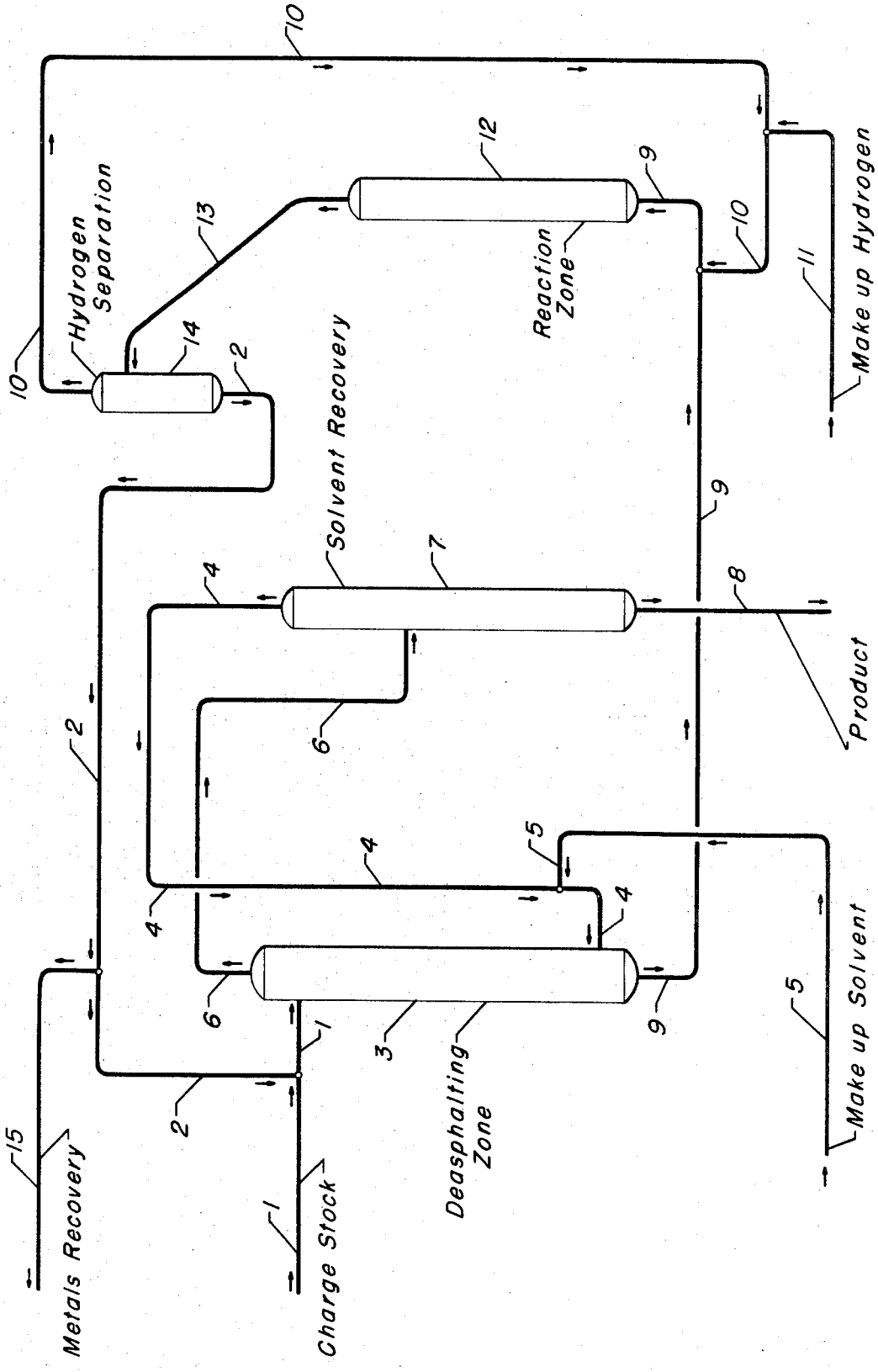
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CONVERSION OF ASPHALTENE-CONTAINING HYDROCARBONACEOUS CHARGE STOCKS

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CONVERSION OF ASPHALTENE-CONTAINING HYDROCARBONACEOUS CHARGE STOCKS

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ABSTRACT OF THE DISCLOSURE

A combination process for effecting the conversion of asphaltene-containing black oils. The charge stock, in admixture with non-stoichiometric vanadium sulfide, and unreacted asphaltenes, is initially subjected to solvent deasphalting to provide a solvent-lean mixture of the vanadium sulfide and the precipitated asphaltenes. This mixture is subsequently reacted with hydrogen to convert the asphaltenes into lower-boiling hydrocarbon products.

