United States Patent

[11] 3,622,503

[72] Inventor **Rudolf H. Hausler**
Rolling Meadows, Ill.

[21] Appl. No. **15,666**
[22] Filed **Mar. 2, 1970**
[45] Patented **Nov. 23, 1971**
[73] Assignee **Universal Oil Products Company**
Des Plaines, Ill.

[54] **HYDROGEN TRANSFER AGENTS FOR SLURRY PROCESSING OF HYDROCARBONACEOUS BLACK OILS**
12 Claims, 1 Drawing Fig.

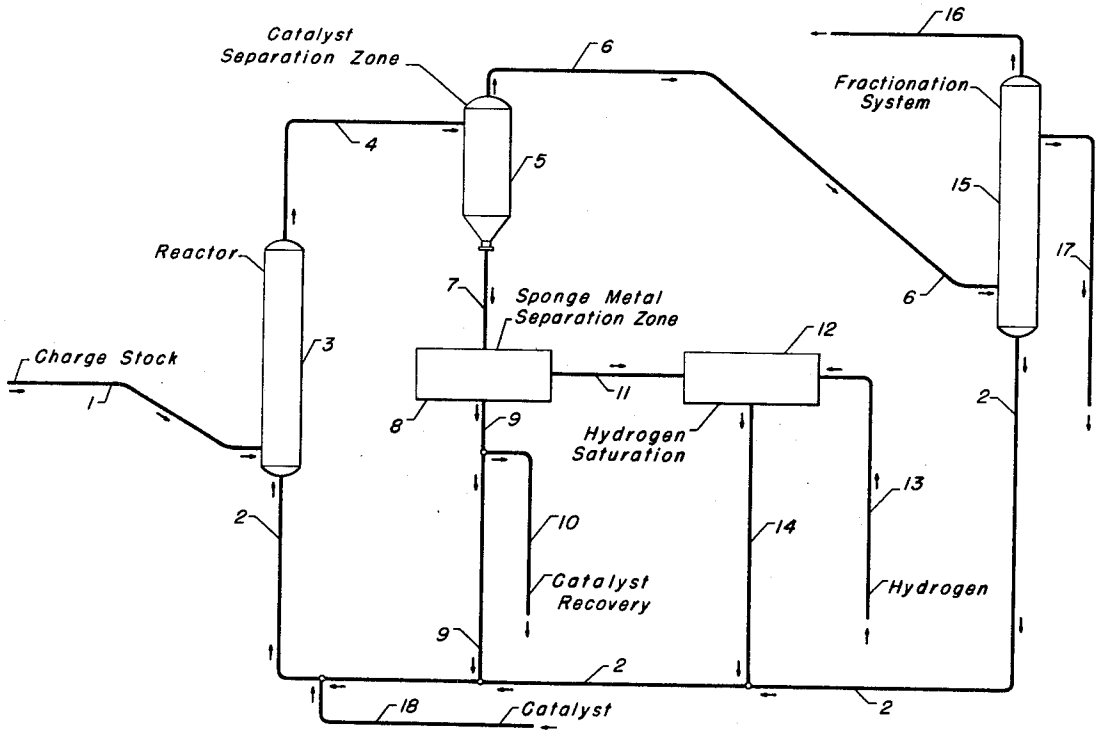
[52] **U.S. Cl.** **208/215,** 208/216, 208/217, 252/477
[51] **Int. Cl.** **C10g 23/02,** C10g 23/06
[50] **Field of Search** 208/217, 215, 209, 216, 213; 252/477, 472

