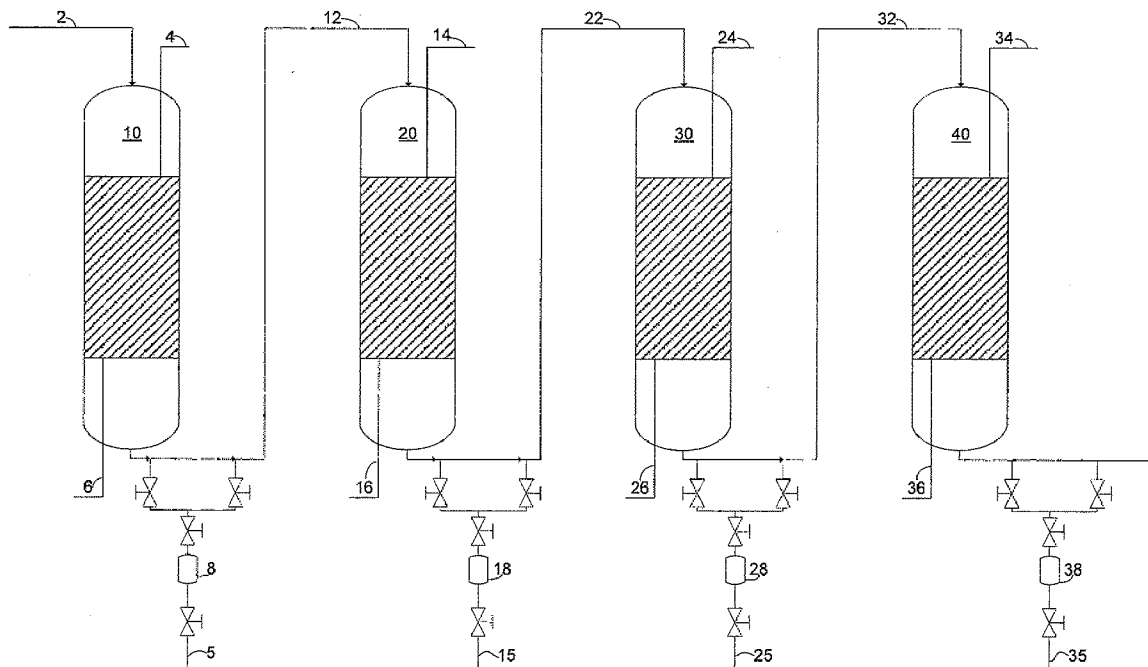




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(19) **United States**(12) **Patent Application Publication**
Kressmann et al.(10) **Pub. No.: US 2010/0018904 A1**(43) **Pub. Date: Jan. 28, 2010**(54) **PREREFINING PROCESS FOR THE
HYDRODESULFURIZATION OF HEAVY
SOUR CRUDE OILS TO PRODUCE SWEETER
LIGHTER CRUDES USING MOVING
CATALYST SYSTEM**(75) Inventors: **Stephane Cyrille Kressmann,**
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Dhahran (SA)(21) Appl. No.: **12/502,590**(22) Filed: **Jul. 14, 2009****Related U.S. Application Data**(60) Provisional application No. 61/080,452, filed on Jul.
14, 2008.**Publication Classification**(51) **Int. Cl.**
C10G 45/00 (2006.01)(52) **U.S. Cl.** **208/210**(57) **ABSTRACT**

A pre-refining catalytic hydrotreating process for the desulfurization, demetallization, and upgrading of heavy, sour crude oils operating at a moderate temperature and pressure through the utilization of moving catalyst bed technology.



