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(54) **SLURRY HYDROPROCESSING FOR HEAVY OIL UPGRADING USING SUPPORTED SLURRY CATALYSTS**

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(57) **ABSTRACT**

A slurry hydroprocessing process (SHP) where a hydrocarbon feedstock is treated at slurry hydrotreating conditions, in the presence of a hydrogen containing treat gas and in the presence of a supported metallic catalyst which is a supported sulfide of a metal selected from the group of non-noble Group VIII metals, Group VIB metals and mixtures thereof where the support is an inorganic oxide and where the catalyst has an average diameter of about 0.5 to about 100 microns to obtain a first product stream comprising the catalyst and a hydroprocessed feedstream; separating the first product into a catalyst-free product stream and a catalyst-containing stream and recycling at least a portion of the catalyst-containing stream back to the hydroprocessing step.

Figure 1

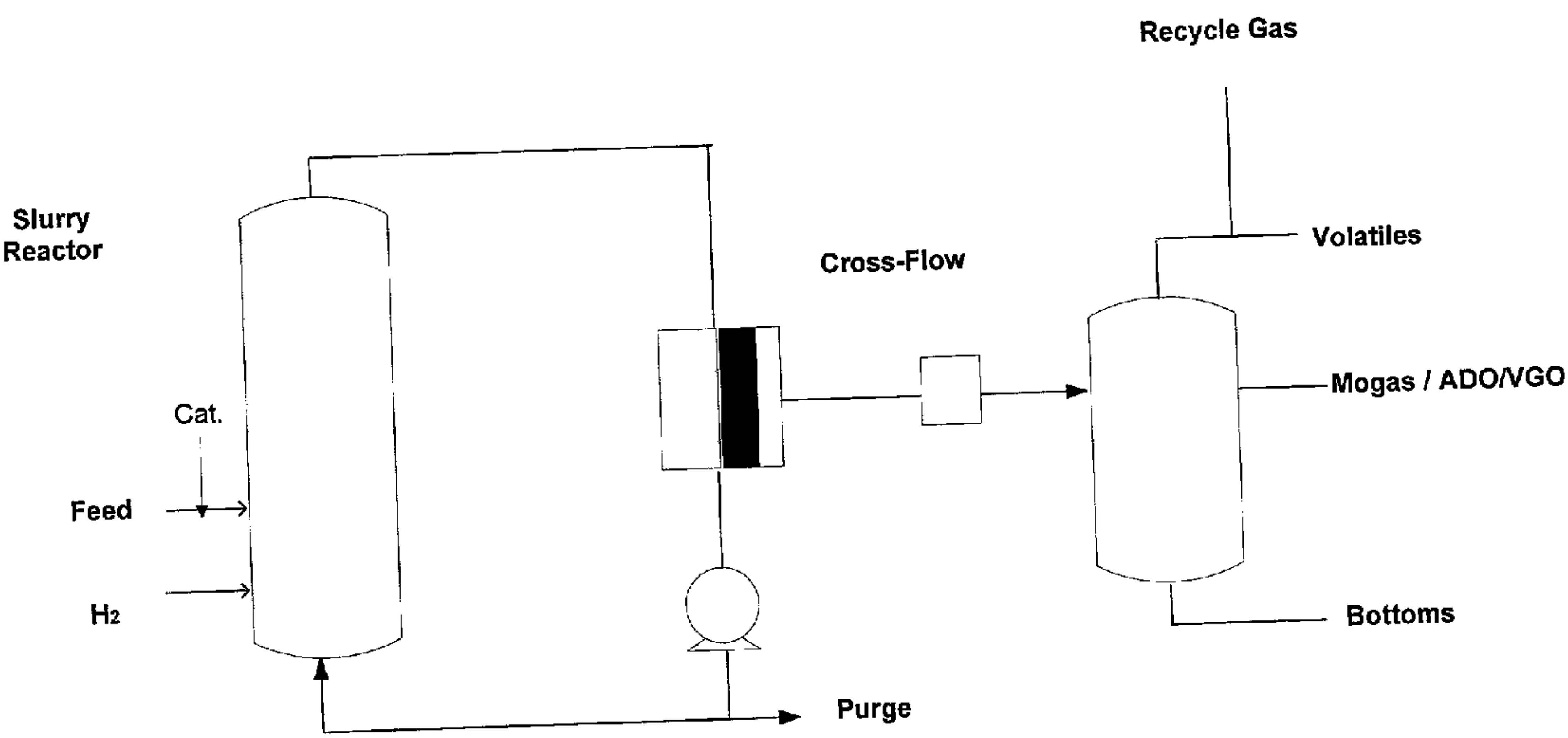


Figure 2

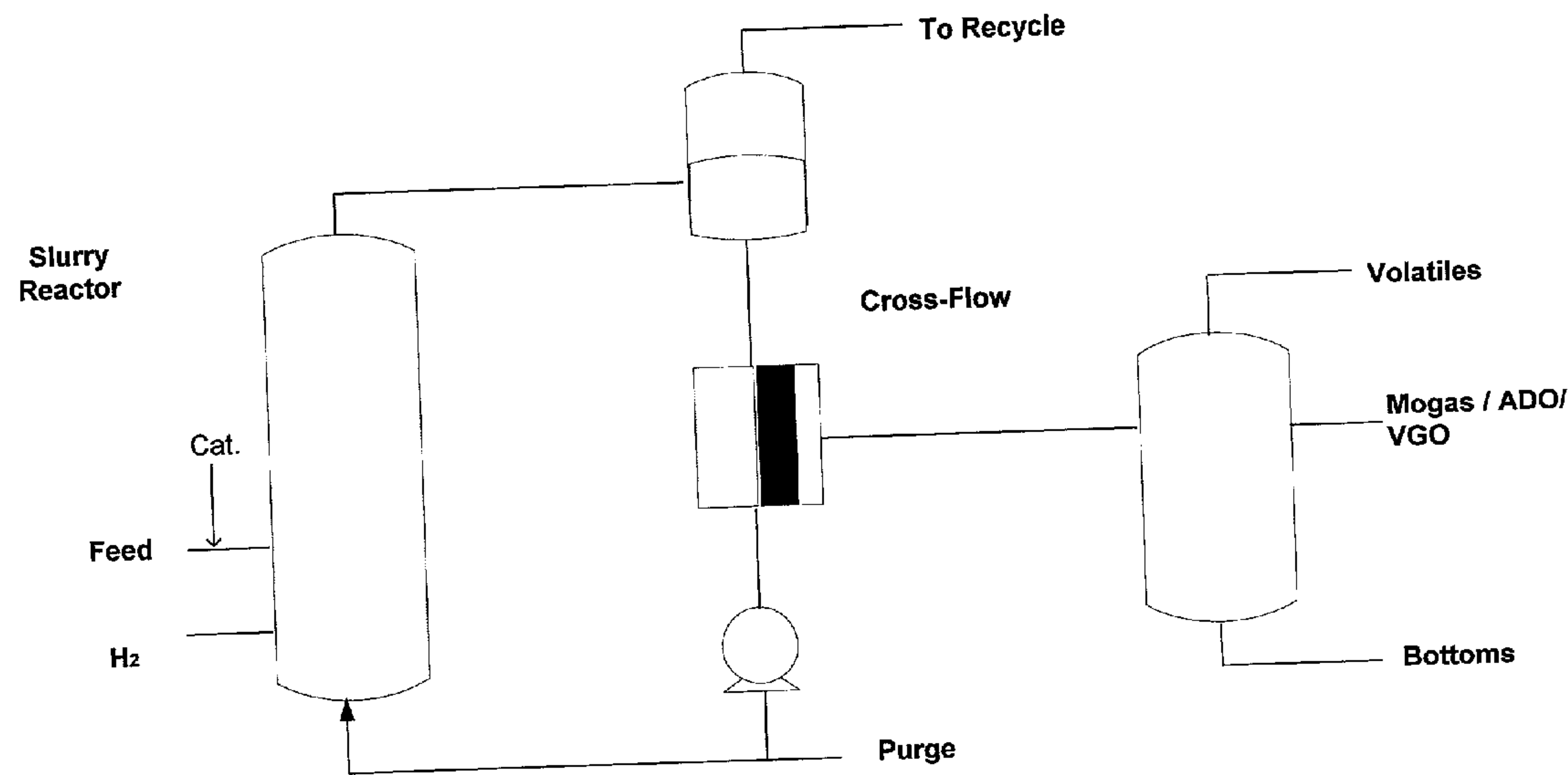
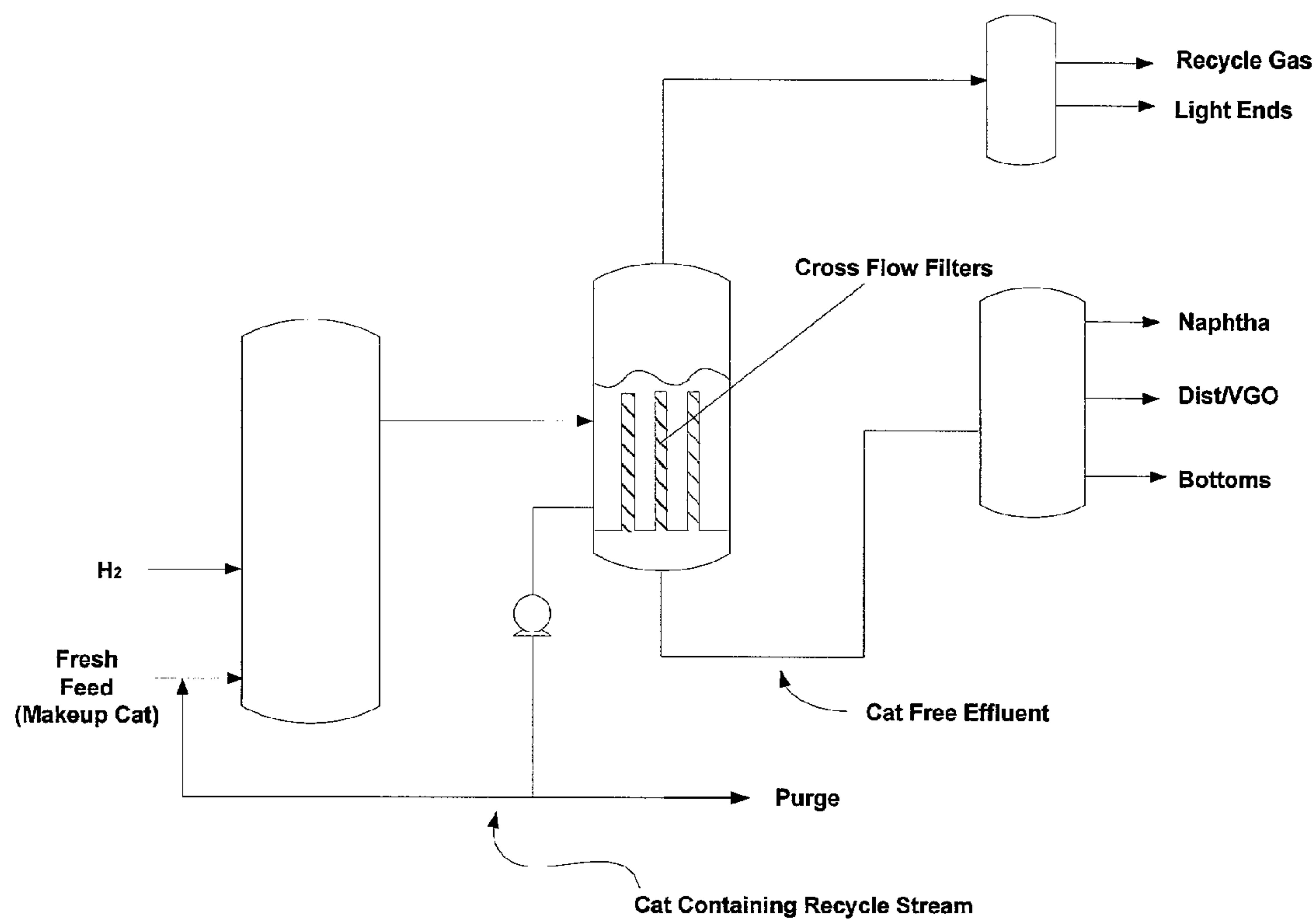


Figure 3



SLURRY HYDROPROCESSING FOR HEAVY OIL UPGRADING USING SUPPORTED SLURRY CATALYSTS

FIELD OF THE INVENTION

[0001] An embodiment of the instant invention is directed to an integrated slurry hydroprocessing process.