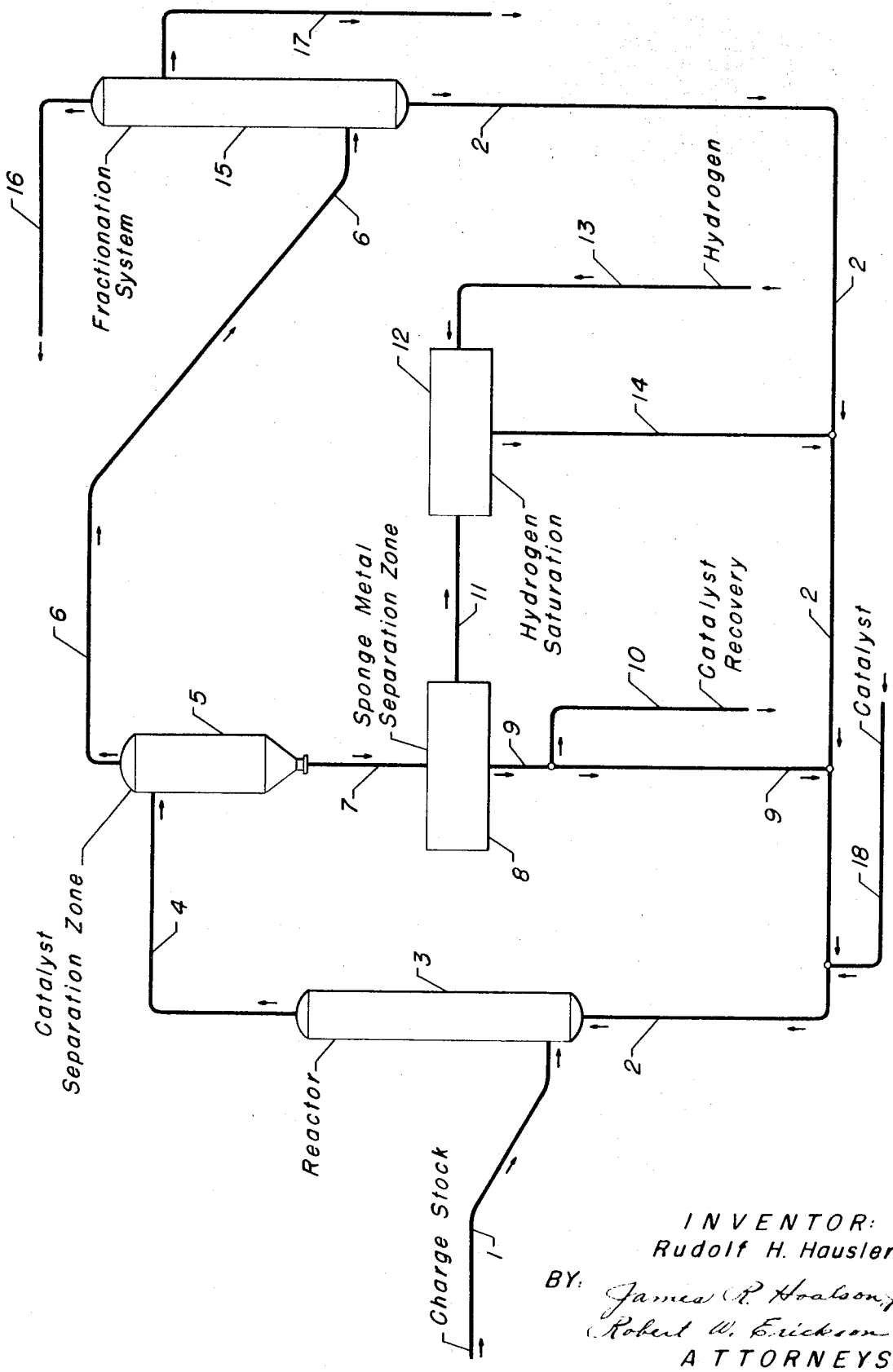
[56] **References Cited**
UNITED STATES PATENTS

3,152,981	10/1964	Berlin et al.	208/217
3,182,016	5/1965	Cole et al.	208/216
3,366,683	1/1968	Johnson et al.	252/472

Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. J. Crasanakis
Attorneys—James R. Hoatson, Jr. and Robert W. Erickson

ABSTRACT: Asphaltene-containing hydrocarbonaceous black oils are hydrogenated in a slurry process utilizing a hydrogen transfer agent. The transfer agent constitutes a finely divided sponge metal, saturated with hydrogen at elevated pressure, and admixed with the charge stock to form a reactive slurry. Preferred sponge metals include titanium, zirconium, vanadium, tungsten and nickel. In a specific embodiment, the reactive slurry also contains a hydrorefining catalyst of an unsupported sulfide of a Group V-B metal.





INVENTOR:
Rudolf H. Hausler

BY: James R. Hoatson, Jr.
Robert W. Erickson
ATTORNEYS

HYDROGEN TRANSFER AGENTS FOR SLURRY PROCESSING OF HYDROCARBONACEOUS BLACK OILS

APPLICABILITY OF INVENTION

The invention described herein encompasses a procedure for effecting the hydrogenation of hydrocarbonaceous black oils in a slurry-type process utilizing a hydrogen transfer agent. The hydrogen transfer agents, herein sometimes referred to as "sponge metals" due to their ability to absorb large volumes of hydrogen, are finely-divided metals in the elemental state. The heavy oils, to which the present invention is applicable, are characterized as containing asphaltenic material and include atmospheric tower bottoms, vacuum tower bottoms, crude oil residuals, topped crude oils, coal oil extracts, crude oils extracted from tar sands, etc.; these are often referred to in the art as "black oils."