APPLICABILITY OF INVENTION

The invention herein described is adaptable to a process for the conversion of asphaltene-containing hydrocarbonaceous charge stocks generally derived from various petroleum crude oils. More specifically, the present invention is directed toward a slurry-type catalytic process for continuously converting atmospheric tower bottoms products, vacuum tower bottoms products (vacuum residuum), crude oil residuum, topped crude oils, coal oil extracts, crude oil extracted from tar sands, etc. Such heavy hydrocarbonaceous mixtures are referred to in the art as "black oils."

Black oils contain high molecular weight sulfurous compounds in exceedingly large quantities and, in addition, excessive amounts of nitrogenous compounds, high molecular weight organometallic complexes, principally comprising nickel and vanadium, and asphaltic material (asphaltenes). Asphaltic material is generally found to be complexed or linked with sulfur and, to a certain extent, with the organometallic compounds. The asphaltic material is concentrated in that fraction of the black oil having a normal boiling point above about 1050° F. An abundant supply of such hydrocarbonaceous material exists, most of which has a gravity less than about 20.0° API; a significant quantity has a gravity less than about 10.0° API. Furthermore, black oils are generally characterized by a boiling range indicating that at least 10.0% by volume has a normal boiling point above a temperature of about 1050° F.

The process of the present invention is a combination process which is particularly directed toward the conversion of black oils into distillable hydrocarbon products. Specific examples of those black oils, illustrative of those to which the present invention is especially applicable, include a vacuum tower bottoms product having a gravity of 7.1° API, containing 4.05% by weight of sulfur and 23.7% by weight of asphaltenes; and, a vacuum residuum having a gravity of 8.8° API, containing 3.0% by weight of sulfur, 4,300 p.p.m. of nitrogen and having a 20.0% volumetric distillation temperature of 1055° F. Through the utilization of the present invention, the conversion of the majority of such material is afforded; such conversion has heretofore been believed virtually impossible. Additionally, the process of the present invention results in a lower rate of catalyst deactivation and to the extent that the process may be conducted effectively for an extended period of time. The principal difficulty, heretofore experienced, resides in the lack of a technique which affords many catalytic composites an acceptable degree

of sulfur stability while simultaneously producing lower-boiling products from the asphaltic material. It is generally conceded that many fixed-bed catalytic processes are available which can process high-boiling sulfurous charge stocks such as heavy vacuum gas oils. These processes fall far short, however, of economical operability when processing asphaltene-containing material.

OBJECTS AND EMBODIMENTS

One object of the present invention is to provide a more efficient process for the hydrogenative conversion of heavy hydrocarbonaceous material containing asphaltics. A corollary objective is to increase the effective life of the catalytic composite utilized in the conversion of asphaltene-containing charge stocks. Another objective is to convert hydrocarbon-insoluble asphaltenes into hydrocarbon-soluble, lower-boiling normally liquid products.

A specific object is to effect the continuous decontamination of asphaltenic black oils by providing a combination process utilizing a solid, unsupported catalyst, in which process there is afforded a decrease in the rate of catalyst deactivation.

Therefore, in one embodiment, the present invention is directed toward a process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock which process comprises the steps of: (a) deasphalting said charge stock, in admixture with non-stoichiometric vanadium sulfide, with a selective solvent in a solvent extraction zone to provide (1) a solvent-rich, normally liquid phase and (2) a solvent-lean mixture of said non-stoichiometric vanadium sulfide and asphaltenes; and, (b) reacting said solvent-lean mixture with hydrogen, in a conversion zone, at conversion conditions selected to convert insoluble asphaltenes into lower-boiling hydrocarbon products.

