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NON-CATALYTIC CRUDE OIL HYDROREFINING PROCESS

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The present invention relates to a process particularly adaptable to the hydrorefining of petroleum crude oils and various hydrocarbon fractions derived therefrom. More specifically, the present invention is directed toward a non-catalytic process for hydrorefining petroleum crude oils, atmospheric tower bottoms products, vacuum tower bottoms product, heavy cycle stocks, crude oil residuum, topped crude oils, oils from tar sands, etc., for the primary purpose of effecting the removal of various contaminating influences therefrom. As hereinafter indicated, the present non-catalytic process is especially advantageous when utilized as a pre-treatment for severely contaminated, heavy hydrocarbonaceous material intended for subsequent processing via catalytic hydrorefining, the ultimate object of which is to provide a substantially contaminant-free normally liquid hydrocarbon product.

Petroleum crude oil, and the other hydrocarbon fractions and/or distillates above described, particularly heavy vacuum gas oils and topped crudes, contain nitrogenous and sulfurous compounds in exceedingly large quantities. In addition, such heavy hydrocarbon fractions contain detrimetally excessive quantities of organo-metallic contaminants which cause deleterious effects with respect to various catalytic composites utilized in a multitude of processes to which the heavy hydrocarbon fraction may be ultimately subjected. Oils extracted from tar sands contain an ash in an amount of about 2.0% by weight; the composition of the ash being about 90.0% silica. The more common of the metallic contaminants are nickel and vanadium, often existing in concentrations in excess of 50 p.p.m., although other metals including iron, copper, etc., may be present. These metals may exist within the hydrocarbon distillate in a variety of forms; they may exist as metal oxides or as sulfides, introduced therein as a form of metallic scale; they may be present in the form of soluble salts of such metals; usually, however, they are present in the form of high molecular weight organo-metallic compounds including metal porphyrins and the various derivatives thereof. Although metallic contaminants, existing as oxide or sulfide scale, may be removed, at least in part by a relatively simple filtering technique, and the water-soluble salts are at least in part removable by washing and a subsequent dehydration procedure, a much more severe treatment is required to effect the destructive removal of the organo-metallic compounds, particularly to the degree which is necessary to produce a heavy hydrocarbon fraction suitable for further processing.

Crude oils contain greater quantities of sulfurous and nitrogenous compounds than are generally found in lighter hydrocarbon fractions such as gasoline, kerosene, light middle-distillates, etc. For example, a Wyoming sour crude oil, having a gravity of 23.28° A.P.I. at 60° F., contains about 2.8% by weight of sulfur and approximately 2700 p.p.m. of total nitrogen, calculated as the elements thereof, in addition to 18 p.p.m. of nickel and 71 p.p.m. of vanadium. Upon being subjected to a catalytic hydrorefining process, the nitrogenous and sulfurous compounds are converted into hydrocarbons, ammonia and hydrogen sulfide. However, the reduction in the concentration of the organo-metallic contaminants is not as easily achieved, and to the extent that the same no longer exert a detrimental effect with respect to further processing of the crude oil. Similarly, a vacuum tower bottoms product, having a gravity, ° API at 60° F., of 7.1, contains 4.05% by weight of sulfur, 6060 p.p.m. of nitrogen, 46 p.p.m. of nickel and 195 p.p.m. of vanadium.

Notwithstanding that the total concentration of these metallic contaminants may be relatively small, for example, less than about 10 p.p.m. of metallic porphyrins, calculated as the elemental metals, subsequent processing techniques will be adversely affected thereby. Thus, when a hydrocarbon charge stock containing metals in excess of about 3.0 p.p.m., is subjected to a cracking process for the purpose of producing lower-boiling liquid hydrocarbon products, the metals become deposited upon the catalyst utilized, steadily increasing in quantity until such time as the composition of the catalytic composite is changed to the extent that undesirable results are obtained. That is to say, the composition of the cracking catalyst is closely controlled with respect to the nature of the charge stock being processed and to the desired product quality and quantity. Such composition is changed drastically as a result of the deposition of the metallic contaminants thereupon, the changed composite inherently resulting in changed catalytic characteristics. Such an effect is undesirable since the deposition of the metallic contaminants results in a lesses quantity of normally liquid hydrocarbon products, and produces large quantities of hydrogen and coke, the latter also producing relatively rapid catalyst deactivation.

