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3,317,420 HYDROREFINING OF PETROLEUM CRUDE OIL

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The present invention relates to a process for hydrorefining of petroleum crude oil, heavy vacuum gas oil, crude tower bottoms, tar sands oil, 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 hydrocarbonanceous material which is severely contaminated by the inclusion 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, 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 catalytic composite 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 as organo-metallic compounds of high molcular weight, such as metal porphyrins and the various derivatives thereof. Notwithstanding 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 thereof 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 2,700 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 about 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, 3,830 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, and 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. 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 the 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 wtih 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 those 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 material, 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, containing asphaltenes, which process comprises admixing said charge stock with a tin salt selected from the group consisting of halides, sulfates, salts of fatty acids and salts of aromatic acids, reacting the resulting mixture with hydrogen at a temperature above 225° C., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

In another broad embodiment, the present invention encompasses a process for hydrorefining a hydrocarbon charge stock, which process comprises admixing said charge stock with a chloride of tin, reacting the resulting mixture with hydrogen at a temperature above about 225° C., removing a metal-containing sludge from the resulting reaction product 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 stannic chloride, calculated as elemental tin, 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 5000 p.s.i.g., removing a metal-containing sludge from the reaction product 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 heavy hydrocarbon charge stock from which the contaminating influences are to be removed. The colloidally dispersed catalytic component is a tin salt, and preferably a chloride of tin, including stannous chloride, stannic chloride and various mixtures thereof. Of these, stannic chloride is particularly preferred, or a mixture of stannic chloride and stannous chloride with the former being in the greater concentration. The quantity of stannic chloride, or other tin salt, 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 tin existed in the elemental state. Lower concentrations may be employed to achieve acceptable results, and lie within the range of from about 1.0% to about 10.0% by weight.

Other tin salts include the sulfates, bromides, fluorides, tin salts of fatty acids such as acetic acid, propionic acid and butyric acid, and tin salts of aromatic acids including benzoic acid, phthalic acid, etc. The chlorides are, however, especially preferred due to their ability to reduce the concentration of sulfurous and nitrogenous compounds while simultaneously converting virtually all the pentane-insoluble asphaltenes.

Briefly, the process is effected by initially admixing the desired quantity of the chloride of tin, for example, stannic chloride, 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 tin, calculated as the element thereof. For this purpose, the stannic chloride should be in the form of a solid, as a finely-divided powder, or as aqueous solution, which forms facilitate the preparation 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 from about 500 to about 5,000 p.s.i.g. An unexpected advantage, resulting from the use of a chloride of tin, resides in the fact that the presence of added hydrogen sulfide, in the hydrogen atmosphere, is not required in order to achieve acceptable results. This is contrary to the results experienced when utilizing other metals, including molybdenum, nickel, tungsten, vanadium, etc., in a similar slurry-type process. With these and other metallic components, hydrogen sulfide is added to the hydrogen atmosphere in an amount of about 5.0% to about 25.0%, prior to effecting the hydrorefining reactions, in order to convert a substantial portion of the asphaltenic material. 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, orignally dispersed in the charge stock, unconverted asphaltenic material, soluble hydrocarbons, porphyrinic material containing nickel and vanadium, metallic contaminants, coke and heavy carbonaceous material, etc. It has been found that the unconverted asphaltenic material consists of from about 10.0% to about 20.0% by weight of the originally-present asphaltenes, which portion 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 component. 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 within 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 reactivate the stannic and/or stannous chloride. Suitable compounds for this purpose include sulfur monochloride, sulfur dichloride, and mixtures thereof. Such reactivation may be readily effected at a comparatively low temperature within the range of 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 portion of the sludge containing the reactivated stannic and/or stannous chloride 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 an organo metallic porphyrin or derivative thereof. Since this vanadium component, when colloidally dispersed within the charge stock as a vanadium chloride, exihibits an acceptable degree of catalytic activity, very little fresh catalyst will be necessary to maintain catalytic activity, and the process may be considered as virtually self-sustaining.

The following example is given to illustrate 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.

Example

The hydrocarbon charge stock was a sour Wyoming crude oil having a gravity, ° API at 60° F., of 23.2, and containing 2,650 p.p.m. of nitrogen, 2.8% by weight of sulfur and 8.3% by weight of pentane-insoluble asphaltenic material. To each of two, 200 gram portions of the crude oil, an aqueous solution of 13.0 grams of stannic chloride was added dropwise at a temperature of about 212° F., at which temperature the water was removed. Each of the resulting colloidal suspensions were placed in individual 1800-milliliter rotating autoclaves, one of which was initially pressured to 10 atmospheres with hydrogen sulfide, and after which both autoclaves were pressured to 100 atmospheres with hydrogen. The contents of each autoclave were heated to a temperature of 400° C., the final pressure in the autoclave containing hydrogen sulfide being about 220 atmospheres, while the final pressure in the second autoclave was about 202 atmospheres. These conditions were maintained for a

period of about four hours, after which the contents of each autoclave were allowed to cool, the autoclaves were 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, resulting from the reaction effected in the absence of added hydrogen sulfide, exhibited a gravity of 30.3° API at 60° F., indicating a considerable degree of conversion into lower-boiling hydrocarbon products, and contains 520 p.p.m. of total nitrogen, 1.2% by weight of sulfur and only 0.47% by weight of pentane-insoluble asphaltenes. The normally liquid hydrocarbon product resulting from the reaction effected in the presence of added hydrogen sulfide indicated a gravity, ° API at 60° F., of 30.7, and contained 576 p.p.m. of nitrogen, 1.5% by weight of sulfur and 0.43% by weight of pentane-insoluble asphaltenes. It is readily ascertained from these results that the addition of hydrogen sulfide, prior to effecting the reaction of the crude oil with hydrogen, does not significantly enhance the activity of the catalytic component.

The foregoing specification and example 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 nitrogeous 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 in order to produce an ultra-clean hydrocarbon product substantially free from nitrogeous and sulfurous compounds.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises colloidally dispersing in said charge stock a tin salt selected from the group consisting of halides, sulfates, salts of fatty acids and salts of aromatic acids, reacting the resulting mixture with hydrogen at a temperature above 225° C., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

2. A process for hydrorefining a hydrocarbon charge stock which comprises colloidally dispersing in said charge stock a chloride of tin, 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.

3. The process of claim 2 further characterized in that said chloride of tin is stannic chloride.

4. The process of claim 2 further characterized in that said chloride of tin is stannous chloride.

5. A process for hydrorefining a hydrocarbon charge stock which comprises colloidally dispersing stannic chloride in said charge stock, 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 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.

6. The process of claim 5 further characterized in that there is colloidally dispersed in said charge stock from about 1.0% to about 30.0% by weight of stannic chloride, calculated as elemental tin.

7. A process for hydrorefining a hydrocarbon charge stock which comprises colloidally dispersing in said stock a tin salt selected from the group consisting of halides and sulfates, reacting the resulting mixture with hydrogen at a temperature above 225° C., removing a metal-containing sludge from the reaction effluent and recovering a hydrorefined liquid product.

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