In another embodiment, the resulting conversion zone effluent, containing the non-stoichiometric vanadium sulfide catalyst in admixture with asphaltenes, is introduced into said solvent extraction zone.

Other embodiments of our invention relate primarily to operating conditions and the use of selected solvents within the solvent extraction zone. In one such embodiment, the charge stock is admixed with non-stoichiometric vanadium sulfide in an amount of at elast 1.5% by weight, calculated as elemental vanadium; the preferred upper limit, for the concentration of non-stoichiometric vanadium sulfide, is about 25.0% by weight.

PRIOR ART

The basic concept involved with the use of unsupported, non-stoichiometric vanadium sulfide as the catalytic agent for the conversion of hydrocarbonaceous black oils, is found in U.S. Pat. No. 3,558,474 (Class 208–108). As indicated in the teachings of this patent, we found that non-stoichiometric vanadium sulfide exhibits an unusual degree of activity with respect to asphaltene conversion, while simultaneously eliminating a significant amount of the sulfurous and nitrogenous compounds. With respect to the present combination process, it should be noted that there exists, in the teachings of this portion of the prior art, no mention of solvent deasphalting, or extraction.

It must necessarily be acknowledged that the prior art is replete with a wide spectrum of techniques for effecting the solvent deasphalting of asphaltene-containing hydrocarbonaceous charge stocks. In the interest of brevity, no attempt will be made herein to tabulate exhaustively the solvent deasphalting art.

Exemplary of such prior art is U.S. Pat. No. 1,948,296 (Class 208–4) in which a combination process is described wherein the separated asphaltic fraction is admixed with an oil and subjected to oxidation to obtain a particularly

good asphalt. The described solvents, for use in precipitating the asphaltic fraction, include light petroleum hydrocarbons such as naphtha, casinghead gasoline, light petroleum fractions composed of propane, butane and isobutane, certain alcohols, ether and mixtures thereof, acetone, etc.

U.S. Pat. No. 2,002,004 (Class 208–14) involves a two-stage deasphalting process wherein the second stage completes the precipitation of asphalts which was partially effected in the first stage. As noted previously, the solvents described include naphtha, gasoline, casinghead gasoline and liquefied normally gaseous hydrocarbons such as ethane, propane, butane and mixtures thereof.

U.S. Pat. No. 2,914,457 (Class 208–79) describes a multiple combination process involving fractionation, vacuum distillationn, solvent deasphalting, hydrogenation and catalytic reforming. Again the suitable liquid deasphalting solvents include liquefied normally gaseous hydrocarbons such as propane, n-butane, isobutane, or mixtures thereof, as well as ethane, ethylene, propylene, n-bptylene, isobutylene, pentane, isopentane, and mixtures thereof.

While the foregoing examples of the deasphalting art serve to indicate the now ancient use of a wide variety of deasphalting solvents, it must be noted that there is no indication of the present combination process wherein the charge stock, in admixture with a finely-divided, non-stoichiometric vanadium sulfide catalyst, is subjected to the deasphalting operation. Furthermore, the prior art appears to be void of any intent to effect asphaltic conversion to lower-boiling hydrocarbon products.

Mention should be made of U.S. Pat. No. 2,975,121 (Class 208–251) wherein the charge stock is initially subjected to hydrogenative cracking, followed by solvent deasphalting of the hydrogen-treated oil to remove suspended solid metal constituents. This reference indicates that the hydrogenation operation, for the initial treatment of the metal-containing charge oil, may be carried out in the presence of a suitable hydrogenation catalyst, and preferably one which is sulfide-resistant. However, the only catalyst contemplated is nickel tungsten sulfide and cobalt molybdate. Furthermore, there is no recognition of the present combination process wherein the catalyst composite is non-stoichiometric vanadium sulfide, the deasphalting operation produces a mixture of the vanadium sulfide with the precipitated asphaltenes and the mixture is subjected to hydrogenative conversion.