BACKGROUND OF THE INVENTION

[0002] Slurry hydroprocessing (SHP) is a technology capable of providing a low cost means for upgrading heavy crudes. Numerous patents exist that teach the use of hydroprocessing to obtain upgraded products from heavy crudes.

[0003] U.S. Pat. Nos. 3,622,495 and 3,622,498 describe a slurry process for effecting the hydroconversion of a hydrocarbonaceous charge stock containing sulfurous compounds. The process utilizes finely divided catalyst selected from the metals of Group V-B, VI-B or VIII of the periodic table. Preferred metallic components are vanadium, chromium, iron, cobalt, nickel, niobium, molybdenum, tantalum, and/or tungsten. The Group VIII noble metals are not generally considered for use. The catalyst may be combined with a refractory inorganic oxide carrier, but the process is said to be facilitated when the sulfide of the metal is unsupported.

[0004] U.S. Pat. No. 4,525,267 is directed to a process for hydrocracking hydrocarbons for residuum conversion. At least part of the catalyst utilized in the hydrocracking is extracted from the reaction zone and subjected to a hydrotreatment regeneration followed by recycle back to the hydrocracking step. The process is said to reduce coke production to a considerable degree.

[0005] While conventional slurry hydroprocessing has met with varying degrees of commercial success, there still remains a need in the art for processes and slurry catalysts that result in improved yields and selectivity.

[0006] As the supply of low sulfur, low nitrogen crudes decrease, refineries are processing crudes with greater sulfur and nitrogen contents at the same time that environmental regulations are mandating lower levels of these heteroatoms in products. Consequently, a need exists for increasingly efficient desulfurization and denitrogenation catalysts.

[0007] What is needed in the art is an improved process and catalysts which upgrade heavy feeds economically and effectively.

SUMMARY OF THE INVENTION

[0008] An embodiment of the instant invention is directed to a process comprising the steps of:

[0009] (a) slurry hydroprocessing (SHP) a hydrocarbon feedstock, at slurry hydroprocessing conditions, in the presence of a hydrogen containing treat gas and in the presence of a supported metallic catalyst comprising a supported sulfide of at least one Group VIII non-noble metal and at least one metal selected from the group consisting of non-noble Group VIII metals, Group VIB metals and mixtures thereof wherein said support is an inorganic refractory oxide carbon or mixtures thereof and wherein said catalyst has an average diameter of about 0.5 to about 100

microns to obtain a first product stream comprising said catalyst and a hydroprocessed feedstream;

[0010] (b) separating said first product into a catalyst-free product stream and a catalyst-containing stream

[0011] (c) recycling at least a portion of the catalyst-containing stream to said hydroprocessing step (a).

BRIEF DESCRIPTION OF THE FIGURES

[0012] FIG. 1 depicts one possible flow scheme for the instant invention. Feed and slurry catalyst enter the hydroprocessing reactor along with hydrogen. The reactor effluent is then passed to a separator zone that may comprises a cross-flow filtration chamber, as shown here, or other separation means, where the effluent is separated into a catalyst-free stream and a catalyst-containing stream. The catalyst containing stream, after withdrawal of a purge stream to control solids concentration in the reactor liquid, is recycled to the hydroprocessing reactor along with fresh feed. The catalyst free stream is then separated into gaseous and liquid products. The gaseous products include hydrogen which can then be recycled to the slurry hydroprocessing reactor.

[0013] FIG. 2 depicts another possible flow scheme where volatiles are removed before the separation of the first product into a catalyst-free and catalyst-containing stream.

[0014] FIG. 3 depicts another possible embodiment where the volatiles are removed from the first product stream during separation into a catalyst free and catalyst containing stream. The effluent from the slurry hydroprocessing reactor can be passed through a cooler (not shown) and introduced into a gas-liquid separator or disengaging means where the hydrogen gas, along with ammonia and hydrogen sulfide by-products from the hydroprocessing reactions, may be separated from the liquid effluent and recycled back for reuse in the hydrogen stream. The recycled gas is usually passed through a scrubber (not shown) to remove hydrogen sulfide and ammonia. This is usually recommended because of the inhibiting effect of such gases on the kinetics of hydrotreating and also to reduce corrosion in the recycle circuit. Fresh make-up hydrogen can be introduced into the recycle circuit. The gas-free liquid from the gas-liquid separator then enters a solids separator, or a filter, vacuum flash, centrifuge or the like, in order to divide the hydrotreating reactor effluent into a catalyst-containing stream and a product stream

DETAILED DESCRIPTION OF THE INVENTION

[0015] An aspect of the instant invention provides an integrated slurry hydroprocessing process which provides a more effective and efficient process by improving separation of product from the slurry.

