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HYDROREFINING OF METAL-CONTAINING BLACK OILS WITH A MOLTEN LEWIS ACID AND A MOLYBDENUM HALIDE

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ABSTRACT OF THE DISCLOSURE

Heavy hydrocarbonaceous charge stocks, commonly referred to as "black oils," are demetallized, reduced significantly in sulfurous and nitrogenous compound concentration, and further converted to reduce the concentration of asphaltenic material—i.e. high molecular weight compounds having a normal boiling point about 1050° F. The black oil is reacted, at superatmospheric hydrogen pressures, with a molten Lewis acid containing a molybdenum halide. The Lewis acid, selected from the halides of aluminum, zinc, antimony and bismuth, are used in an amount of 5.0% to 50.0% by weight of the black oil. The molybdenum halide is employed in an amount of from 5.0% to 50.0% by weight of the quantity of Lewis acid admixed with the black oil.

APPLICABILITY OF INVENTION

The present invention relates to a process for effecting the decontamination, or hydrorefining of petroleum crude oil, heavy vacuum gas oil, shale oil extract, crude tower bottoms, tar sands oil, vacuum tower bottoms product, coal oil extracts, 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 liquid-liquid catalytic process for hydrorefining heavy hydrocarbonaceous material severally 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 light hydrocarbon-insoluble 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 fraction contain quantities of metallic contaminants which exhibit the tendency to exert detrimental effects upon a 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 organometallic compounds of high molecular weight, and include metal porphyrins and 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 of the catalyst is changed to the extent that undesirable results are obtained.

In addition to the contaminating influences exemplified by nitrogenous and sulfurous compounds, and organometallic 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, 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 soluble liquid hydrocarbon products. Furthermore, the presence of excessive quantities of asphaltenes in the charge appears to inhibit the activity of a hydrorefining catalyst with respect to its ability to effect the removal of sulfur and nitrogen through conversion thereof to hydrogen sulfide, ammonia and hydrocarbons.

OBJECTS AND EMBODIMENTS

An object of the present invention is to provide a process for removing organometallic compounds from black oils while simultaneously converting asphaltenes into light hydrocarbon-soluble products. A corollary object is to desulfurize and effect denitrification to the extent that subsequent fixed-bed processing is feasible.

Another object is to provide a liquid contacting type hydrorefining process utilizing a molten Lewis acid from the group consisting of the halides of zinc, aluminum, antimony and bismuth, the Lewis acid containing a molybdenum halide.

A fixed bed catalytic process, or a fixed-fluidized bed process, is virtually precluded, as a technique for hydrorefining black oil, 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 errosive, thereby causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a catalytic liquid useful for a liquid-liquid contacting process. The catalyst of the present invention is particularly advantageous for effecting the conversion of pentane-insoluble asphaltenic material, while simultaneously converting a high percentage of the nitrogenous and sulfurous compounds into ammonia, hy-

drogen sulfide and hydrocarbons. The process of the present invention yields a liquid hydrocarbon product substantially free from pentane-insoluble asphaltenes and organometallic compounds, and significantly reduced in nitrogen and sulfur concentration to the extent that a subsequent fixed-bed catalytic process, intended to result in an ultraclean hydrocarbon product, is economically feasible.

In a broad embodiment, therefore, the present invention relates to a process for hydrorefining a black oil charge stock containing asphaltenes and organometallic compounds, which process comprises reacting said black oil at superatmospheric hydrogen pressure with a liquid mixture of a molybdenum halide with a molten Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth.

A more limited embodiment of my invention is directed toward a process for hydrorefining a black oil, containing asphaltenes and organometallic compounds, which process comprises reacting said black oil with from 10.0% to 20.0% by weight of a molten Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth, said molten Lewis acid containing from 10.0% to about 30.0% by weight of molybdenum chloride; said process further characterized in that said black oil and Lewis acid are contacted at a superatmospheric hydrogen pressure of from 1,000 to about 5,000 p.s.i.g. and a temperature of from about 300° C. to about 450° C.

SUMMARY OF THE INVENTION

From the foregoing embodiments, it is readily ascertained that the method of the present invention involves contacting the heavy hydrocarbon charge stock, from which the contaminating influences are to be removed, with a liquid catalytic component. The liquid catalytic component is a molten Lewis acid from the halides of aluminum, zinc, antimony and bismuth, having a melting point less than 300° C., and containing a molybdenum halide. The molten Lewis acid may, therefore, be 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, especially mixtures of zinc chloride with the stated antimony halides. Suitable halides of molybdenum include MoF_3, $MoCl_5$, $MoCl_3$, $MoCl_4$, $MoBr_2$, $MoBr_3$, $MoBr_4$, etc. The contacting of the selected liquid catalytic agent with the heavy hydrocarbon charge stock, at the foregoing stated conditions, may be effected in any suitable reaction zone, or vessel, and either countercurrently, or cocurrently.