SUMMARY OF INVENTION

As indicated in U.S. Pat. No. 3,558,474, unsupported vanadium sulfide catalyst, colloidally dispersed in the hydrocarbonaceous charge stock, has been found to be an effective hydrorefining catalyst. The catalyst is non-stoichiometric, and is prepared "in situ" from the catalyst precursor, vanadium tetrasulfide. The indicated procedure is to disperese finely-divided vanadium tetrasulfide in the charge stock, thermally decomposing the same in the presence of hydrogen to yield the non-stoichiometric vanadium catalyst. We have found that, when the catalyst is separated from the product effluent including unreacted asphaltenes and heavy oil, and rerun with additional charge stock, a marked decrease in catalyst activity takes place.

Unsupported, non-stoichiometric vanadium sulfide catalyst has little, if any, internal surface area, and, therefore, the desired reactions must be effected on the external surface. As a consequence, the activity of the catalyst is principally dependent upon particle size. A high degree of catalytic actiivty is initially obtained when the catalyst is formed from the catalyst precursor, vanadium tetrasulfide. The finely-dispersed vanadium tetrasulfide breaks down into even smaller particles when thermally decomposed in the presence of hydrogen. The present inventive concept is founded upon recognition of the fact that, as the catalyst precursor is thermally decomposed in the presence of hydrogen and asphaltenes, the resulting non-stoichiometric vanadium sulfide particles become associated with the asphaltenes and the latter serve to keep the catalyst colloidally dispersed. High catalytic activity can be maintained provided the catalyst particles are not permitted to agglomerate which is the case when the once-used catalyst is rerun to combine with additional charge stock.

Where a high asphaltene conversion is obtained, resulting in an insufficient quantity of asphaltenes to associate with the vanadium sulfide catalyst particles, or if the catalyst is separated from the liquid product in a manner which removes the catalyst from any asphaltenes associated with it, the catalyst particle will subsequently agglomerate resulting in a loss of external surface and, consequently, a decrease in catalytic activity. If, on the other hand, a too low asphaltene conversion is obtained, leading to coke deposition on the catalyst from the thermal decomposition of asphaltenes, or if the catalyst is separated from the liquid product in a manner such that carbonization of the catalyst is effected, a similar decrease in catalytic activity results.

We have found that the activity of the non-stoichiometric vanadium sulfide catalyst, when it is re-used with fresh hydrocarbonaceous black oil, can be maintained close to the same level as when the catalyst is initially formed from the catalyst precursor, vanadium tetrasulfide. This is accomplished by subjecting a mixture of the vanadium sulfide catalyst and the hydrocarbonaceous charge stock, to a solvent deasphalting operation such that the catalyst particles appear in the heavy phase containing the asphaltenes and heavy oil constituents. This heavy phase is then subjected to conversion in the presence of hydrogen with the result that lower-boiling hydrocarbon products are produced from the asphaltenes and heavy oils. Following separation of the hydrogen, from the conversion zone effluent, the remainder of the effluent including unreacted asphaltenes and the vanadium sulfide catalyst is introduced into the solvent extraction zone. As the process continues in operation, 100.0% by weight of the virgin asphaltenes will be converted; however, this is not to be construed as stating that 100.0% by weight of all the asphaltenes entering the conversion zone are so converted. In this manner, the non-stoichiometric vanadium sulfide catalyst is constantly maintained in intimate association with asphaltenes, and, therefore, remains colloidally dispersed. There then exists no tendency of the finely-divided vanadium sulfide catalyst to form large agglomerates which inherently lead to a decline in catalyst activity.