In addition to the foregoing described contaminating influences, crude oils and other heavy hydrocarbon fractions contain excessive quantities of pentane-insoluble asphaltenic material. For example, the Wyoming sour crude described above contains about 8.3% by weight of pentane-insoluble asphaltenes, whereas the vacuum tower bottoms contains as much as 23.7% by weight of pentane-insoluble asphaltenes. Asphaltenic material consists of hydrocarbonaceous compounds considered to coke precursors having the tendency to become immediately deposited within the reaction zone and onto the catalytic composite in the form of a high molecular weight, gummy residue. Since this constitutes a relatively large loss of charge stock, it is economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions, thereby increasing the liquid yield of desired product, based upon the quantity of oil charged to the process. Furthermore, the presence of excessive quantities of pentane-insoluble asphaltenic material and organo-metallic contaminants adversely affects the activity of a catalytic composite with respect to the destructive removal of nitrogenous and sulfurous compounds.

The object of the present invention is to provide a non-catalytic process for hydrorefining heavier hydrocarbonaceous material, and particularly petroleum crude oil and crude tower bottoms product, whereby the degree of contamination is lessened to the extent that a catalytic process becomes economically feasible. The term "hydrorefining," as employed herein, connotes the catalytic treatment, in an atmosphere of hydrogen, of a hydrocarbon fraction or distillate for the purpose of eliminating and/or reducing the concentration of various contaminating influences previously described. The present invention encompasses a non-catalytic process which affords unusual advantages when utilized as a pre-treatment process in combination with a subsequent catalytic hydrorefining system. The present process yields a liquid hydrocarbon product which is more suitable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing contaminants. The present process is particularly advantageous for ef-

fecting the conversion of the organo-metallic contaminants without significant product yield loss while simultaneously converting pentane-insoluble material into pentane-soluble liquid hydrocarbon products.

In a broad embodiment, therefore, the present invention relates to a process for hydrorefining a hydrocarbon charge stock which comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide at hydrorefining conditions.

Another broad embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock, which process comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide at a temperature above about 200° C. and under a pressure greater than about 500 p.s.i.g.

More specifically, the present invention is directed toward a process for hydrorefining a hydrocarbon charge stock boiling at a temperature above the gasoline boiling range, which process comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide, at a temperature of from about 200° C. to about 500° C. and under a pressure within the range of from about 500 to about 5000 p.s.i.g.

From the foregoing embodiments, it will be noted that the method of the present invention involves a non-catalytic process for hydrorefining hydrocarbons boiling at a temperature above the normal gasoline boiling range. Thus, the process of the present invention is adaptable to the decontamination of various hydrocarbon mixtures, fractions and/or distillates containing substantial concentrations of hydrocarbons boiling at temperatures above about 425° F., which level is considered to be the maximum temperature of a gasoline or naphtha fraction. However, it is not intended to limit the process of the present invention to hydrocarbon charge stocks essentially devoid of hydrocarbons boiling within the gasoline boiling range. As hereinbefore set forth the present invention is particularly adaptable to petroleum crude oils and the heavier hydrocarbon fractions derived therefrom.