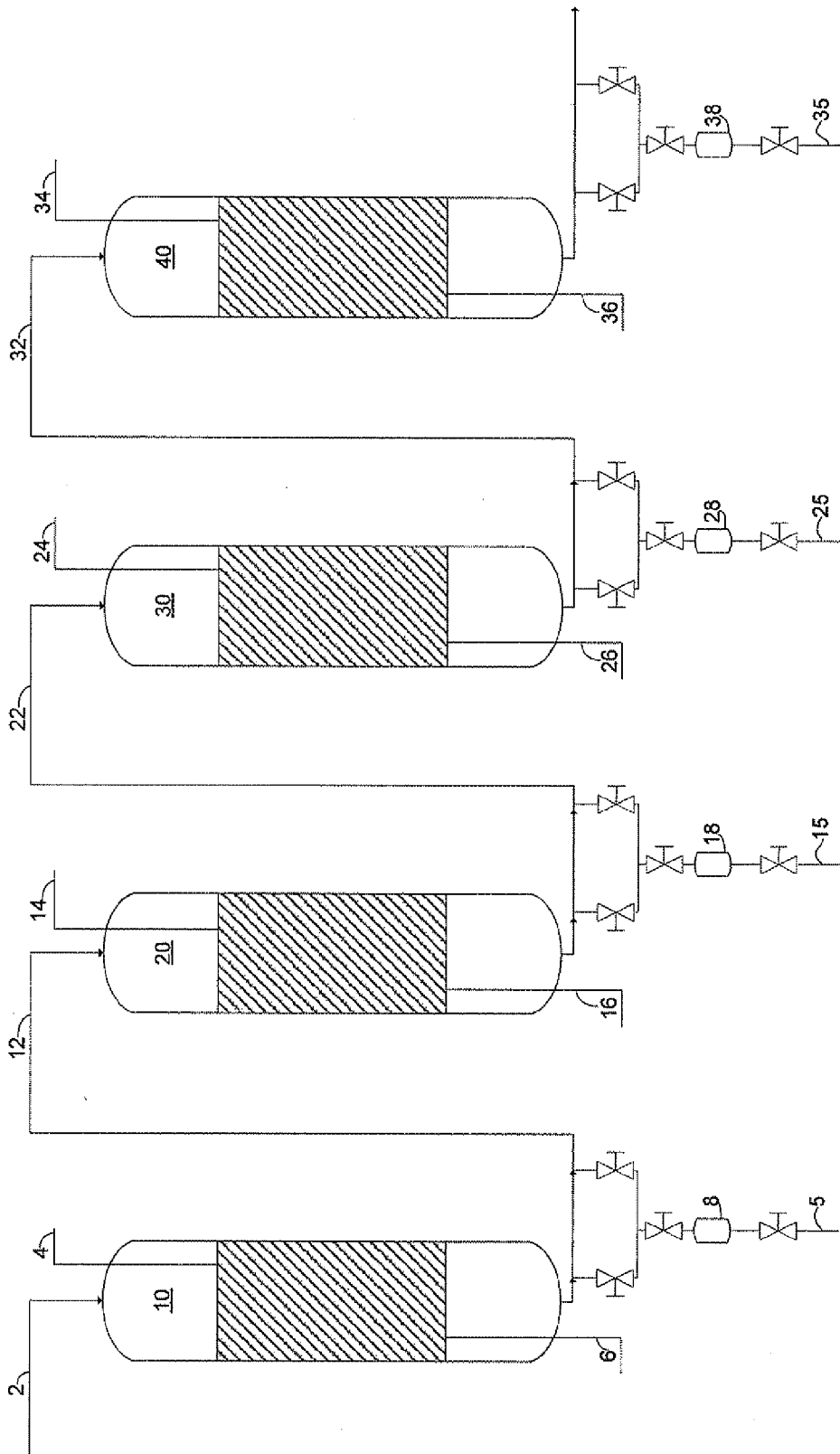


FIG. 1

**PREREFINING PROCESS FOR THE
HYDRODESULFURIZATION OF HEAVY
SOUR CRUDE OILS TO PRODUCE SWEETER
LIGHTER CRUDES USING MOVING
CATALYST SYSTEM**

RELATED APPLICATIONS

[0001] This patent application claims priority to U.S. Provisional Patent Application Ser. No. 61/080,452 filed on Jul. 14, 2008, which is incorporated by reference in its entirety.

TECHNICAL FIELD OF THE INVENTION

[0002] The present invention relates to a pre-refining process for the upgrading of heavy sour crude oils using a catalytic hydrotreating process employing Hydrotodemetalization (HDM), Hydrodesulfurization (HDS), and Hydroconversion (HDC), to produce sweeter, lighter crudes using a series of moving catalyst beds in discrete reactors.

BACKGROUND OF THE INVENTION

[0003] The removal of sulfur compounds from crude oil and its fractions has been of significant importance for several decades, but has become even more important in recent years due to tightening environmental legislation. While much of the prior art focuses on the desulfurization of individual crude oil fractions, a large segment of the art today and in the past has addressed the requirement for hydroprocessing of whole crude oil. The majority of the interest in recent years has been on the upgrading of very heavy (API gravity <20) crude oil, shale and tar-sands to produce light sweet synthetic crudes. The major driving force for these processes is the demand for light crude oils in refineries and the low value of highly viscous feedstocks. Furthermore, demand is shifting from high sulfur fuel oils to low-and ultra-low sulfur fuel oil products, having a sulfur content of less than about 1 wt % (LSFO) and 0.5 wt % (ULSFO). Therefore, the ability to produce LSFO or ULSFO instead of high sulfur fuel oils is advantageous.

[0004] One of the major technical challenges posed when hydrotreating heavy oil fractions or whole crude is the effect of minor concentrations of contaminants such as organic nickel and vanadium compounds. These organometallic components have been proven to detrimentally impact the activity of hydrotreating catalysts.

[0005] Another major challenge faced by processing whole crude oil is that the concentration of coke precursors can be very high. These coke precursors, such as asphaltenic plates detrimentally impact the activity of the hydro-desulfurization (HDS) catalysts in question. This means that the performance of a conventional process would decrease over time, requiring catalyst replacement to ensure continued operation. This catalyst replacement can be both costly and time consuming, significantly impacting the economic feasibility of such a process.

[0006] Deactivation of catalyst within a hydroprocessing unit can occur via two primary mechanisms: (1) metal deposition and (2) coke formation. For both of these mechanisms, increasing the operating temperature helps to maintain the catalyst performance; however, all process units have maximum temperature limits normally based upon the metallurgy of the process unit. These maxima limit the time for that a catalyst can operate without being replaced with fresh catalyst. Furthermore, replacement of spent catalyst with fresh

catalyst usually requires complete shutdown of the process unit in order to unload the deactivated spent catalyst and load a fresh batch of catalyst into the process. This shutdown time reduces the on-stream time and therefore negatively impacts the economics of the process.

SUMMARY OF THE INVENTION

[0007] One embodiment of the present invention provides a process for prerrefining heavy sour crude oils by admixing whole crude oil feedstock with hydrogen at a pressure in the range of about 30 and 150 bars to create a premixture. This premixture is heated to a first temperature, wherein the first temperature is within a range of about 300 and 500° C. The heated premixture is introduced into a first reactor vessel through a first vessel inlet, wherein the first reactor vessel is operable to receive a first catalyst. The first catalyst enters the first reactor vessel through a first catalyst inlet and exits the first reactor vessel through a first catalyst outlet. The heated premixture can be contacted with the first catalyst within the first reactor vessel such that the premixture is at least partially demetallized, forming a first effluent. The first effluent is characterized as having a lower amount of metal content than the heated premixture.

