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**HYDROREFINING A HYDROCARBONACEOUS
CHARGE STOCK WITH A MOLTEN LEWIS
ACID AND MOLYBDENUM SULFIDE**

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ABSTRACT OF THE DISCLOSURE

Decontamination, or hydrorefining, of heavy hydrocarbonaceous material commonly referred to as "black oil." While the principal targets of the slurry-type process described are asphaltenic compounds and high molecular weight organo-metallic contaminants, considerable denitrification and desulfurization is effected. The charge stock, under superatmospheric hydrogen pressure, is reacted with a Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth, and which have a melting point below about 300° C. The liquid, molten Lewis acid contains from about 5.0% to about 50.0% by weight of molybdenum sulfide.

APPLICABILITY OF INVENTION

The present invention relates to a process for effecting the decontamination, or hydrorefining, of petroleum crude oil, heavy vacuum gas oil, crude tower bottoms, tar sands oil, coal oil extracts, vacuum tower bottoms product, visbreaker product effluent, heavy cycle stocks, and other high-boiling hydrocarbon fractions and/or distillates commonly referred to in the petroleum art as "black oils." More specifically, the present invention is directed toward a catalytic, slurry-type process for hydrorefining heavy hydrocarbonaceous material 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 a significant amount of nitrogenous and sulfurous compounds, and particularly for the conversion of the insoluble asphaltenic portion of such charge stock into useful 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 black oils contain metallic contaminants which exhibit the tendency to exert detrimental effects upon any catalytic composite which may be utilized in a process to which the crude oil, or portion thereof, is 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 molecular weight, such as metal porphyrins and 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 adversely affected thereby. For example, when a hydrocarbon charge stock containing metals in excess of about 10.0 p.p.m. by weight is subjected to a cracking process for the purpose of producing lower-boiling, normally liquid hydrocarbons, the metals

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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 insoluble asphaltenic 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- or heptane-insoluble asphaltenic fraction in an amount of about 8.4% 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, 3,800 p.p.m. of total nitrogen, about 85 p.p.m. of total metals and about 10.9% 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 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 supported hydrorefining catalyst with respect to its ability to effect the removal of sulfur and nitrogen by conversion thereof to hydrogen sulfide, ammonia and hydrocarbons.

OBJECTS AND EMBODIMENTS

An object of the present invention is to provide a process for hydrorefining, or decontaminating petroleum crude oil and other heavy hydrocarbon fractions.

A corollary objective is to effect decontamination in a liquid catalyst system utilizing a molten Lewis acid from the group consisting of the halides of aluminum, zinc, antimony and bismuth.

A specific object of the present invention resides in the use of a molten Lewis acid containing molybdenum sulfide in the hydrorefining of black oils.

A fixed-bed catalytic process, or a fixed-fluidized bed process, is virtually precluded for hydrorefining black oils 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 use of a liquid, unsupported catalytic component in a liquid-liquid contacting process. The catalyst of the present invention is particularly advantageous for effecting the conversion of insoluble asphaltenic 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 insoluble asphaltenes and organo-metallic compounds, and reduced in nitrogen and sulfur

concentration to the extent that a subsequent fixed-bed catalytic process, intended to produce an ultra-clean hydrocarbon product, is economically feasible.

In a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbonaceous charge stock, containing asphaltenes and organo-metallic compounds, which process comprises reacting said charge stock at superatmospheric hydrogen pressure with a molten Lewis acid selected from the group consisting of the halides of aluminum, zinc, bismuth and antimony, having a melting point below about 300° C., in admixture with from 5.0% to about 50.0% by weight of molybdenum sulfide.

A more specific embodiment of our invention provides a process for hydrorefining a hydrocarbonaceous charge stock containing asphaltenes and organo-metallic compounds, which process comprises reacting said charge stock with a molten Lewis acid consisting of zinc chloride and containing 10.0% to about 20.0% by weight of molybdenum sulfide, at reaction conditions including a temperature in the range of 300° C. to about 450° C. and a pressure of from 1500 to 3000 p.s.i.g., removing a metal-containing sludge from the reaction product effluent, and recovering a hydrorefined liquid product.

SUMMARY OF INVENTION

From the foregoing embodiments, it is readily ascertained that the method of the present invention involves a liquid catalytic component of molybdenum sulfide and a molten Lewis acid, contacting the heavy hydrocarbon charge stock from which the contaminating influences are to be removed. The molten Lewis acid is selected from the group of halides of aluminum, zinc, antimony and bismuth, being limited to those having melting points less than 300° C. The Lewis acids are, therefore, aluminum chloride, bismuth bromide, antimony fluoride, aluminum bromide, antimony iodide, bismuth chloride, aluminum iodide, zinc chloride, antimony bromide, antimony chloride and mixtures of two or more, and especially mixtures of zinc chloride with antimony halides.

The quantity of Lewis acid employed is from about 5.0% to about 50.0% by weight, and at least an amount equivalent to the weight percent asphaltenes in the charge stock. In a preferred embodiment, for further decreasing the quantity of residual sulfurous and nitrogenous compounds, the molten Lewis acid contains molybdenum sulfide in an amount in the range of from 5.0% to about 50.0%. Intermediate quantities of molybdenum sulfide are suitable, and are in the range of 10.0% to 20.0% by weight. The concentrations of molybdenum sulfide are computed on the basis of elemental molybdenum, whereas the Lewis acid, for example antimony trifluoride, is computed on the basis of the metallic halide.