Black oils contain high molecular weight sulfurous compounds in exceedingly large quantities. In addition, they contain excessive quantities of nitrogenous compounds, high molecular weight organometallic complexes, principally comprising nickel and vanadium, and asphaltenic material. The asphaltenic material is generally found to be complexed with, or linked to sulfur, and, to a certain extent, with the organometallic contaminants. An abundant supply of such hydrocarbonaceous material exists, most of which has a gravity less than 20.0° API, and which is further characterized by a boiling range indicating that 10.0 percent by volume and generally more, boils above a temperature of about 1050° F.

Difficulties encountered in processing black oils, utilizing a fixed-bed of a supported catalyst, have indicated that a more advantageous route resides in a slurry process wherein an unsupported catalytic component and hydrogen are admixed with the charge stock. The principal difficulty with a fixed-bed system is the lack of a suitable technique which affords the various fixed-bed catalysts sufficient sulfur stability in the presence of the asphaltenic and organometallic compounds. Not only does the catalyst deactivate rapidly, as a result of the formation of the carbon thereon, but the metallic contaminants become deposited upon the catalyst, steadily increasing in quantity until such time as the composition of the catalyst is changed to the extent that undesirable results are obtained. The asphaltenic fraction consists primarily of high molecular weight, nondistillable coke precursors, insoluble in light hydrocarbons such as propane, pentane, or heptane. A significant characteristic of asphaltenic material is the extremely low hydrogen to carbon atomic ratio. The hydrogen to carbon atomic ratio of most native asphaltenes is less than 1.0:1.0. In order to convert this asphaltenic material into lower-boiling hydrocarbon products, it is necessary to increase the hydrogen to carbon atomic ratio by way of hydrogenation.

The primary purpose of the present invention is to provide an efficient and economical scheme for effecting the hydrogenation of asphaltene-containing hydrocarbonaceous black oils. My invention is particularly directed toward the use of hydrogen transfer agents in the form of finely divided sponge metals capable of absorbing large volumes of hydrogen. Although the present application of hydrogen transfer agents is specifically directed toward the slurry processing of hydrocarbonaceous black oils, the technique is well suited for use in other processes in which hydrogenation assumes a dominant role. Such other processes include, but not by way of limitation, smoke point improvement of kerosene fractions, desulfurization, denitrification, aromatic and olefinic saturation, hydrotreating of naphtha fractions, etc.

OBJECTS AND EMBODIMENTS

A principal object of my invention is to provide a slurry process for hydrogenating an asphaltene-containing hydrocarbonaceous charge stock. A corollary object is to utilize a finely divided sponge metal as a hydrogen transfer agent to effect intimate dispersion of hydrogen within the charge stock.

Another object of my invention is to improve the operation of a catalytic slurry process in which the catalyst is an unsupported sulfide of a metal from Group V-B of the Periodic Table.

Therefore, in one embodiment, my invention provides a process for hydrorefining an asphaltene-containing hydrocarbonaceous charge stock which comprises saturating a finely divided sponge metal with hydrogen at a pressure greater than about 500 p.s.i.g. and a temperature in the range of about 175° to about 350° C., admixing the hydrogen-saturated sponge metal with said charge stock and reacting the resulting slurry at a pressure greater than about 500 p.s.i.g. and a temperature above about 350° C.

Other objects and embodiments of my invention, relating to specific and preferred hydrogen transfer agents, and operating conditions and techniques, will become apparent from the following detailed summary of the invention. For example, another embodiment involves saturating the sponge metal with hydrogen at a pressure in the range of 1,000 to about 5,000 p.s.i.g., and reacting the sponge metal/charge stock slurry at a temperature in the range of 350° to about about 500° C. and a pressure from about 1,000 to about 5,000 p.s.i.g.