The concentration of non-stoichiometric vanadium sulfide, within the heavy phase recovered from the solvent extraction zone, is at least about 1.5% by weight, calculated on the basis of elemental vanadium. Excessive concentrations do not appear to enhance the overall result, even with extremely contaminated charge stocks exhibiting a high asphaltene content. Therefore, the upper limit of vanadium sulfide is about 25.0% by weight. The charge stock/non-stoichiometric vanadium sulfide mixture is introduced into an upper portion of a solvent deasphalting zone, wherein it countercurrently contacts a suitable selective solvent which is introduced into a lower portion thereof. The solvent deasphalting zone will function at a temperature in the range of about 50° F. to about 500° F., and preferably from about 100° F. to about 300° F.; the pressure will be maintained within the range of about 100 to about 1,000 p.s.i.g., and preferably from about 200 to about 600 p.s.i.g. The precise operating conditions will generally depend upon the physical characteristics of the charge stock as well as the selected solvent. In general, the temperature and pressure are selected to maintain the deasphalting operation in liquid phase, and to insure that all the catalyst particles are removed in the solvent-lean heavy phase.

Suitable solvents include those hereinbefore described in the discussion of the prior art. Thus, it is contemplated that the solvent will be selected from the group of light hydrocarbons such as ethane, methane, propane, butane, isobutane, pentane, isopentane, neopentane, hexane, isohexane, heptane, etc. Similarly, the solvent may be a normally liquid naphtha fraction containing hydrocarbons having from about 5 to about 14 carbon atoms per molecule, and preferably a naphtha fraction having an end boiling point below about 200° F. The solvent-rich normally liquid phase is introduced into a suitable solvent recovery system, the design and techniques of which are thoroughly described in the prior art.

The solvent-lean heavy phase, from the deasphalting zone, containing the vanadium sulfide catalyst, asphaltenes and heavy oil constituents, is admixed with hydrogen in an amount above about 5,000 s.c.f./bbl. The practical upper limit for hydrogen concentration is about 50,000 s.c.f./bbl. Following suitable heat-exchange with various hot effluent streams, the temperature of the mixture is further increased to the level desired at the inlet to the reaction zone. Since the reactions being effected are principally exothermic in nature, the temperature of the effluent from the reaction zone will be considerably higher than the inlet temperature. Therefore, the inlet temperature will be controlled in the range of about 325° C. to about 400° C. The residence time in the reaction zone is such that the effluent temperature is not substantially higher than about 500° C. Although suitable results are obtained at a maximum reaction temperature of 500° C., a preferred mode of operation limits the maximum reaction temperature to about 450° C. The reaction zone will be maintained under an imposed pressure of about 500 to about 5,000 p.s.i.g.

Although the present process may be effected in an elongated reaction zone with the slurry and hydrogen being introduced into the upper portion thereof, the effluent being removed from a lower portion, an upflow system offers advantages. One principal advantage resides in the fact that the extremely heavy portion of the charge stock, particularly that portion boiling above a temperature of about 1050° F., will have an appreciably longer residence time within the reaction zone, with the result that a greater degree of conversion thereof becomes attainable.

The product effluent, including the vanadium sulfide catalyst and unreacted asphaltenes, is introduced into a suitable separation system from which a hydrogen-rich gaseous phase is recovered for purposes of recycle to combine with the material being introduced into the reaction zone. The hydrogen separation system is not considered an essential feature of the present combination process, and may consist of one or more suitably operated vessels from which the hydrogen is recovered; other normally gaseous streams may be separately recovered, including, for example, a methane/ethane concentrate and a propane/butane concentrate. The remainder of the product effluent is introduced into the upper portion of the solvent deasphalting zone.

The conversion of hydrocarbonaceous black oils appears to be beneficially affected when carried out in the presence of hydrogen sulfide. Therefore, it is within the scope of the present invention that from about 2.50 to about 25.0 mol percent hydrogen sulfide will be present in the hydrogen entering the conversion reaction zone.

DESCRIPTION OF DRAWING

One embodiment of the present invention is presented in the accompanying drawing by means of a simplified flow diagram in which details such as pumps, instrumentation and controls, heat-exchange and heat-recovery circuits, valving, start-up lines and similar hardware have been omitted as not essential to an understanding of the techniques involved. The utilization of such miscellaneous appurtenances, to modify the illustrated process flow, is well within the purview of those skilled in the art.