[0016] The process may also include separating said catalyst-free product stream into gaseous and liquid hydrocarbon components prior to said step (c).

[0017] A wide range of petroleum and chemical hydrocarbon feedstocks can be hydroprocessed in accordance with the present invention. Suitable feedstocks, which will typically contain both nitrogen and sulfur, include whole and reduced petroleum crudes, atmospheric and vacuum residua, asphaltenes, deasphalted oils, cycle oils, FCC tower bot-

toms, gas oils, including atmospheric and vacuum gas oils and coker gas oils, light to heavy distillates including raw virgin distillates, hydrocrackates, hydrotreated oils, dewaxed oils, slack waxes, Fischer-Tropsch waxes, raffinates, naphthas, and mixtures thereof.

[0018] The heavy feeds which may be treated in accordance with the teachings herein are heavy feeds, defined as feeds having an API gravity of $<10-15^\circ$ with a viscosity of ≥ 60 centistokes at 60 C, including heavy crude oils and vacuum resid.

[0019] The light feeds which can be processed herein include feeds such as kerosene, home heating oil, straight run atmospheric gas oils, straight run vacuum gas oils etc. and mixtures thereof. Typically, such feeds will have a boiling point in the range of about 60 to about 1050° F. (about 16 to about 566° C.).

[0020] In an embodiment of the instant invention (illustrated in **FIG. 2**, a feedstream and slurry hydroprocessing (SHP) catalyst, along with hydrogen are fed to a reactor, which includes an external pump-around line and crossflow filter chamber. The crossflow filter chamber, which operates at reactor pressure and temperature, consists of a vapor zone and liquid zone. Hydrogen and gaseous products are removed from the vapor zone to a downstream separator. Upgraded catalyst-free liquid is withdrawn through the crossflow filter, and the resultant catalyst-containing liquid is recycled to the reactor, after removal of a suitable purge stream to control solids level in the reactor. The recycle stream can be fed directly to the reactor or premixed with the fresh feed stream. Additionally, fresh catalyst may be used in combination with the recycled catalyst.

[0021] Catalysts which may be utilized in the invention are supported catalysts. The supports may comprise inorganic refractory oxides such as silica, alumina and mixtures thereof, carbon and mixtures of carbon and inorganic refractory oxides. The catalyst will preferably comprise sulfides of molybdenum, nickel, tungsten, cobalt, or mixtures thereof. The catalyst will have an average diameter ranging from about 0.5 to about 100 microns and can be prepared directly from pre-sized inorganic oxide materials or obtained by reducing the size of commercially available hydrotreating catalysts.

[0022] Preferably, the catalysts will be prepared ex-situ by crushing commercially available catalysts and catalyst supports to obtain the desired catalyst diameter. It is believed that the selection and control of the particle size distribution of the catalyst enhances solid-liquid separation and significantly improves the hydrodesulfurization process. The ex-situ preparation provides flexibility to control the particle hardness and attrition resistance, intrinsic catalyst activity and other catalyst properties important to the process performance and physical separation.

[0023] An example of a useable catalyst is a supported sulfided material prepared from a precursor represented by the formula: $(X)_b(Y)_c$ where X is a Group VIII non-noble metal and Y is a Group VIII non noble metal or a VIB metal. The molar ratio described as the ratio of b:c is 0.1/1 to 3/1, preferably 0.25/1 to 2/1, more preferably 0.35/1 to 1/1, and most preferably 0.4/1 to 0.7/1.

[0024] Another useable sulfided catalyst comprises at least three metals wherein at least one of said metals is a Group

VIII non-noble metal and at least one of said metals is a Group VIB metals where the ratio of Group VIB metal to Group VIII non-noble metal is from about 10:1 to about 1:10, supported on an inorganic oxide.