SUMMARY OF INVENTION

Previous investigations into the slurry processing of hydrocarbonaceous black oils for hydrogenation and/or hydrorefining, the terms being used synonymously, have indicated that significant problems and difficulties exist. One principal difficulty involves bringing the charge stock into simultaneous contact with the hydrogen, or with the unsupported catalyst and hydrogen. When hydrogen is brought into the reaction system, whether separate from, or in conjunction with the charge stock, it tends to coalesce to form large bubbles. This problem is not solved through the use of mechanical feed devices such as spray nozzles, bayonets, high speed mixing valves, etc., since the coalescing will continue to take place in the initial section of the reaction zone with the result that the actual reaction time becomes severely limited. The primary purpose of the present invention is to provide a method whereby a greater quantity of hydrogen is made available for reaction with the charge stock over the entire length of the reaction chamber.

As hereinbefore stated, the present invention contemplates the simultaneous use of the hydrogen transfer agent and unsupported catalyst of a sulfide of a Group V-B metal. Slurry processing with unsupported catalytic components have indicated that a preferred form is a metallic sulfide, as distinguished from other compounds such as metallic oxides, metallic sulfates, etc. Furthermore, it has been found that the sulfides of the metals of Group V–B vanadium, niobium and tantalum, yield more advantageous results, with a vanadium sulfide being particularly preferred. Furthermore, the catalytic vanadium sulfide is nonstoichiometric and is produced in situ within the reaction chamber by initially employing vanadium tetrasulfide in slurry admixture with the charge stock.

The use of the term "unsupported," is intended to connote a catalyst, or catalytic component which is not an integral part of a composite with a refractory inorganic oxide carrier material. That is, the catalyst is a vanadium sulfide without the addition thereto of extraneous material. Although the precise atomic ratio of sulfur to vanadium is not known with accuracy, analyses have indicated that the nonstoichiometric, catalytic sulfide has a ratio of sulfur to vanadium not less than 0.8:1, nor greater than 1.8:1. This is not intended to mean that the vanadium sulfide has but a single specific sulfur/vanadium atomic ratio, but rather refers to a mixture of vanadium sulfides having nonstoichiometric atomic ratios within the aforesaid range. Although four oxidation states are known for vanadium, 2, 3, 4 and 5, Periodic Table of the Elements, E. H. Sargent and Company, 1964, only three stoichiometric vanadium sulfides are sufficiently stable for identification. These are: monovanadium sulfide, VS; sesquivanadium sulfide

V_2S_3; and, pentavanadium sulfide, V_2S_5; Handbook of Chemistry and Physics, Chemical Rubber Publishing Company, 42nd Edition, Page 680, 1960–1961. The literature is replete with references to many identifiable nonstoichiometric vanadium sulfides which are specific compounds in their own right, possibly the most common being the tetrasulfide, VS_4. It has previously been found that the catalytic vanadium sulfide is not identifiable as any of the stoichiometric vanadium sulfides, or as VS_4. The catalytic, nonstoichiometric vanadium sulfide is, however, produced in the reaction zone in situ through the conversion of the tetrasulfide at reaction conditions. It is within the scope of my invention to employ discrete particles consisting of the hydrogen transfer agent and the sulfide of the Group V–B metal.

A wide variety of metals can be utilized as the hydrogen transfer agent, or sponge metal, in accordance with my invention. The metals are employed in a finely divided state, generally from about 0.05 mm. to about 3.0 mm., and include magnesium, titanium, zirconium, strontium, barium, hafnium, vanadium, niobium, tantalum, chromium, tungsten, manganese, iron, nickel, and tin. Group VIII noble metals, as well as other metals, are suitable, and may be used to advantage as the hydrogen transfer agent. The generally high cost of these metals, however, precludes their use from an economic standpoint. Of the foregoing metals, those preferred include titanium, zirconium, vanadium, tungsten and nickel. In accordance with my invention, the finely divided sponge metal, for example titanium, is saturated with hydrogen at a pressure greater than about 500 p.s.i.g., and preferably from about 1,000 to about 5,000 p.s.i.g., and at a temperature in the range of about 175° to about 350° C. The hydrogen-saturated sponge metal is admixed with the hydrocarbonaceous charge stock and the resulting slurry is reacted in an elongated reaction chamber at a pressure greater than about 500 p.s.i.g. and a temperature above about 350° C. A preferred pressure range is from 1,000 to about 5,000 p.s.i.g., while the preferred temperature is in the range of about 350° to about 500° C.

