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HYDROREFINING OF PETROLEUM CRUDE OIL WITH VANADIUM HALIDES

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The present invention relates to a process for hydrorefining of petroleum crude oil, heavy vacuum gas oil, crude tower bottoms, vacuum tower bottoms product, visbreaker product effluent, heavy cycle stocks, and other high-boiling hydrocarbon fractions and/or distillates. More specifically, the present invention is directed toward a catalytic, slurry-type process for hydrorefining heavy hydrocarbonaceous material severely contaminated by the inclusion therein of excessive quantities of deleterious substances.

In one of its embodiments, the present invention involves a process for effecting the decontamination, or hydrorefining, of a heavy hydrocarbon charge stock for the primary purpose of effecting the destructive removal of nitrogenous and sulfurous compounds, and particularly for the conversion of the pentane-insoluble portion of such charge stock into useful pentane-soluble hydrocarbon products. Crude petroleum oil, and other heavy hydrocarbon fractions and/or distillates, which boil at temperatures above the gasoline and middle-distillate boiling ranges, such as crude tower bottoms, vacuum gas oil, heavy cycle stocks, black oil, etc., generally contain nitrogenous and sulfurous compounds in large quantities. In addition, these high-boiling hydrocarbon fractions contain quantities of metallic contaminants which exhibit the tendency to exert detrimental effects upon a catalyst utilized in a process to which the crude oil, or portion thereof, is ultimately subjected. The more common of such metallic contaminants are nickel and vanadium, although other metals including iron, lead, arsenic, copper, etc., may be present. Although the metallic contaminants may exist in a variety of forms, they are usually found in the form of organo-metallic compounds of high molecular weight, such as metal porphyrins and the various derivatives thereof. Nothwithstanding that the total concentration of these metallic contaminants is relatively small, often less than about 10 p.p.m. calculated as the elemental metal, subsequent processing techniques are easily adversely affected thereby. For example, when a hydrocarbon charge stock, containing metals in excess of about 10.0 p.p.m., is subjected to a cracking process for the purpose of producing lower-boiling, normally liquid hydrocarbons, the metals become deposited upon the catalyst employed, steadily increasing in quantity until such time as the composition of the catalytic composite is changed to the extent that undesirable results are obtained.

In addition to the contaminating influences exemplified by nitrogenous and sulfurous compounds, and organo-metallic complexes, crude oils and other heavy hydrocarbon fractions generally consist of a significant quantity of high-boiling, pentane-insoluble material. For example, a full boiling range Wyoming sour crude oil, having a gravity of 23.2° API at 60° F., not only is contaminated by about 2.8% by weight of sulfur, approximately 2700 p.p.m. of total nitrogen, a total of about 100 p.p.m. of metallic porphyrins (computed as elemental nickel and vanadium), but contains a pentane-insoluble asphaltenic fraction in an amount of 8.39% by weight. Similarly, a crude-tower bottoms product, having a gravity, ° API at 60° F. of 14.3, is contaminated by the presence of about 3.0% by weight of sulfur, 3830 p.p.m. of total nitrogen, about 85 p.p.m. of total metals and about 10.93% by weight of asphaltenic compounds. A much more difficult charge stock to convert into valuable, normally liquid hydrocarbons, is a vacuum tower bottoms product having a gravity, ° API at 60° F. of 7.0, containing more than 6,000 p.p.m. of nitrogen, about 4.0% by weight of sulfur, over 450 p.p.m. of metallic contaminants, and about 24.0% by weight of pentane-insoluble asphaltenic material. Such asphaltenic material consists of high molecular weight hydrocarbons which are considered to be coke-precursors having the tendency to become immediately deposited within the reaction zone and other process equipment, and onto the catalytic composite in form of a gummy, heavy hydrocarbonaceous residue. Since this in effect constitutes a large loss of charge stock, it is economically desirable to convert such asphaltenes into pentane-soluble liquid hydrocarbon products. Furthermore, the presence of excessive quantities of asphaltenes appears to inhibit the activity of a hydrorefining catalyst with respect to its ability to effect the removal of sulfur and nitrogen by conversion thereof to hydrogen sulfide, ammonia and hydrocarbons.

The object of the present invention is to provide a more efficient process for hydrorefining, or decontaminating petroleum crude oil and other heavy hydrocarbon fractions, than the processes currently employed. A fixed-bed catalytic process, or a fixed-fluidized bed process is virtually precluded due to the difficulty in maintaining the catalyst in an active condition. Various moving-bed processes employing catalytically active metallic components, composited with a highly refractory inorganic oxide material, are extremely erosive, thereby causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a colloidally dispersed, unsupported catalytic component useful in a slurry process. The catalyst of the present invention is particularly advantageous for effecting the conversion of pentane-insoluble materials into pentane-soluble liquid hydrocarbons, while simultaneously converting a high percentage of the nitrogenous and sulfurous compounds into ammonia, hydrogen sulfide and hydrocarbons. The process of the present invention yields a liquid hydrocarbon product substantially free from pentane-insoluble asphaltenes, and significantly reduced in nitrogen and sulfur concentration to the extent that a subsequent fixed-bed catalytic process intended to result in an ultra-clean hydrocarbon product is economically feasible.