[0008] The first effluent can be introduced into a second reactor vessel through a second vessel inlet, wherein the second reactor vessel is operable to receive a second catalyst. The second catalyst enters the second reactor vessel through a second catalyst inlet and exits the second reactor vessel through a second catalyst outlet. The first effluent is contacted with the second catalyst within the second reactor vessel thereby forming a second effluent. The second effluent is characterized as having a lower amount of metal and sulfur content than the first effluent.

[0009] The second effluent is introduced into a third reactor vessel through a third vessel inlet, wherein the third reactor vessel is operable to receive a third catalyst. The third catalyst enters the third reactor vessel through a third catalyst inlet and exits the third reactor vessel through a third catalyst outlet. The second effluent is contacted with the third catalyst within the third reactor vessel thereby forming a third effluent. The third effluent is characterized as having a lower amount of sulfur content than the second effluent.

[0010] The third effluent is introduced into a fourth reactor vessel through a fourth vessel inlet, wherein the fourth reactor vessel is operable to receive a fourth catalyst. The fourth catalyst enters the fourth reactor vessel through a fourth catalyst inlet and exits the fourth reactor vessel through a fourth catalyst outlet. The third effluent is contacted with the fourth catalyst within the fourth reactor vessel thereby forming a fourth effluent. The fourth effluent is characterized as having a reduced amount of metal and sulfur content than the third effluent. In one embodiment, the fourth effluent has a sulfur content between about 0.1 and 1.0 wt %, as well as an increased API gravity of more than one degree as compared to whole crude oil feedstock. The rate of addition of said catalysts to said reactors is defined as the Catalyst Replacement Rate.

[0011] In another embodiment of the present invention, the process includes introducing a heated-pressurized mixture of the whole crude oil feedstock and hydrogen into an HDM reaction zone through an HDM reaction inlet, wherein the heated-pressurized mixture is at a first temperature within a range of about 300 to 500° C. Additionally, the heated-pressurized mixture is at a first pressure within a range of about 30

to 200 bar. Furthermore, the HDM reaction zone further includes an HDM moving bed, and the HDM reaction zone is operable to receive an HDM catalyst through an HDM catalyst inlet. The HDM reaction zone has an HDM catalyst outlet that is operable to emit the HDM catalyst from the HDM reaction zone. The HDM catalyst is introduced into the HDM reaction zone through the HDM catalyst inlet. Next, the premixture is contacted with the HDM catalyst within the HDM reaction zone such that the premixture is at least partially demetallized, forming the first effluent, with the first effluent being characterized as having a reduction of about 30 to 90% of the amount of metals as compared to the whole crude oil feedstock.

[0012] The first effluent can be introduced into an HDM/HDS reaction zone through an HDM/HDS reaction inlet. The HDM/HDS reaction zone further includes an HDM/HDS moving bed, and the HDM/HDS reaction zone is operable to receive an HDM/HDS catalyst through an HDM/HDS catalyst inlet. Furthermore, the HDM/HDS reaction zone has an HDM/HDS catalyst outlet, with the HDM/HDS catalyst outlet being operable to emit the HDM/HDS catalyst from the HDM/HDS reaction zone. The HDM/HDS catalyst can be introduced into the HDM/HDS reaction zone through the HDM/HDS catalyst inlet, wherein the first effluent is contacted with the HDM/HDS catalyst within the HDM/HDS reaction zone to form the second effluent, wherein the second effluent has a reduced metals and sulfur content as compared to the first effluent.

[0013] The second effluent can be introduced into an HDS reaction zone through an HDS reaction inlet, wherein the HDS reaction zone further comprises an HDS moving bed. The HDS reaction zone is operable to receive an HDS catalyst through an HDS catalyst inlet, and the HDS reaction zone has an HDS catalyst outlet, with the HDS catalyst outlet being operable to emit the HDS catalyst from the HDS reaction zone. The HDS catalyst is introduced into the HDS reaction zone through the HDS catalyst inlet where it is contacted with the second effluent within the HDS reaction zone to form the third effluent, wherein the third effluent has a reduced sulfur content as compared to the second effluent.

[0014] The third effluent can then be introduced into an HDC reaction zone through an HDC reaction inlet, wherein the HDC reaction zone further comprises an HDC moving bed. The HDC reaction zone is operable to receive an HDC catalyst through an HDC catalyst inlet, and the HDC reaction zone has an HDC catalyst outlet, with the HDC catalyst outlet being operable to emit the HDC catalyst from the HDC reaction zone. The HDC catalyst is introduced into the HDC reaction zone through the HDC catalyst inlet where it is contacted with the third effluent within the HDC reaction zone to form the fourth effluent, wherein the fourth effluent is characterized as having an increased API Gravity of at least about 1° greater than the whole crude oil feedstock and a reduced amount of metal and sulfur content as compared to the whole crude oil feedstock.

[0015] In another embodiment, the first temperature is within a range of about 340 and 390° C. and the first pressure is within a range of about 30 and 150 bar. In another embodiment, the HDM catalyst, the HDM/HDS catalyst, and the HDS catalyst are selected from the group consisting of sulfides of the group VB, VIB and VIIIB metals on an inorganic oxide support, wherein the inorganic oxide support is selected from the group consisting of alumina, silica alumina, and combinations thereof. As used herein, group VB metals refers

to the group consisting of vanadium, niobium, and tantalum. As used herein, group VIB metals refers to the group consisting of chromium, molybdenum, or tungsten. As used herein, group VIIIB metals refers to iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, or platinum, preferably iron, cobalt and nickel. The HDC catalyst can be in the form of extrudates, spheres, cylinders or pellets or a combination thereof. In yet another embodiment of the present invention, the HDM catalyst, the HDM/HDS catalyst, and the HDS catalyst are selected from the group consisting of Nickel promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof.