The titanium releases its hydrogen, which is evenly distributed therein, within the reactor in a form which facilitates rapid reaction. Since the titanium particles are sufficiently small, hydrogen diffusion within the particle is not limiting upon a reaction rate. Similarly, where convection within the reaction chamber is similar to that of a fluidized bed system, hydrogen diffusion within the oil phase is not rate limiting either, since the titanium particles carry the hydrogen where it is required for the reaction. This type of system enhances the advantages of an upflow slurry operation which is not very efficient when hydrogen is brought into the reaction chamber in a vaporous state. The reason for this resides in the fact that the titanium powder will be more finely divided than hydrogen bubbles, and the latter tend to coalesce, while the titanium powder will remain finely divided. Titanium, for example, absorbs about 1,500 times its own volume of hydrogen, which is virtually equivalent to a pressure of 1,500 atmospheres. The absorption takes place at temperatures in the range of about 175° to about 350° C., whereas the release of hydrogen commences at about 350° C., and takes place rather rapidly at 450° C. In order to adjust the temperature at which hydrogen is absorbed and released, titanium may be alloyed with other metals, or other metals can be used in and of themselves. Thus, for example, uranium will decrease the hydrogen release temperature. When the process of the present invention is effected in conjunction with an unsupported sulfide of a Group V-B metal as a hydrorefining catalyst, the slurry will generally contain about 1.0 to about 25.0 percent by weight of said metal sulfide. The total reaction product effluent is separated to provide (1) an asphaltenic sludge containing the hydrogen transfer agent and (2) a product stream of normally gaseous and normally liquid hydrocarbons. The latter may be additionally separated to concentrate the hydrogen which is then utilized to resaturate the hydrogen transfer agent. Where a catalytic metal sulfide is utilized in conjunction with the hydrogen transfer agent, a series of separation techniques is effected. Although both the metal sulfide and hydrogen transfer agent may be introduced into the hydrogen saturation zone, a preferred technique involves separation of the hydrogen transfer agent from the metal sulfide whereby at least a portion of the latter may be removed from the process for regeneration and/or metal recovery. Such separation may be effected through any of the suitable, common separation techniques including floatation, settling, etc.

DESCRIPTION OF A PREFERRED EMBODIMENT

The illustration of a preferred embodiment involves the utilization of both a hydrogen transfer agent and a catalytic vanadium sulfide. This type scheme is diagrammatically presented in the accompanying drawing as a simplified flow scheme. In the drawing, various flow valves, control valves, instrumentation and startup lines, coolers, pumps and/or compressors, etc., have either been eliminated, or reduced in number; only those vessels and connecting lines considered necessary for a complete understanding of the present invention are shown. The use of such miscellaneous appurtenances are well within the purview of one having skill in the art of petroleum processing techniques.

The fresh feed charge stock in this illustrative embodiment is a vacuum tower bottoms product having a gravity of 9.8° API, and a 30.0 percent volumetric distillation temperature of about 1050° F. Contaminating influences include about 5.2 percent by weight of heptane-insoluble asphaltenes, 3.06 percent by weight of sulfur, 4.030 p.p.m. by weight of nitrogen and a total metals concentration of about 100 p.p.m.

With reference now to the drawing, the charge stock enters the process by way of line **1** and is introduced into a lower portion of elongated reactor **3**. Also, introduced into reactor **3**, via line **2**, is a mixture of hydrogen-saturated sponge metal and about 4.0 percent by weight of vanadium sulfide catalyst. The saturation of the sponge metal, titanium, is effected at a temperature of about 300° C. and a pressure of about 3,500 p.s.i.g. The temperature at the lower portion of reactor **3** is about 380° C. and the pressure is slightly less than about 3,500 p.s.i.g. as a result of the normal pressure drop experienced due to fluid flow through the system. In view of the fact that the reactions being effected are exothermic in nature, the temperature at the outlet of reactor **3** is about 450° C. The reaction zone effluent is withdrawn by way of line **4** into catalyst separation zone **5**. The catalyst separation zone is illustrated as a single vessel in order to simplify the flow scheme. In actual practice, for example, a hot flash system, functioning at essentially the same pressure as the reaction chamber in a first stage, and at a slightly reduced pressure in a second stage, serves to separate the product effluent into a vaporous phase, the principal portion of which boils below about 800° F. and a liquid phase containing unconverted asphaltenic material, titanium and the catalytic vanadium sulfide. The latter is indicated as emanating from catalyst separation zone **5** by way of line **7**, and introduced therethrough to sponge metal separation zone **8**. The separated titanium is introduced, by way of line **11**, into hydrogen saturation zone **12**, wherein the same absorbs hydrogen from line **13** at a pressure of about 3,500 and a temperature of about 300° C. The substantially titanium-free stream, from sponge metal separation zone **8**, containing unconverted asphaltenes and the vanadium sulfide, is removed by way of line **9** and recycled to the reaction chamber by way of line **2**. Although this stream may be totally recycled to combine with the fresh hydrocarbonaceous charge stock, a preferred operating technique involves withdrawing a drag stream, through line **10**, containing at least about 10.0 percent by weight of the vanadium sulfide. Any suitable means may be utilized to separate solid catalyst and unreacted asphaltenic material from the liquid phase hydrocarbons, including filtration, settling tanks, a series of centrifuges, etc. A like quantity of fresh vanadium tetrasulfide is then added by way of line **18** in order to maintain the selected catalyst content of the slurry. The principally vaporous phase from