In a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbon charge stock, which process comprises admixing said charge stock with a halide of vanadium, preferably a chloride, reacting the resulting mixture with hydrogen at a temperature above about 225° C., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

A more limited embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock, which process comprises admixing said charge stock with from about 1.0% to about 30.0% by weight of vanadium trichloride, calculated as elemental vanadium, reacting the resulting mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure within the range of from about 500 to about 5,000 p.s.i.g., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

From the foregoing embodiments, it is readily ascertained that the method of the present invention involves the preparation of a colloidally-dispersed catalytic component within the hydrocarbon charge stock from which the contaminating influences are intended to be removed.

The colloidally dispersed catalytic component is a halide of vanadium, and may be vanadium dichloride, vanadium trichloride, vanadium bromide, vanadium iodide, vanadium fluoride, vanadium tetrachloride, or mixtures thereof. Of these, vandium dichloride and vanadium trichloride are preferred, with vanadium trichloride being particularly preferred due to the degree of contaminant removal experienced through the use thereof. The quantity of vanadium chloride utilized is such that the colloidal suspension, or dispersion, resulting upon admixture with the hydrocarbon charge stock, comprises from about 1.0% to about 30.0% by weight, calculated as if the vanadium existed in the elemental state. Lower concentrations of the vanadium chloride may be employed, to achieve acceptable results, and lie within the range of from about 1.0% to about 10.0% by weight.

Briefly, the process is effected by initially admixing the desired quantity of the chloride of vanadium, for example, vanadium trichloride, with the hydrocarbon charge stock, in an amount such that the resulting colloidal suspension, or dispersion contains from about 1.0% to about 10.0% by weight of vanadium, calculated as the element thereof. For this purpose, it is preferred that the vanadium trichloride be in the form of a solid, as a finely-divided powder, which form facilitates the formation of the colloidal suspension. The resulting colloidal dispersion is then passed into a suitable reaction zone maintained at a temperature within the range of from about 225° C. to about 500° C. and under a hydrogen pressure of about 500 to about 5,000 p.s.i.g. The presence of added hydrogen sulfide in the hydrogen atmosphere, has been found to enhance the catalytic activity of the vanadium trichloride, and such hydrogen sulfide is added in an amount within the range of from about 5.0% to about 25.0%, prior to effecting the hydrorefining reactions. The process may be effected as a batch-type operation, or in a continuous manner in either upward flow or downward flow. The normally liquid hydrocarbons are separated from the total reaction zone product effluent by any suitable means, for example, through the utilization of a centrifuge, or settling tanks, the remaining metal-containing sludge being treated as hereinafter set forth.

The metal-containing sludge is a viscous fluid consisting of the catalytically active metallic component, originally dispersed in the charge stock, unconverted asphaltenic material, soluble hydrocarbons, porphyrinic material containing nickel, vanadium, metallic contaminants, coke and heavy carbonaceous material, etc. I have found that the unconverted asphaltenic material consists of from about 10.0% to about 20.0% by weight of the originally-present asphaltenes, which material is significantly more resistant to conversion, thereby causing an inordinately large proportion of the difficulties experienced when the crude oil, or heavy fraction derived therefrom, is subjected to hydrorefining and/or hydrocracking. This asphaltenic material is that which possesses the tendency to become virtually immediately transformed into coke and gummy polymerization material, as a result of which the remaining portion of the asphaltenes fails to come into contact with the active catalyst components. It is, therefore, expedient and economical to remove about 10.0% to about 20.0% of the total asphaltenic material originally present in the hydrocarbon charge stock, from the catalyst-containing sludge, prior to recirculating the same to combine with the fresh charge stock. Furthermore, the active catalytic components may then be recombined with the charge stock, to form a colloidal suspension or dispersion, thereby effecting additional refining of the charge stock.

Following the separation of the normally liquid hydrocarbons from the catalyst-containing sludge, the latter is treated with a suitable organic solvent for the purpose of dissolving residual organic-soluble material such as pentane-soluble hydrocarbon products resulting from the conversion of the pentane-insoluble asphaltenic compounds. Any well-known organic solvent may be employed for the dissolution of the organic-soluble material in the sludge, and the resulting solution may be subjected to further reaction with hydrogen by recycling the same to combine with fresh hydrocarbon charge stock. The remainder of the sludge is then treated with a compound having the propensity to regenerate the vanadium trichloride. Suitable compounds for this purpose include sulfur monochloride, sulfur dichloride, and their mixtures. Such regeneration may be readily effected at a comparatively low temperature within the range of from about 250° C. to about 450° C., the sulfur chlorides being employed in an amount of from about 0.1% to about 25.0% by weight of the material to be treated. The sludge containing regenerated vanadium trichloride is combined with fresh hydrocarbon charge stock, and reacted with hydrogen as aforesaid. The regenerated catalyst-containing sludge will contain the original metallic components utilized as the catalyst, and, in addition thereto, at least a portion of the vanadium originally existing within the charge stock as a porphyrin or a derivative thereof. Since the vanadium component, when colloidally dispersed within the charge stock exhibits an acceptable degree of catalytic activity, very little fresh catalyst is necessary to maintain catalytic activity, and in many instances the catalyst may be considered to be self-sustaining.