[0025] In yet another preferred embodiment the supported sulfided metallic catalyst has a precursor represented by the formula: $(X)_b(Mo)_c(W)_dO_z$; wherein X is a non-noble Group VIII metal, and the molar ratio of b to (c+d) is 0.1/1 to 3/1; the molar ratio of c to d is $\geq 0.01/1$; and $z=[2b+6(c+d)]/2$.

[0026] In another preferred embodiment of the present invention the Group VIII non-noble metal is selected from Ni and Co.

[0027] In still another preferred embodiment of the present invention the Group VIII metal is Ni, and the X-ray diffraction pattern of the catalyst is essentially amorphous with crystalline peaks at $d=2.53$ Angstroms and $d=1.70$ Angstroms.

[0028] In yet another preferred embodiment of the present invention the molar ratio of b to (c+d) is 0.25/1 to 2.0/1 and the molar ratio of c to d is 1/10 to 10/1.

[0029] Desired catalysts that are used to process heavy feeds have median pore diameters between 10.0 and 35.0 nm. For distillate boiling range feeds, preferred median pore diameters are between 12.0 and 20.0 nm; and most preferred median pore diameters are between 14.0 and 18.0 nm. For heavy feeds, preferred median pore diameters are ≥ 30 nm. These median pore diameters are typically determined by Hg porosimetry.

[0030] The process conditions in the hydroprocessing reactor will depend on such things as the particular feed being treated. Such conditions are readily adjustable by the skilled artisan within the ranges herein taught. General process conditions for SHP include temperatures of about 500° to about 900° F. (about 260 to about 482° C.), preferably about 650 to about 850° F. (about 385 to about 454° C.) and most preferably about 725 to about 850° F. (about 343 to about 454° C.) and pressures from about 300 to about 2500 psig (about 2170 to about 17,339 kPa), preferably about 500 to about 2500 psig (3,549 to about 17,339 kPa) and most preferably about 800 to about 1000 psig (about 5,617 kPa to about 6996 kPa). The hydrogen treat gas rate is suitably about 200 to 2000 SCF/B (standard cubic feet per barrel) (36 to 360 m^3/m^3), preferably about 500 to 1500 SCF/B (90 to 270 m^3/m^3). The residence time is suitably from about 0.5 to 4 hours and preferably about 1 to 2 hours. For heavy feeds, it is preferable to attain about 1025+° F. to 1025-° F. ($552+^\circ$ C. to $552-^\circ$ C.) conversion of at least about 30%, preferably about 40%, and most preferably from about 50 to 60%. Catalyst concentration on feed will range from about 1 wt % to 30 wt %, preferably about 5 to about 20 wt %.

[0031] It is to be understood that the hydroprocessing of the present invention can be practiced in one or more reaction zones and can be practiced in either countercurrent flow or cocurrent flow mode. By countercurrent flow mode we mean a process mode wherein the feedstream flows countercurrent to the flow of hydrogen-containing treat gas.

[0032] The slurry hydroprocessing process of the present invention can be practiced by introducing a given feedstock

into a slurry hydroprocessing reactor. Before being passed to the hydroprocessing reactor, the feed may be mixed with a hydrogen containing gas stream and heated to a reaction temperature in a furnace or preheater. Alternatively, the hydrogen gas can be introduced directly into the hydroprocessing reactor. The reactor contains the slurried catalyst as previously described. Recycle of the reactor effluent via a pump is optional to provide mixing within the reactor zone.

[0033] In the preferred embodiment, the catalyst/solids separation from the product oil is accomplished by a cross-flow filtering step integrated with a pump around loop in the slurry reactor. In the turbulent cross-flow filtration zone there is minimal build-up of filter cake, which minimizes problems associated with filter binding. Other established separation steps such as gravity settling, centrifugation and other commonly known techniques may also be employed in combination with cross-flow filtration to enhance the process performance.

[0034] The most efficient process will employ a catalyst particle size and functionality that has been selected for the reactor conversion objectives and the cross-flow filtering system. The skilled artisan can readily select such parameters. In the most preferred embodiment, catalyst particle diameters on the order of 0.5 to 25 microns in size will be utilized. The performance of the cross-flow filtering step may be enhanced by the use of filter media aids. These filter media aids can be specially sized particles in the size range of about 5 to 200 microns that are used to pre-coat the filter media surface to enhance filter performance. Filter design can either be a back-flushed or continuously purged configuration.