catalyst separation zone 5 is withdrawn by way of line 6, and, following its use as heat exchange medium, is introduced thereby into fractionation system 15. It is understood that catalyst separation zone 5 may function to remove all distillable hydrocarbons boiling below desired temperatures other than 800° F., such temperatures typically including 750° F., 950° F., 1050° F., etc. With respect to fractionation system 15, one typical separation involves removing butanes and lower-boiling normally gaseous components as an overhead stream in line 16, pentane, and other normally liquid hydrocarbons are removed by way of line 17. The illustrated flow diagram also presents another technique whereby a normally liquid recycle stream is removed from fractionation system 15 by way of line 2, being utilized to facilitate the transfer of the hydrogen-saturated titanium, from line 14 and the separated catalytic vanadium sulfide, from line 9, to the lower portion of reaction chamber 3.

Analyses of the normally liquid product effluent, withdrawn from fractionation system 15 by way of line 17, indicate greater than about 98.0 percent heptane-insoluble conversion, less than about 10.0 p.p.m. of organometallic complexes and a gravity of about 18.2 API. Furthermore, the analyses indicate about 55.0 to about 70.0 percent conversion of sulfurous and nitrogenous compounds into hydrogen sulfide, ammonia and hydrocarbons.

I claim as my invention:

1. A process for hydrorefining an asphaltene-containing hydrocarbonaceous charge stock which comprises saturating a finely divided sponge metal with hydrogen at a pressure greater than about 500 p.s.i.g. and a temperature in the range of about 175° to about 350° C., said sponge metal being selected from the group consisting of titanium, zirconium, vanadium, tungsten and nickel, admixing the hydrogensaturated sponge metal with said charge stock and reacting the resulting slurry at a pressure greater than about 500 p.s.i.g. and a temperature above about 350° C.

2. The process of claim 1 further characterized in that said sponge metal is hydrogen-saturated at a pressure from 1,000 to about 5,000 p.s.i.g., and the resulting slurry is reacted at a temperature in the range of 350° to about 500° C. and a pressure from 1,000 to about 5,000 p.s.i.g.

3. The process of claim 1 further characterized in that said sponge metal is titanium.

4. The process of claim 1 further characterized in that said sponge metal is zirconium.

5. The process of claim 1 further characterized in that said sponge metal is vanadium.

6. The process of claim 1 further characterized in that said sponge metal is tungsten.

7. The process of claim 1 further characterized in that said sponge metal is nickel.

8. The process of claim 1 further characterized in that said slurry contains, as a hydrorefining catalyst, an unsupported sulfide of a Group V–B metal.

9. The process of claim 8 further characterized in that said Group V–B metal sulfide is a vanadium sulfide.

10. The process of claim 8 further characterized in that said slurry contains from 1.0 percent to about 25.0 percent by weight of said Group V–B metal sulfide.

11. A process for hydrorefining an asphaltene-containing hydrocarbonaceous charge stock which comprises saturating a finely divided sponge metal with hydrogen at a pressure greater than about 500 p.s.i.g. and a temperature in the range of about 175° to about 350° C., admixing with the charge stock said hydrogen-saturated sponge metal and a hydrorefining catalyst comprising an unsupported sulfide of a Group V–B metal, and reacting the resulting slurry at a pressure greater than about 500 p.s.i.g. and a temperature above about 350° C.

12. The process of claim 11 further characterized in that said Group V–B metal sulfide is a vanadium sulfide.

* * * * *