With reference now to the drawing, the charge stock in line **1** is admixed with a mixture of non-stoichiometric vanadium sulfide and unreacted asphaltenes in line **2**, the mixture continuing through line **1** into deasphalting zone **3**. A selected solvent, for example a mixture of isobutane and n-butane, is introduced into a lower portion of deasphalting zone **3** by way of line **4**, and is inclusive of make-up solvent from line **5**. The solvent-rich, normally liquid hydrocarbon phase is removed through line **6**, and introduced thereby into a suitable solvent recovery system **7**. The isobutane/n-butane solvent is recycled through line **4**, while the normally liquid product of the process is removed by way of line **8**.

The solvent-lean mixture of non-stoichiometric vanadium sulfide, precipitated asphaltenes and high-boiling heavy oil components, is withdrawn from deasphalting zone **3** by way of line **9** and introduced into the lower portion of reaction zone **12**. The product effluent is withdrawn through line **13**, and introduced into hydrogen separation system **14**, from which a hydrogen-rich recycle gas stream is recovered in line **10** and recycled, along with make-up hydrogen from line **11**, to combine with the charge to the reaction zone in line **9**. The non-stoichiometric vanadium sulfide, unreacted asphaltenes, and the normally liquid product effluent, for example hexane-plus, is removed from hydrogen separation system **14** through line **2**, and is introduced by way of line **1** into deasphalting zone **3**. In order to prevent undue metals build-up within the system, a drag stream is withdrawn through line **15** and sent to a suitable metals recovery facility.

It will be noted, from the flow just described, that the non-stoichiometric vanadium sulfide is constantly maintained in intimate association with asphaltenes. Thus, there is afforded a significant decrease in the rate of catalyst deactivation as indicated by analyses of the product in line **8**. Being devoid of metalic contaminants and high molecular weight asphaltenes, the product in line **8** is suitable for direct utilization as the charge stock to a fixed-bed system for complete removal of the remaining sulfurous and nitrogenous compounds. Furthermore, since the charge stock/vanadium sulfide mixture is initially subjected to a deasphalting technique, the size of the subsequent reaction zone will be significantly decreased.

EXAMPLES

The following examples are presented for the sole purpose of illustrating the process of the present invention, and it is not intended that the invention be limited to the specifics involved. The hydrocarbonaceous charge stock employed was a vacuum column bottoms product having a gravity of 6.2° API, an initial boiling point of 546° F. and a 10.0% volumetric distillation temperature of 958° F.; 24.0% by volume was distillable at a temperature of 1050° F. The charge stock contained 13.3% by weight of asphaltenes, 4.88% by weight of sulfur, 0.48% by weight of nitrogen, 400 p.p.m. of vanadium and 70 p.p.m. of nickel, the latter existing as organometallic porphyrins.

Example I

In this example, the charge stock was employed in an amount of 200 grams per hour, and was admixed with 18.9 s.c.f./hour of hydrogen (15,000 s.c.f./bbl.); the mol percent hydrogen sulfide in the recycle gas was 17.0. The reaction zone was maintained at a pressure of 3,000 p.s.i.g. and a peak (maximum) reaction zone temperature of 443° C. The normally liquid portion of the product effluent was subjected to solvent deasphalting, utilizing propane, at a temperature of 67° C. and a pressure sufficient to maintain the deasphalting operation in liquid phase.

The catalyst was first employed in an amount of about 3.2% by weight for the conversion of a topped crude oil having a gravity of 8.0° API. The crude contained 10.53%

by weight of asphaltenes, 2.80% by weight of sulfur and 578 p.p.m. of metals. The non-stoichiometric vanadium sulfide catalyst was rerun twice following removal of all the benzene-soluble material and asphaltenes. Results of this operation are presented in the following Table I:

TABLE I.—TOPPED CRUDE PROCESSING

Run number	Gravity, °API	Asphaltics	Sulfur, wt. percent
1	19.5	0.19	0.95
2	17.8	2.01	1.49
3	16.7	2.40	1.81

Catalyst deactivation is readily apparent from the foregoing tabulation; by the time of the second rerun (run No. 3) the gravity had decreased to 16.7 and the residual asphaltics had increased to 2.40% by weight.