The quantity of Lewis acid utilized is in the range of from about 5.0% to about 50.0% by weight of the charge stock, preferably from about 10.0% to about 30.0%, and, in any event, at least an amount equivalent to the weight percent asphaltenes in the charge stock. The molten Lewis acid contains a molybdenum halide in an amount in the range of from 5.0% to about 50.0%. Intermediate quantities of molybdenum halide are suitable, and are in the range of 10.0% to 30.0% by weight. The concentrations of the molybdenum halides 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 Lewis acid, containing a molybdenum halide in the given amount, for example, zinc chloride containing molybdenum 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, which 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 molten Lewis acid and molybdenum halide, resides in the fact that the presence of added hydrogen sulfide, in the hydrogen atmosphere, is not required in order to achieve acceptable results. 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 molten Lewis acids form complexes with the more basic constitutents in the black oil, and especially with the asphaltenes, heteropolycyclic compounds and the high molecular weight organometallic 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, in the presence of the molybdenum chloride, and are disassociated 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 chloride, is further hydrogenated at 1,000 to 5,000 p.s.i.g. hydrogen pressure, and an elevated temperature in the range of 40° C. to about 50° C. After this treatment, the organic matter separates from the Lewis acid containing the molybdenum chloride, 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 organic-soluble material such as heptane- and/or heptane-soluble hydrocarbon products resulting from the conversion of the 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. Suitable solvents include low molecular weight paraffins having from four to eight carbon atoms per molecule, aromatics, especially benzene, and naphthalene and anthracene, etc.

EXAMPLES

The following examples are presented to illustrate the present invention and the effectiveness thereof in converting asphaltenic material and organometallic 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 containing 2.0 grams of molybdenum pentachloride is added. Each of the resulting mixtures is placed in individual 1800-milliliter rotating autoclave, one of which is initially pressured to 10 atmospheres with hydrogen sulfide, and after which both are pressured to 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 215 atmospheres, while the final pressure in the second autoclave is about 204 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 depressured, 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 presence of added hydrogen sulfide, has a gravity of about 30.8° API at 60° F., indicating considerable degree of conversion into lower-boiling hydrocarbon products, and contains about 676 p.p.m. of total nitrogen, 1.35% by weight of sulfur and only about 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 30.2, and contains 715 p.p.m. of nitrogen, 1.53% by weight of sulfur and about 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, an aqueous solution of 20.0 grams of aluminum bromide, containing 2.5 grams of molybdenum trichloride 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 207 atmospheres. Following a period of four hours, the normally liquid hydrocarbons are separated from the sludge. Analysis indicate an API gravity of 31.6°, residual sulfur in an amount of about 1.2% by weight, nitrogenous compounds of about 560 p.p.m., metals content "nil" and asphaltenes decreased to about 0.30% by weight.

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 hydrodcarbon 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 resulting decontaminated product effluent is well suited for further processing in contact with a fixed-bed of solid catalyst particles in order to produce an ultraclean hydrocarbon product substantially free from nitrogenous and sulfurous compounds.

I claim as my invention:

1. A process for hydrorefining a black oil containing asphaltenes and organometallic contaminants which comprises reacting said black oil at a hydrogen pressure of from about 1,000 to about 5,000 p.s.i.g. with a molten mixture of a molybdenum halide and a Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth, said acid having a melting point less than about 300° C.

2. The process of claim 1 further characterized in that said solution contains from 5.0% to about 50.0% of a molybdenum halide.

3. The process of claim 1 further characterized in that said molten Lewis acid is admixed with said black oil in an amount at least equivalent to the quantity of asphaltenes in said black oil.

4. The process of claim 1 further characterized in that said molten Lewis acid is admixed with said black oil in an amount within the range of from about 5.0% to about 50.0% by weight.

5. A process for hydrorefining a black oil containing asphaltenes and organometallic compounds which comprises reacting said black oil with from 10.0% to 20.0% by weight of a molten Lewis acid selected from the group consisting of the halides of aluminum, zinc, antimony and bismuth, said Lewis acid having a melting point less than about 300° C., and containing from 10.0% to about 30.0% by weight of molybdenum chloride, based on the weight of the elemental molybdenum; said process further characterized in that said black oil and molten Lewis acid are reacted at a superatmospheric hydrogen pressure of from 1,000 to about 5,000 p.s.i.g. and a temperature in the range of from 300° C. to about 450° C.

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