[0035] The cross-flow filtration step can be either close coupled to the reactor in an external pump around loop or integrated into the reactor design as a section of the reactor in combination with a pump around zone (not shown in the figures).

[0036] In most slurry hydroprocessing operations it is desirable to separate substantially all of the catalyst from the liquid hydrocarbon product. Thus, the separation step is typically carried out under conditions which maximize separation to produce a recyclable active catalyst product having a maximum concentration which can be pumped or conveyed to the feed. This is typically in the range of from about 5 weight percent ("wt. %") to about 75 wt. %, preferably in the range of from about 10 wt. % to about 50 wt. %, and even more preferably in the range of from about 15 wt. % to about 35 wt. %. Except for cross-flow filtration, the separation step may comprise the use of centrifuges, cyclones, filters or even settling and draw-off.

[0037] The following examples are meant to be illustrative and not limiting.

EXAMPLE 1

[0038] A supported slurry catalyst was prepared by reducing the size of commercially available NiMo catalyst (Catalyst A). A sample of Catalyst A was wet-ball milled overnight and dried at 100-110° C. for 3-4 hours. After calcining at 400° C. for 3 hours, a fine powdered catalyst sample was obtained with measured average particle size at 3.6 microns. Prior to hydrotreating tests, it was pre-treated with hydrogen and hydrogen sulfide under 1000 psig (6996 kPa) of total

pressure (H₂/H₂S=90/10, v/v) at 725° F. (385° C.) for 60 minutes both to sulfide and to activate the catalyst. Table 1 provides additional physical properties of this catalyst.

TABLE 1

Physical Properties of Pre-treated Slurry Catalyst A	
Physical Properties of Slurry Catalyst A	
Mo, wt %	5.9
Ni, wt %	1.73
Surface Area, m ² /g	121
Pore Volume, cc/g	0.41
Median Particle Size, μm	3.6

EXAMPLE 2

[0039] A typical hydroprocessing experiment involved charging an autoclave with 100 g of resid (ALVR, Brent VR), and appropriate amount of catalyst chosen on the basis of wt % metal on feed. The mixture was stirred at 1500 RPM at 775° F. (413° C.) under 1000 psig (6996 kPa) of hydrogen pressure for 2 hours. Hydrogen was flowed through during the test to maintain an effective hydrogen partial pressure of about 900 psig (6307 kPa). The autoclave was then cooled to 300° F. (149° C.) and vented, and the liquid containing the catalyst was discharged. The product was separated by filtration through a two-layer of filter composed of one sheet of #2 and one sheet of #3 Whatman filter papers. The solid was washed with toluene and dried under vacuum overnight. The product oil was analyzed for metals, sulfur and Microcarbon Residue (MCR).

TABLE 2

Mild Slurry hydroprocessing tests of supported slurry Catalyst A. Conditions 775° F. (413° C.), 1000 psig H ₂ (6996 kPa), 2 hours. The catalyst was charged at 12 wt % on feed equivalent to 0.5 wt % Mo on feed.				
Total Liquid Product	Brent Vacuum Resid		Arab Light Vacuum Resid	
	Feed	Cycle 1	Feed	Cycle 2
Ni, ppm	10	3.67	27.3	16.0
V, ppm	38	1.77	95.7	18.7
S wt %	1.17	0.26	4.18	1.37
MCR wt %	14.9	9.68	24.3	12.8

[0040]

TABLE 3

Limited Catalyst Recycle Tests of the Supported Slurry Catalyst A on ALVR. Conditions: 775° F. (413° C.), 1000 psig (6996 kPa) H ₂ , 2 hours, the catalyst was charged at 12 wt % on feed for the first cycle, equivalent to 0.6 wt % Mo on feed.				
Total Liquid Product	ALVR	Slurry Hydroprocessing		
	Feed	Cycle 1	Cycle 2	Cycle 3
Ni, PPM	27.1	14.5	20.5	21.6
V, PPM	95.7	18.6	23.9	25.3
S, wt %	4.18	1.44	1.64	1.70
CCR, wt %	24.3	13.5	14.5	14.8

[0041] In summary, it has been demonstrated that the supported slurry catalysts could be utilized to improve the

quality of feeds. In the case of the slurry Catalyst A (Table 2), better upgrading results were achieved for both Brent VR and ALRV, and HDS was particularly higher due to Ni components of the catalyst. The recycle test, though not under optimum conditions, indicated that the supported slurry catalyst could provide reasonable recycle activity maintenance (Table 3). In addition, since the supported slurry catalysts are made ex-situ, their particle size can be better controlled and the size distribution can be made particularly narrow, thus providing for better solid-liquid separation relative to soft, small particle catalysts.