At this point, the charge stock was changed to the vacuum column bottoms previously described. Again the vanadium sulfide catalyst, in the increased amount of about 7.9% by weight, was rerun (four times) following removal of the benzene-soluble material and the residual asphaltenes. In the following Table II there are presented the results of the last three catalyst rerun operations.

TABLE II.—VACUUM BOTTOMS PROCESSING

Run number	Gravity, °API	Asphaltics	Sulfur, wt. percent
4	17.9	1.74	1.62
5	18.8	1.74	1.73
6	19.6	1.70	1.79

Catalyst deactivation is particularly noticeable with respect to the residual asphaltics concentration; with fresh catalyst, more than 99.0% of the virgin asphaltenes were converted, while the above figures indicate only about 87.0% asphaltene conversion.

Example II

In accordance with the present invention, the charge stock/vanadium sulfide slurry is admixed with unreacted asphaltenes, and subjected to a n-butane deasphalting operation at a temperature of about 70° C. and a pressure sufficient to maintain the operation in liquid phase. Approximately 20.0% by volume of the original charge stock is removed in a solvent-rich phase and introduced into a suitable solvent recovery system. The remaining heavy oil constituents, non-stoichiometric vanadium sulfide, in an amount of about 3.0% by weight, and precipitated asphaltenes are introduced into the lower portion of a reaction zone maintained at a maximum temperature of about 425° C. and under an imposed pressure of about 3,000 p.s.i.g. The charge is admixed with a hydrogen-rich gas in an amount of about 17,000 s.c.f./bbl., containing about 15.0 mol percent of hydrogen sulfide.

Following separation of the reaction product effluent, to concentrate the hydrogen for recycle to the reaction zone, the remainder is admixed with fresh hydrocarbon charge stock and introduced into the solvent deasphalting zone. After a period of about 100 hours, approximately 10.0% of the reaction product effluent is withdrawn and, following removal of hydrocarbon-soluble products, is sent to a metals recovery system.

Analyses of the normally liquid product effluent including that recovered from the drag stream when applicable, indicate a recovery of the initial catalyst activity. At about fifty hours of operation, the residual asphaltene concentration is about 1.25%; at 142 hours, it has dropped to about 0.50%; at 175 hours, the residual asphaltics amount to about 0.25%; and, after about 200 hours, the concentration is about 0.10%.

The foregoing clearly indicates the method by which the present invention is effected and the benefits to be afforded through the utilization thereof.

We claim as our invention:

1. A process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock which comprises the steps of:
   (a) deasphalting said charge stock, in admixture with non-stoichiometric vanadium sulfide, with a selective solvent in a solvent extraction zone to provide (1) a solvent-rich, normally liquid phase and (2) a solvent-lean mixture of said non - stoichiometric vanadium sulfide and asphaltenes; and,
   (b) reacting said solvent-lean mixture with hydrogen, in a conversion zone, at conversion conditions selected to convert insoluble asphaltenes into lower-boiling hydrocarbon products.

2. The process of claim 1 further characterized in that the resulting conversion zone effluent is introduced into said solvent extraction zone.

3. The process of claim 1 further characterized in that said conversion conditions include a temperature from about 300° C. to about 500° C. and a pressure in the range of about 500 p.s.i.g. to about 5,000 p.s.i.g.

4. The process of claim 1 further characterized in that said charge stock is admixed with non-stoichiometric vanadium sulfide in an amount of at least 1.5% by weight, calculated as elemental vanadium.

5. The process of claim 1 further characterized in that the hydrogen concentration, in said conversion zone, is at least about 5,000 s.c.f./bbl.

6. The process of claim 1 further characterized in that said selective solvent is a light hydrocarbon containing from one to about seven carbon atoms.

7. The process of claim 1 further characterized in that said selective solvent is a normally liquid naphtha fraction containing hydrocarbons having from about five to about fourteen carbon atoms per molecule.

8. The process of claim 1 further characterized in that the volume ratio of said selective solvent to said charge stock is from about 3:1 to about 15:1.

9. The process of claim 6 further characterized in that said selective solvent comprises n-butane.

10. The process of claim 7 further characterized in that said naphtha fraction has an end boiling point below about 200° F.

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