The use of the term "hydrorefining conditions" is intended to encompass those conditions of temperature and pressure at which hydrorefining reactions are effected. That is, conditions at which pentane-insoluble asphaltenic material is converted into pentane-soluble liquid hydrocarbon products, nitrogenous compounds are converted into ammonia and hydrocarbons, and sulfurous compounds are converted into sulfur and hydrocarbons, which reactions are accompanied by the destructive removal of organo-metallic compounds. Thus, hydrorefining conditions are intended to include temperatures above about 200° C., with an upper limit of about 500° C., and pressures greater than about 500 p.s.i.g., having an upper limit of about 5000 p.s.i.g. Under the foregoing conditions, the hydrocarbon charge stock is reacted with a gaseous mixture of hydrogen containing hydrogen sulfide. The composition of the gaseous mixture is such that hydrogen is in the greater concentration, hydrogen sulfide being present therein in an amount within the range of about 5.0% to about 25.0%. Although it may be conducted in a batch-wise fashion, the process readily lends itself to continuous processing in an enclosed vessel through which the mixture of hydrocarbon charge stock, hydrogen and hydrogen sulfide is passed. When conducted as a continuous process, it is particularly preferred to introduce the gaseous mixture into the vessel countercurrently to the flow of charge stock therethrough, the latter passing through the vessel in downward flow. The internals of the vessel may be constructed in any suitable manner capable of providing intimate contact between the liquid charge stock and the gaseous mixture passing therethrough. In many instances it may be desirable to provide the reaction zone with a packed bed of inert material such as particles of granite, porcelain, Berl saddles, sand, aluminum and other metal turnings, etc. Although not considered an essential feature of the present invention, the flow rate of the charge stock and gaseous mixture are such that hydrogen is present in an amount within the range of from about 1000 to about 100,000 s.c.f./bbl. of liquid hydrocarbons.

The following examples are given to illustrate the present invention, and to indicate the unexpected effectiveness thereof in hydrorefining a petroleum crude oil to remove a significant proportion of the various contaminating influences hereinbefore described. It is not intended to limit the present invention to the batch-type method employed, the concentrations of material, the particular charge stock and/or the specific conditions of operation utilized in presenting these examples.

Example I

The charge stock employed in this example was the Wyoming sour crude having a gravity of 23.2° API at 60° F., and containing about 2.8% by weight of sulfur, 2700 p.p.m. of total nitrogen, 18 p.p.m. of nickel, 71 p.p.m. of vanadium and 8.3% by weight of pentane-insoluble asphaltenes. 200 grams of the crude oil were placed within an 1800 cc. rocker-type autoclave fabricated from stainless steel. The contents of the vessel were initially pressured to 10 atmospheres with hydrogen sulfide, then to a total pressure of 100 atmospheres with hydrogen, and slowly heated to a temperature of 425° C., resulting in a final pressure of about 200 atmospheres; these conditions were maintained for a period of about 8 hours. The autoclave was allowed to cool, was depressured, and the normally liquid hydrocarbons separated from the metal-containing heavy hydrocarbonaceous sludge. The normally liquid hydrocarbon product indicated a gravity of 32° API at 60° F., and contained 2160 p.p.m. of nitrogen, 1.75% by weight of sulfur, 5.6 p.p.m. of nickel and 13 p.p.m. of vanadium, and only 3.0% by weight of pentane-soluble asphaltenes.

This example indicates the much improved character of the hydrocarbon charge stock in that there has been effected a significant decrease in the concentration of the various contaminating influences. That the crude oil is significantly more suitable for further processing, and particularly catalytic processing, will be immediately recognized by those possessing skill within the art of petroleum refining processing and techniques.

