of claim 7, whereby petroleum, residua is selected from the group consisting of crude oil atmospheric distillation column bottoms or vacuum distillation column bottoms.

9. The process of claim 8, crude oil atmospheric distillation column bottoms is selected from the group consisting of reduced crude oil or atmospheric column residuum.

10. The process of claim 1, whereby at least one reaction zone is designed for onstream catalyst regeneration.

11. The process of claim 1, whereby the operating conditions for hydrodesulfurization processes include a reaction zone temperature in the range from 600° F. to 900° F., a pressure in the range of from 200 to 3000 psig, and a hydrogen feed rate of 500 to 15000 SCF per barrel of oil feed.

12. The process of claim 10, in which at least one catalyst in one or more of the reaction zones is a macroporous catalyst suitable for onstream catalyst regeneration.

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