[0016] In one embodiment, the inorganic oxide support is selected from the group consisting of alumina, silica alumina, and combinations thereof. Additionally, the HDC catalyst can be selected from the group consisting of sulfides of the group VB, VIB and VIIIB metals on an inorganic oxide support, wherein the inorganic oxide support is selected from the group consisting of alumina, silica alumina, a zeolite, and combinations thereof. The HDC catalyst can preferably be in the form of extrudates, spheres, cylinders, pellets, and combinations thereof. Furthermore, each catalyst can have a flow rate within its respective moving bed, wherein the flow rate of each of said catalysts is at a rate of approximately 0.5% to 5% of the Tan-Tan height of the reactor per day. The process can be configured in such a way that each of said moving beds can be operated in a co-current or countercurrent fashion.

[0017] In a preferred embodiment, the HDM catalyst has a HDM catalyst flow rate, and the first effluent has a baseline effluent metal concentration, such that the process can include monitoring a metal concentration of the first effluent and increasing the HDM catalyst flow rate whenever the metal concentration of the first effluent exceeds the baseline effluent metal concentration. Likewise, the HDM/HDS catalyst can have an HDM/HDS catalyst flow rate, the second effluent can have a second baseline effluent metal concentration, and the second effluent can have a baseline sulfur concentration. Both a metal and a sulfur concentration of the second effluent can be monitored, and whenever the metal concentration of the second effluent exceeds the second baseline effluent metal concentration or whenever the sulfur concentration of the second effluent exceeds the baseline sulfur concentration, the HDM/HDS catalyst flow rate can be increased.

[0018] In another preferred embodiment, the HDS catalyst has an HDS catalyst flow rate, and the third effluent has an HDS baseline sulfur concentration. The process preferably includes monitoring of a sulfur concentration of the third effluent and increasing the HDS catalyst flow rate whenever the sulfur concentration of the third effluent exceeds the baseline sulfur concentration.

[0019] In yet another preferred embodiment, the HDC catalyst has an HDC catalyst flow rate, and the whole crude oil feedstock and the fourth effluent have a baseline API gravity. The process further includes monitoring the baseline API gravity of the whole crude oil feedstock and the fourth effluent and increasing the HDC catalyst flow rate whenever the difference between the baseline API gravity of the fourth effluent and the baseline API gravity of the whole crude oil feedstock does not exceed 1°.

[0020] In another embodiment of the present invention, the third effluent is characterized as having a sulfur content of between about 0.1 and 1.0 weight percent. Additionally, the process can further include separating the whole crude oil feedstock into two fractions prior to introducing the heated-pressurized mixture into the HDM reaction zone. In this embodiment, the first fraction has a maximum boiling point of about 210° C., and the second fraction has a minimum boiling point of greater than about 210° C. Additionally, the first fraction can bypass said reaction zones and can be combined with the fourth effluent, wherein the second fraction is mixed with the hydrogen to form the heated-pressurized mixture.

[0021] In another embodiment of the present invention, the process can further include introducing a first effluent slip stream to an HDM sampling vessel, introducing a second effluent slip stream to an HDM/HDS sampling vessel, introducing a third effluent slip stream to an HDS sampling vessel, and introducing a fourth effluent slip stream to an HDC sampling vessel. The HDM sampling vessel, the HDM/HDS sampling vessel, the HDS sampling vessel, and the HDC sampling vessel are each operable to allow for sampling of their respective slip streams while the process is in operation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] So that the manner in which the above-recited features, advantages, and objectives of the invention, as well as others that will become apparent, are attained and can be understood in detail, more particular description of the invention briefly summarized above may be had by reference to the embodiments thereof that are illustrated in the drawings that form a part of this specification. It is to be noted, however, that the appended drawings illustrate only several embodiments of the invention and are, therefore, not to be considered limiting of the invention's scope, for the invention may admit to other equally effective embodiments.

[0023] FIG. 1 is a schematic representation of an embodiment of the present invention.

DETAILED DESCRIPTION

[0024] For purposes of this application, hydrometallization, hydrodesulfurization and hydroconversion will be shortened to HDM, HDS, and HDC, respectively. The present invention provides a pre-refining process for the upgrading of heavy, sour crude oils through HDM, HDS, and HDC of the crude oils to unexpectedly produce sweeter, lighter crudes using a moving catalyst system. In FIG. 1, which represents an embodiment of the present invention, heavy oil feedstock, such as a whole crude oil feedstock, is admixed with hydrogen (not shown) at a pressure of between about 30 bars and 200 bars, and more preferably about 60 bars to 100 bars, creating a premixture. In an alternate embodiment, the heavy oil feedstock and hydrogen are admixed at a pressure of between about 80 and 110 bar. The premixture is preferably heated (not shown) to a first temperature of between about 300° C. and 500° C., and more preferably, the premixture is heated in the range of about 350° C. and 450° C. The premixture is introduced via line [2] into HDM reactor [10], which contains a first catalyst. The first catalyst is an HDM catalyst. Preferred catalysts include sulfides of the group VB, VIB and VIIB metals, optionally in supported form on γ -alumina and/or γ -alumina and silica in the form of extrudates, spheres, cylinders and/or pellets. More preferred first catalysts can