Briefly, the process is effected by initially admixing the desired quantity of the molten Lewis acid, for example, zinc chloride, with the hydrocarbon charge stock, in an amount such that the resulting mixture contains from about 5.0% to about 50.0% by weight of zinc chloride. The resulting mixture is then passed into a suitable reaction zone maintained at a temperature within the range of from about 300° C. to about 450° C., and under a hydrogen pressure of from about 1,000 to about 5,000 p.s.i.g. An unexpected advantage, resulting from the use of the Lewis acid, 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 nickel, tungsten, vanadium, noble metals from Group VIII, etc., in a similar 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 present 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 produce 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 Lewis acids form complexes with the more basic constituents in the black oil, and especially with the asphaltenes, heteropolycyclic compounds and the high molecular weight organo-metallic compounds, at least some of which exist in the black oil as heteropolycyclics. These complexes are readily hydrogenated when heated at elevated temperature and high hydrogen pressure, and disassociate into a hydrogenated organic portion and an inorganic portion.

Following separation of the normally gaseous and liquid hydrocarbons from the reaction product effluent, the resulting sludge, containing the Lewis acid and the molybdenum sulfide, is further hydrogenated at 1,000 to 5,000 p.s.i.g. hydrogen pressure, and an elevated temperature in the range of 400° C. to about 550° C. After this treatment, the organic matter separates from the molten Lewis acid containing molybdenum sulfide, the latter being recycled to the process. The remaining sludge, containing unconverted asphaltenic material, some soluble hydrocarbons, porphyrinic material containing nickel and vanadium, other metallic contaminants, coke and heavy hydrocarbonaceous material, is treated with a suitable organic solvent for the purpose of dissolving residual organo-soluble material such as heptane- and/or pentane-soluble hydrocarbon products resulting from the conversion of the asphaltenic compounds. Any well-known organic solvent may be employed for the dissolution of the organo-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. Suitable solvents include low molecular weight paraffins having from four to eight carbon atoms per molecule, aromatics, especially benzene, naphthalene and anthracene, etc.

EXAMPLES

The following examples are presented to illustrate the present invention and the effectiveness thereof in converting asphaltenic material and organo-metallic compounds while simultaneously effecting the conversion of sulfurous and nitrogenous compounds, in a significant degree, 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 I

The hydrocarbon charge stock was a sour Wyoming crude oil having a gravity, API at 60° F., 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, 20.0 grams of zinc chloride and 10.0 grams of molybdenum sulfide is added. Each of the resulting mixtures is placed into an individual 1800-milliliter rotating autoclave, one of which is initially pressured to 10 atmospheres with hydrogen sulfide, and after which both autoclaves are pressured to a total of 100 atmospheres with hydrogen. The contents of each autoclave are 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 is about 202 atmospheres. These conditions are maintained for a period of about four hours, after which the contents of each autoclave are allowed to cool, the autoclaves de-pressured, and the contents subjected to centrifugal separation to remove the 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, has a gravity of

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about 30.7 API at 60° F., indicating a considerable degree of conversion into lower-boiling hydrocarbon products: the normally liquid portion contains 720 p.p.m. of total nitrogen; 1.4% by weight of sulfur; and, only 0.45% by weight of insoluble asphaltenes; the metals content being essentially "nil." The normally liquid hydrocarbon product resulting from the reaction effected in the presence of added hydrogen sulfide indicates a gravity, API at 60° F., of about 30.3, and contains 776 p.p.m. of nitrogen, 1.7% by weight of sulfur and 0.47% 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 results obtained.

EXAMPLE II

To a single 200-gram portion of the Wyoming sour crude, 20.0 grams of aluminum chloride, containing 2.0 grams of molybdenum sulfide, is added. The resulting mixture is placed into the 1800-milliliter rotating autoclave, and pressured to 100 atmospheres with hydrogen. After raising the temperature to 400° C., the autoclave pressure is about 205 atmospheres. Following a period of four hours, the normally liquid hydrocarbons are separated from the sludge. Analyses indicate an API gravity of 31.3°, and residual sulfur in an amount of about 1.15% by weight. Nitrogenous compounds remain in an amount of about 520 p.p.m., the metals content is "nil," and the asphaltenes have been decreased to about 0.36% by weight.

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 nitrogenous compounds. It will be readily recognized by those possessing skill within the art of petroleum refining processing, and particularly the hydrotreating 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

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order to produce an ultra-clean hydrocarbon product substantially free from nitrogenous and sulfurous compounds.

We claim as our invention:

1. A process for hydrotreating a hydrocarbonaceous charge stock containing asphaltenes and organo-metallic compounds which comprises reacting said charge stock at a hydrogen pressure of from about 1,000 to about 5,000 p.s.i.g. with a molten mixture comprising a Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth, said acid having a melting point below about 300° C., and from 5.0 to 50.0% molybdenum sulfide by weight based on the weight of the elemental molybdenum.
2. The process of claim 1 further characterized in that said Lewis acid is added to said charge stock in an amount at least equivalent to the weight percent asphaltenes in said charge stock, and is in the range of from about 5.0% to about 50.0%.
3. A process for hydrotreating a hydrocarbonaceous charge stock in accordance with claim 1 wherein said Lewis acid is zinc chloride and which contains therein 10.0% to 20.0% by weight of molybdenum sulfide based on the weight of the elemental molybdenum, at a reaction temperature in the range of 300° C. to 450° C. and a pressure of from 1,500 to about 3,000 p.s.i.g.

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