Example II

The charge stock employed in this example was a vacuum tower bottoms product having a gravity, ° API at 60° F., of 7.1, and containing 23.7% by weight of pentane-insoluble asphaltenes, 6060 p.p.m. of nitrogen, 4.05% by weight of sulfur, 46 p.p.m. of nickel and 195 p.p.m. of vanadium. 204 grams of the vacuum tower bottoms were placed within the 1800 cc. rocker-type autoclave, and initially pressured to 10 atmospheres with hydrogen sulfide. The pressure was raised to 100 atmospheres with hydrogen, and the contents of the vessel slowly heated to a temperature of about 425° C., the final pressure being about 200 atmospheres. The contents of the vessel were allowed to cool, were depressured, and separated by centrifugal separation to provide a normally liquid hydrocarbon product. Upon analysis, the normally liquid hydrocarbons, having a gravity of 30.3° API at 60° F., were found to contain 5.5% by weight of pentane-insoluble asphaltenes, 2727 p.p.m. of nitrogen, 1.7% by weight of sulfur, and less than about 10.0 p.p.m. of both nickel and vanadium, calculated as the elemental metals.

Example III

The charge stock employed in this example was an oil from the McMurray Tar Sand formation. The gravity, ° API at 60° F., was 6.7, and the oil contained 16.5% by weight of pentane-insoluble asphaltenes, 4100 p.p.m. of nitrogen, 5.56% by weight of sulfur, 2530 p.p.m. of iron,

100 p.p.m. of nickel and 200 p.p.m. of vanadium and a total of 2.5% ash containing up to 90% silica. 200 grams of the vacuum tower bottoms were placed within the 1800 cc. rocker-type autoclave, and initially pressure to 10 atmospheres with hydrogen sulfide. The pressure was raised to 100 atmospheres with hydrogen, and the contents of the vessel slowly heated to a temperature of about 425° C., the final pressure being about 220 atmospheres. The contents of the vessel were allowed to cool, were depressured, and separated by centrifugal separation to provide a normally liquid hydrocarbon product. Upon analysis, the normally liquid hydrocarbons, having a gravity of 25.4° API at 60° F., were found to contain 2.2% by weight of pentane-insoluble asphaltenes, 1868 p.p.m. of nitrogen, 1.59% by weight of sulfur, 5.0 p.p.m. of nickel and 13.7 p.p.m. of vanadium, calculated as the elemental metals.

The foregoing specification and examples clearly indicate the benefits afforded a process for hydrorefining heavy hydrocarbonaceous material through the use of the non-catalytic process of the present invention. The contaminating influences have been removed to the extent required for further processing without incurring the deleterious effects otherwise resulting.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock containing asphaltenes and organo-metallic contaminants which comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and hydrogen sulfide at a temperature above about 200° C. and under a pressure greater than about 500 p.s.i.g. to remove a substantial portion, at least, of said asphaltenes and organo-metallic contaminants from the charge stock.

2. A process for hydrorefining a hydrocarbon charge stock containing asphaltenes and organo-metallic contaminants which comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to 25.0% of hydrogen sulfide, at a temperature above about 200° C. and under

a pressure greater than about 500 p.s.i.g. to remove a substantial portion, at least, of said asphaltenes and organo-metallic contaminants from the charge stock.

3. A process for hydrorefining a hydrocarbon charge stock containing asphaltenes and organo-metallic contaminants which comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to 25.0% of hydrogen sulfide, at a temperature within the range of from about 200° C. to about 500° C. and under a pressure of from about 500 to about 5000 p.s.i.g. to remove a substantial portion, at least, of said asphaltenes and organo-metallic contaminants from the charge stock.

4. A process for hydrorefining a hydrocarbon charge stock boiling at a temperature above the gasoline boiling range and containing asphaltenes and organo-metallic contaminants, which process comprises reacting said charge stock, in the absence of a catalytic composite, with a gaseous mixture of hydrogen and from about 5.0% to about 25.0% of hydrogen sulfide, at a temperature of from about 200° C. to about 500° C. and under a pressure within the range of about 500 to about 5000 p.s.i.g. to remove a substantial portion, at least, of said asphaltenes and organo-metallic contaminants from the charge stock.

5. The process of claim 4 further characterized in that said charge stock is petroleum crude oil.

6. The process of claim 4 further characterized in that said charge stock is a crude tower bottoms product.

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