include Nickel promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof. In certain embodiments, the active metal species on the surface of the catalyst is the sulfide form of the metal. One exemplary first catalyst utilizes Nickel sulfide and Molybdenum sulfide active species, wherein the weight ratio of Ni to (Ni+Mo) is greater than about 0.15. Preferably, the inorganic oxide support material is selected from the group consisting of alumina, silica alumina, and combinations thereof. In certain embodiments, the first catalyst is supported on a γ -alumina based support having a surface area of between about 100 and 300 m²/g, preferably between about 140 and 240 m²/g. The catalyst can be described as generally having a high pore volume, which in certain embodiments is greater than about 0.5 cc/g, preferably greater than about 1 cc/g. The pore volume is believed to facilitate the uptake of active metals on the catalyst surface. In one embodiment, the first catalyst is introduced into HDM reactor [10] via line [6] and exits HDM reactor [10] via line [4]. In another embodiment, the flow of the first catalyst can be reversed such that the first catalyst is introduced into HDM reactor [10] via line [4] and exits HDM reactor [10] via line [6]. The exit stream from HDM reactor [10] defines the first effluent.

[0025] In one embodiment of the present invention, a slipstream of the first effluent can be sampled via line [5] in order to monitor the effectiveness of the first catalyst by measuring the metal concentration (for instance Nickel and Vanadium) of the slipstream. For example, for a fixed Weighted Average Bed Temperature (WABT), whenever the metal concentration of the slipstream exceeds a desired level, the Catalyst Replacement Rate of the first catalyst is increased until the metal concentration within the slipstream has returned to desired levels. In one embodiment, the Catalyst Replacement Rate of the first catalyst is between about 0.05 to 10 wt %, more preferably between about 0.05 to 0.5 wt %, of the total catalyst inventory per day. The first catalyst can be replaced as a function of the total metals content (e.g., nickel and vanadium) detected at the outlet of the HDM reactor [10].

[0026] Upon exiting HDM reactor [10], the first effluent is introduced via line [12] into HDM/HDS reactor [20], which contains the second catalyst. The second catalyst is an HDM/HDS catalyst. Preferred catalysts include sulfides of the group VB, VIB and VIIB metals optionally supported on γ -alumina and/or γ -alumina and silica in the form of extrudates, spheres, cylinders and/or pellets. In one exemplary embodiment, the second catalyst includes a γ -alumina support. More preferred second catalyst can include Nickel promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof. In one exemplary embodiment, the second catalyst includes Nickel and Molybdenum, wherein the weight ratio of nickel to (nickel+molybdenum) is up to about 0.3. Preferably, the inorganic oxide is selected from the group consisting of alumina, silica alumina, and combinations thereof. In one embodiment, the second catalyst is introduced into HDM/HDS reactor [20] via line [16] and exits HDM/HDS reactor [20] via line [14]. In another embodiment, the flow of the second catalyst is reversed such that the second catalyst is introduced into HDM/HDS reactor

[20] via line [14] and exits HDM/HDS reactor [20] via line [16]. The exit stream from HDM/HDS reactor [20] defines the second effluent.

[0027] In one embodiment of the present invention, a slipstream of the second effluent can be sampled via line [15] in order to monitor the effectiveness of the second catalyst by measuring the metal and sulfur concentration of the slipstream. For example, for a fixed WABT, whenever the metal and/or sulfur concentrations of the slipstream exceeds a desired level, the Catalyst Replacement Rate of the second catalyst can be increased until the metal and/or sulfur concentrations within the slipstream have returned to desired levels. In certain embodiments, similar to what is done with respect to the replacement of the first catalyst, the second catalyst can typically be replaced as a function of the total metals content (e.g., nickel and vanadium) or the total sulfur content detected at the outlet of the HDM/HDS reactor [20]. Preferably, the second effluent would have approximately 30 to 90% less metals than the heavy oil feedstock.

[0028] Upon exiting HDM/HDS reactor [20], the second effluent is introduced via line [22] into HDS reactor [30], which contains the third catalyst. The third catalyst is an HDS catalyst. Preferred catalysts include sulfides of the group VB, VIB and VIIIB metals, optionally supported on γ -alumina and/or γ -alumina and silica, the catalysts being in the form of extrudates, spheres, cylinders and/or pellets. More preferred third catalysts include Nickel promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof. In an exemplary embodiment, the third catalyst includes Nickel and Molybdenum, wherein the weight ratio of Ni to (Ni+Mo) is between about 0.1 and 0.3. Preferably, the inorganic oxide support is selected from the group consisting of alumina, silica alumina, and combinations thereof. In certain embodiments, the HDS catalyst support is a γ -alumina support having a surface area of between about 150 and 300 m²/g, preferably between about 180 and 240 m²/g. The catalyst can be described as generally having a pore volume that is smaller than the pore volume of the HDM catalyst, for example, the HDS catalyst can have a pore volume that is less than about 1 cc/g. The pore volume is believed to facilitate the uptake of metals on the catalyst surface. In one embodiment, the third catalyst is introduced into HDS reactor [30] via line [26] and exits HDS reactor [30] via line [24]. In another embodiment, the flow of the third catalyst is reversed such that the third catalyst is introduced into HDS reactor [30] via line [24] and exits HDS reactor [30] via line [26]. The stream from HDS reactor [30] defines the third effluent.