What is claimed is:

1. A process comprising the steps of:
 - (a) slurry hydroprocessing (SHP) a hydrocarbon feedstock, at slurry hydroprocessing conditions, in the presence of a hydrogen containing treat gas and in the presence of a supported metallic catalyst comprising a supported sulfide of at least one Group VIII non-noble metal and at least one metal selected from the group consisting of non-noble Group VIII metals, Group VIB metals and mixtures thereof wherein said support is an inorganic refractory oxide, carbon and mixtures thereof, and wherein said catalyst has an average diameter of about 0.5 to about 100 microns to obtain a first product stream comprising said catalyst and a hydroprocessed feedstream;
 - (b) separating said first product into a catalyst-free product stream and a catalyst-containing stream;
 - (c) recycling at least a portion of the catalyst-containing stream to said hydroprocessing step (a).
2. The process of claim 1 wherein said hydrocarbon feedstock is selected from the group consisting of heavy feeds, distillates, asphaltenes, deasphalted oils, cycle oils, FCC tower bottoms, gas oils, hydrocrackates, dewaxed oil, slack waxes, Fischer Tropsch waxes, raffinates, naphthas, hydrotreated oils and mixtures thereof.
3. The process of claim 1 wherein said catalyst is selected from a supported sulfided metallic catalyst wherein said metal is selected from molybdenum, nickel, tungsten, cobalt and mixtures thereof.
4. The process of claim 1 wherein said inorganic refractory oxide catalyst support is selected from alumina, silica and mixtures thereof.
5. The process of claim 1 wherein said catalyst is a supported sulfided material prepared from a precursor rep-

resented by the formula $(X)_b(Y)_c$ where X is a Group VIII non-noble metal and Y is a Group VIII non-noble metal or a VIB metal and the molar ratio of b to c is 0.1/1 to 3/1.

6. The process of claim 1 wherein said catalyst comprises at least three metals and wherein at least one of said metals is a group VIII non-noble metal and at one of said metals is a group VIB metals where the ratio of group VIB metal to group VIII non-noble metal is from about 10:1 to about 1:10.

7. The process of claim 1 wherein said catalyst is prepared from a precursor is represented by the formula $(X)_b(MO)_c(W)_dO_z$; wherein X is a non-noble Group VIII metal, and the molar ratio of b to (c+d) is 0.5/1 to 3/1; the molar ratio of c:d is $\geq 0.01/1$; and $z=[2b+6(c+d)]/2$.

8. The process of claim 1 wherein said Group VIII non-noble metal is nickel.

9. The process of claim 8 wherein said catalyst has an essentially amorphous x-ray diffraction pattern with crystalline peaks at $d=2.53$ Angstroms and $d=1.70$ Angstroms.

10. The process in claim 1 wherein said separation of said first product into a catalyst free and catalyst containing stream is accomplished using a cross-flow filtering step.

11. The process of claim 10 wherein said catalyst has a particle size of about 0.5 to 25 microns.

12. The process of claim 10 wherein filter media aids comprising particles in the size range of about 5 to about 200 microns are utilized.

13. The process of claim 10 wherein said cross-flow filtering step is integral to said slurry hydroprocessing step.

14. The process of claim 1 wherein said process further comprised separating volatiles from said first product stream prior to said separation step (b).

15. The process of claim 1 further comprising removing gaseous overheads during said separation step (b).

16. The process of claim 15 wherein when said overheads comprise a hydrogen containing gas, further comprising recycling said hydrogen containing gas to said step (a).

17. The process of claim 1 further comprising separating said catalyst-free product stream into gaseous and liquid hydrocarbon components prior to said step (c).

18. The process of claim 1 wherein said supported metallic catalyst has a median pore diameter of between 10.0 and 35.0 nm.

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