The following examples are given to illustrate the process of the present invention, and the effectiveness thereof in converting pentane-insoluble asphaltenes, while simultaneously effecting the conversion of sulfurous and nitrogenous compounds into sulfur-free and nitrogen-free hydrocarbons. It is not intended that the present invention be unduly limited to the method, catalyst, charge stock and/or operating conditions employed in this illustration.

The hydrocarbon charge stock was a heavy vacuum tower bottoms product having a gravity, °API at 60° F., of 7.0, and contaminated by the presence of 6,060 p.p.m. of total nitrogen, 4.05% by weight of sulphur, more than 450 p.p.m. of organo-metallic contaminants, and consisted of about 24.0% by weight of pentane-insoluble asphaltenic material.

Example I

12.0 grams of finely-divided, powdered vanadium dichloride were intimately admixed with 185 grams of the vacuum tower bottoms hereinabove described. The resulting colloidal suspension, comprising 2.75% by weight of vanadium, was placed in an 1800-milliliter rotating autoclave, pressured to 10 atmospheres with hydrogen sulfide, and then to 100 atmospheres with hydrogen. The contents of the autoclave were heated to a temperature of 425° C., the final pressure being about 210 atmospheres, which conditions were maintained for a period of about eight hours. The contents of the autoclave were allowed to cool, the autoclave was depressured, and the contents subjected to centrifugal separation to remove the metal-containing sludge from the normally liquid hydrocarbon product. Upon analysis, the normally liquid hydrocarbon product exhibited a gravity, °API at 60° F., of 30.5, indicating a considerable degree of conversion into lower-boiling hydrocarbon products, and contained 2.2% by weight of pentane-insoluble asphaltenic material.

Example II

15.0 grams of vanadium trichloride, in a finely-divided, powdered form, were admixed with 185 grams of the vacuum tower bottoms, to produce a colloidal dispersion containing 2.6% by weight of vanadium. The mixture was placed in a rotating autoclave, and maintained therein for a period of eight hours at the conditions set forth in the foregoing Example I. The analysis of the normally liquid hydrocarbon product, following separation from the metal-containing sludge, indicated a gravity, °API of 60° F. of 35.9, contained 484 p.p.m. of total nitrogen, 0.91% by weight of sulfur, and no pentane-insoluble as-

phaltenic material. Furthermore, following the dissolution of the organic soluble material from the metal-containing sludge, only 6.0 grams of sludge, containing coke, unconverted asphaltenic material, polymerization products, etc., remained.

A second experiment was conducted utilizing 195 grams of the vacuum tower bottoms and 15 grams of the vanadium trichloride to yield a colloidal dispersion containing 2.5% by weight of vanadium. Upon analysis, the normally liquid hydrocarbon product, following an eight-hour period in the rotating autoclave, indicated a gravity of 33.8° API at 60° F., 0.2% by weight of pentane-insoluble asphaltenes, 434 p.p.m. of nitrogen and 0.88% by weight of sulfur. In both instances, when utilizing the vanadium trichloride, the normally liquid hydrocarbon product, following separation from the metal containing sludge, indicates the continued presence of organo-metallic compounds in an amount less than about 10.0 p.p.m.

The foregoing specification and examples clearly illustrate the method by which the present invention is effected, and the benefits to be afforded through the utilization thereof. The normally liquid hydrocarbon product is substantially free from asphaltenic material, and has been significantly decreased with respect to the concentration of sulfurous and nitrogenous compounds. It will be readily recognized by those possessing skill within the art of petroleum refining processing, and particularly the hydrorefining of contaminated hydrocarbon charge stocks, that the product effluent is highly suited for further processing in contact with a fixed-bed of solid catalyst particles to produce an ultra-clean hydrocarbon product substantially free from nitrogenous and sulfurous compounds.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with a chloride of vanadium, reacting the resulting mixture with hydrogen at a temperature above about 225° C., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

2. The process of claim **1** further characterized in that said chloride of vanadium is vanadium dichloride.

3. The process of claim **1** further characterized in that said chloride of vanadium is vanadium trichloride.

4. A process for hydrorefining a hydrocarbon charge stock which comprises admixing said charge stock with vanadium trichloride, reacting the resulting mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure within the range of from about 500 to about 5,000 p.s.i.g., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

5. The process of claim **4** further characterized in that said charge stock is admixed with from about 1.0% to about 30.0% by weight of vanadium trichloride, calculated as elemental vanadium.

6. The process of claim **4** further characterized in that said mixture is reacted with hydrogen in the presence of about 5.0% to about 25.0% of added hydrogen sulfide.

References Cited by the Examiner

UNITED STATES PATENTS

3,161,585	12/1964	Gleim et al.	208—264
3,165,463	1/1965	Gleim et al.	208—264
3,196,104	7/1965	Gleim et al.	208—264
3,231,488	1/1966	Gatsis et al.	208—213
3,240,718	3/1966	Gatsis	208—264

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