[0029] In one embodiment of the present invention, a slipstream of the third effluent can be sampled via line [25] in order to monitor the effectiveness of the third catalyst by measuring the sulfur concentration of the slipstream. For example, for a fixed WABT, whenever the sulfur concentration of the slipstream exceeds a desired level, the Catalyst Replacement Rate of the third catalyst is increased until the sulfur concentration within the slipstream has returned to desired levels. In one embodiment, the Catalyst Replacement Rate of the second catalyst is between about 0.01 to 5 wt %, more preferably between about 0.05 to 0.5 wt %, of the total catalyst inventory per day. Generally, the replacement rate of the third catalyst can be based on a function of the total sulfur content of the effluent from HDS reactor [30].

[0030] Upon exiting HDS reactor [30], the third effluent is introduced via line [32] into HDC reactor [40], which contains the fourth catalyst. The fourth catalyst is an HDC catalyst. Preferred catalysts include sulfides of the group VB, VIB and VIIIB metals, optionally supported form on γ -alumina and/or γ -alumina and silica and/or a zeolite in the form of extrudates, spheres, cylinders and/or pellets. Preferably, the zeolite is selected from the group consisting of zeolite Y, ZSM-5, LWZ-15, AWLZ-15, and combinations thereof. Generally, the support utilized for the fourth catalyst is more acidic than the supports utilized for each of the first, second and third catalysts. An exemplary catalyst support includes silica in conjunction with γ -alumina, wherein the alumina can be present in an amount of between about 1 and 40% by weight. Similarly, the catalyst support can include silica and a zeolite, wherein the zeolite can be present in an amount of between about 1 and 40% by weight. More preferred fourth catalysts include Nickel promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof. In certain exemplary embodiments, the catalyst includes Nickel and Molybdenum, or Nickel and Tungsten, wherein the weight ratio of nickel to (nickel and the second metal) is between about 0.25 and 0.5, wherein the second metal is either Molybdenum or Tungsten. Preferably, the inorganic oxide is selected from the group consisting of alumina, silica alumina, zeolite, zeolite Y, AWLZ-15, and any combination thereof. In one embodiment, the fourth catalyst is introduced into HDC reactor [40] via line [36] and exits HDC reactor [40] via line [34]. In another embodiment, the flow of the fourth catalyst is reversed such that the fourth catalyst is introduced into HDC reactor [40] via line [34] and exits HDC reactor [40] via line [36]. The e stream from HDC reactor [40] defines the fourth effluent. It is believed that the addition of the HDC reactor [40] to the process results in further hydroconversion and deeper hydrodesulfurization of the heavy oil feedstock, thereby resulting in a more improved product. Without wishing to be bound to any specific theory, it is believed that the fourth catalyst may facilitate ring opening, thereby improving the removal of bound sulfur.

[0031] In one embodiment of the present invention, a slipstream of the fourth effluent is sampled via line [35] in order to monitor the effectiveness of the fourth catalyst by measuring the API gravity and/or sulfur content of the slipstream. For example, for a fixed WABT, whenever the API gravity of the slipstream is below a desired level and/or the sulfur content of the slipstream is above a desired level, the Catalyst Replacement Rate of the fourth catalyst is increased until the API gravity and/or the sulfur content within the slipstream have met the desired levels. In certain embodiments, the replacement rate of the HDC catalyst can be a function of the conversion of, or the presence of, the 540° C. +material present in the effluent of the HDC reactor [40]. In certain embodiments, once the catalyst has become stabilized (i.e., reached a coke equilibrium), the amount of catalyst removed from the reactor should approximately match the amount of catalyst added to the reactor.

[0032] In another embodiment of the present invention, the fourth effluent can be introduced to a liquid gas separator (not shown) in order to separate any gaseous products, wherein the

liquid product is a synthetically produced crude oil having reduced metal and sulfur content, and an increased API gravity.

[0033] The reaction between the respective feed streams and the respective catalysts is exothermic. Therefore, the temperature proximate the feed stream inlet of each reactor will be less than the temperature proximate the exit stream of each reactor. The temperature of the catalyst bed, known as the Weighted Average Bed Temperature (WABT) is defined as being:

$$WABT = T_i + \frac{(T_o - T_i)}{2}$$

wherein T_i is the inlet temperature and T_o is the outlet temperature. In one embodiment of the present invention, the WABT is used as a control point for improved catalyst performance. For example, in an embodiment of the present invention, the WABT for each reactor can be increased or decreased as appropriate to maintain the desired level of HDM, HDS or HDC within each reactor. The WABT is controlled by controlling the inlet temperature for each reactor. Due to the exothermic nature of the HDM, HDM/HDS, HDS and HDC reactions, the reactor outlet temperature is higher than the inlet temperature. The WABT is therefore the weighted average. In operation, the WABT will be set by optimization between the Catalyst Replacement Rate and the WABT to achieve the target for each section. In an embodiment of the present invention, each of the reactors is adiabatic and there is no external heating. In another embodiment of the present invention, the fourth effluent will pass through a feed/effluent heat exchanger in order to cool the fourth effluent while simultaneously preheating the premixture or the crude oil feedstock. Preferably, the premixture is preheated to a temperature within the range of about 300° C. to 500° C. In one embodiment, optional HDM sampling vessel [8], HDM/HDS sampling vessel [18], HDS sampling vessel [28] and HDC sampling vessel [38] are provided upstream of their respective sampling lines.

[0034] The WABTs of HDM reactor [10], HDM/HDS reactor [20], and HDS reactor [30] are preferably maintained within the range of about 350° C. and 420° C. The WABT of HDC reactor [40] is preferably within the range of about 350° C. and 450° C., preferably within the range of about 380° C. and 425° C. In certain embodiments, the WABT of the HDC reactor [40] is greater than the WABTs of the HDM reactor [10], the HDM/HDS reactor [20] and the HDS reactor [30]. In an exemplary embodiment, the HDM reactor [10] is operated at a temperature of between about 370° C. and 415° C., the HDS reactor [30] is operated at a temperature of between about 370° C. and 410° C., and the HDC reactor [40] is operated at a temperature of between about 380° C. and 425° C. Optionally, the HDM/HDS reactor [20] is operated at a temperature that is less than the operating temperature of the HDC reactor [40].

[0035] In an additional embodiment of the present invention, the heavy oil feedstock is separated into first and second fractions prior to introduction into HDM reactor [10], with the first fraction having a maximum boiling point of about 210° C. or less and the second fraction containing the volumetric balance of the whole crude oil. The first fraction can then bypass HDM reactor [10], HDM/HDS reactor [20], HDS

reactor [30], and HDC reactor [40], and instead be optionally processed separately prior to recombining with the fourth effluent.

Example

Production of Low Sulfur Crude Oil

[0036] An Arab Heavy Feedstock having properties as shown in Table I below was processed in accordance with an embodiment of the present invention.

TABLE I

Properties of Arab Heavy Feedstock		
Crude Origin	Units	Arabian Heavy Export
Density at 15° C.	g/ml	0.89
API Gravity	°	27
CCR	wt %	8.2
Vanadium	wtppm	56.4
Nickel	wtppm	16.4
Sulphur	wt %	2.83
NaCl content	wtppm	<5
C	wt %	84.9
H	wt %	11.89

[0037] The specific conditions include the following: total hydrogen pressure of the reactor system is maintained at 100 bar; hydrogen to hydrocarbon ratio is maintained at 800 normal liters of hydrogen per liter of Arab Heavy Feedstock; temperature of the catalyst system was operated at between 370° C. and 380° C.; and the liquid hourly space velocity for the combined four reactors was 0.5 per hour. The Catalyst Replacement Rate for the first catalyst was maintained within the range of 0.05 to 0.5 weight percent of the total catalyst inventory per day. The Catalyst Replacement Rate for the third catalyst was maintained within the range of 0.01 to 5 weight percent of the total catalyst inventory per day. The resulting product was analyzed, with the results shown in Table II below.

TABLE II

Properties of Resulting Product		
Crude Origin	Units	Synthetic Crude Oil Produced
Refractive index		1.4948
Density at 15° C.	g/ml	0.8762
API Gravity	°	29.9
CCR	wt %	—
Vanadium	Wtppm	23.4
Nickel	Wtppm	8.7
Sulphur	wt %	0.5547
NaCl content	Wtppm	—

[0038] As shown in Table II, the final product is a synthetic crude oil having a lower density; increased API gravity; and, reduced amounts of CCR, vanadium, nickel, and sulfur.

[0039] As will be readily apparent to those skilled in the art, the present invention may easily be produced in other specific forms without departing from its spirit or essential characteristics. The present embodiment is, therefore, to be considered as merely illustrative and not restrictive, the scope of the invention being indicated by the claims rather than the foregoing description, and all changes which come within the meaning and range of equivalence of the claims are therefore

intended to be embraced therein. Furthermore, the present invention may suitably comprise, consist or consist essentially of the elements disclosed and may be practiced in the absence of an element not disclosed.

We claim:

1. A process for prerefining heavy sour crude oils, the process comprising:

introducing a heated-pressurized mixture of whole crude oil feedstock and hydrogen into an HDM reaction zone through an HDM reaction inlet, wherein the heated-pressurized mixture is at a first temperature within a range of about 300 to 500° C., wherein the heated-pressurized mixture is at a first pressure within a range of about 30 to 200 bar, wherein the HDM reaction zone further comprises an HDM moving bed, the HDM reaction zone being operable to receive an HDM catalyst through an HDM catalyst inlet, the HDM reaction zone having an HDM catalyst outlet, the HDM catalyst outlet being operable to emit the HDM catalyst from the HDM reaction zone;

introducing the HDM catalyst into the HDM reaction zone through the HDM catalyst inlet;

contacting the premixture with the HDM catalyst within the HDM reaction zone such that the premixture is at least partially demetallized, forming a first effluent, the first effluent being characterized as having 30 to 90% reduced amounts of metals as compared to the whole crude oil feedstock;

introducing the first effluent into an HDM/HDS reaction zone through an HDM/HDS reaction inlet, wherein the HDM/HDS reaction zone further comprises an HDM/HDS moving bed, the HDM/HDS reaction zone being operable to receive an HDM/HDS catalyst through an HDM/HDS catalyst inlet, the HDM/HDS reaction zone having an HDM/HDS catalyst outlet, the HDM/HDS catalyst outlet being operable to emit the HDM/HDS catalyst from the HDM/HDS reaction zone;

introducing the HDM/HDS catalyst into the HDM/HDS reaction zone through the HDM/HDS catalyst inlet;

contacting the first effluent with the HDM/HDS catalyst within the HDM/HDS reaction zone to form a second effluent, wherein the second effluent has a reduced metals and sulfur content as compared to the first effluent;

introducing the second effluent into an HDS reaction zone through an HDS reaction inlet, wherein the HDS reaction zone further comprises an HDS moving bed, the HDS reaction zone being operable to receive an HDS catalyst through an HDS catalyst inlet, the HDS reaction zone having an HDS catalyst outlet, the HDS catalyst outlet being operable to emit the HDS catalyst from the HDS reaction zone;

introducing the HDS catalyst into the HDS reaction zone through the HDS catalyst inlet;

contacting the second effluent with the HDS catalyst within the HDS reaction zone to form a third effluent, wherein the third effluent has a reduced sulfur content as compared to the second effluent;

introducing the third effluent into an HDC reaction zone through an HDC reaction inlet, wherein the HDC reaction zone further comprises an HDC moving bed, the HDC reaction zone being operable to receive an HDC catalyst through an HDC catalyst inlet, the HDC reac-

tion zone having an HDC catalyst outlet, the HDC catalyst outlet being operable to emit the HDC catalyst from the HDC reaction zone;

introducing the HDC catalyst into the HDC reaction zone through the HDC catalyst inlet;

contacting the third effluent with the HDC catalyst within the HDC reaction zone to form a fourth effluent, wherein the fourth effluent is characterized as having an increased API Gravity of at least 1° greater than the whole crude oil feedstock and a reduced amount of metal and sulfur content as compared to the whole crude oil feedstock.

2. The process of claim 1, wherein the first temperature is within a range of about 340 and 390 degrees Celsius.

3. The process of claim 1, wherein the first pressure is in a range of about 30 and 150 bar.

4. The process of claim 1, wherein the HDM catalyst, the HDM/HDS catalyst, and the HDS catalyst comprise at least one metal sulfide selected from the group consisting of sulfides of the group VB, VIB and VIIIB metals supported on an inorganic oxide, wherein the inorganic oxide is selected from the group consisting of alumina, silica alumina, and combinations thereof, wherein the fourth catalyst is in the form of extrudates, spheres, cylinders or pellets or a combination thereof.

5. The process of claim 1, wherein the HDM catalyst, the HDM/HDS catalyst, and the HDS catalyst are selected from the group consisting of Nickel promoting Molybdenum supported on an inorganic oxide, Nickel promoting Tungsten supported on an inorganic oxide, Cobalt promoting Molybdenum supported on an inorganic oxide, Cobalt promoting Tungsten supported on an inorganic oxide, and combinations thereof.

6. The process of claim 5, wherein the inorganic oxide is selected from the group consisting of alumina, silica alumina, and combinations thereof.

7. The process of claim 1, wherein the HDC catalyst comprises a metal selected from the group consisting of sulfides of the group VB, VIB and VIIIB metals on an inorganic oxide, wherein the inorganic oxide is selected from the group consisting of alumina, silica alumina, a zeolite, and combinations thereof, wherein the fourth catalyst is in the form of extrudates, spheres, cylinders, pellets, and combinations thereof.

8. The process of claim 1, wherein each catalyst has a flow rate within its respective moving bed, wherein the flow rate of each of said catalysts is at a rate of approximately 0.5% to 5% of the Tan-Tan height of the reactor per day.

9. The process of claim 8, wherein each of said moving beds can be operated in a co-current or countercurrent fashion.

10. The process of claim 1, wherein the HDM catalyst has a HDM catalyst flow rate, wherein the first effluent has a baseline effluent metal concentration, the process further comprising monitoring a metal concentration of the first effluent and increasing the HDM catalyst flow rate whenever the metal concentration of the first effluent exceeds the baseline effluent metal concentration.

11. The process of claim 1, wherein the HDM/HDS catalyst has an HDM/HDS catalyst flow rate, wherein the second effluent has a second baseline effluent metal concentration, wherein the second effluent has a baseline sulfur concentration, the process further comprising monitoring a metal concentration and a sulfur concentration of the second effluent and increasing the HDM/HDS catalyst flow rate whenever the

metal concentration of the second effluent exceeds the second baseline effluent metal concentration or whenever the sulfur concentration of the second effluent exceeds the baseline sulfur concentration.

12. The process of claim 1, wherein the HDS catalyst has an HDS catalyst flow rate, wherein the third effluent has an HDS baseline sulfur concentration, the process further comprising monitoring a sulfur concentration of the third effluent and increasing the HDS catalyst flow rate whenever the sulfur concentration of the third effluent exceeds the baseline sulfur concentration.

13. The process of claim 1, wherein the HDC catalyst has an HDC catalyst flow rate, wherein the whole crude oil feedstock and the fourth effluent have a baseline API gravity, the process further comprising monitoring the baseline API gravity of the whole crude oil feedstock and the fourth effluent and increasing the HDC catalyst flow rate whenever the difference between the baseline API gravity of the fourth effluent and the baseline API gravity of the whole crude oil feedstock does not exceed 1°.

14. The process of claim 1, wherein the third effluent is characterized as having a sulfur content of between 0.1 and 1.0 weight percent.

15. The process of claim 1, further comprising separating the whole crude oil feedstock into two fractions prior to introducing the heated-pressurized mixture into the HDM reaction zone, wherein the first fraction has a maximum boiling point of about 210° C., wherein the second fraction has a minimum boiling point of greater than about 210° C., wherein the first fraction bypasses said reaction zones and is combined with the fourth effluent, wherein the second fraction is mixed with the hydrogen to form the heated-pressurized mixture.

16. The process of claim 1, further comprising:
introducing a first effluent slip stream to an HDM sampling vessel;
introducing a second effluent slip stream to an HDM/HDS sampling vessel;
introducing a third effluent slip stream to an HDS sampling vessel; and
introducing a fourth effluent slip stream to an HDC sampling vessel, wherein the HDM sampling vessel, the HDM/HDS sampling vessel, the HDS sampling vessel, and the HDC sampling vessel are all operable to allow for sampling of their respective slip streams while the process is in operation.

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