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HYDROREFINING CRUDE OILS WITH COLLOIDALLY DISPERSED CATALYST

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This invention relates to the hydrorefining of heavy hydrocarbon charge stocks, particularly petroleum crude oils, to effect the conversion of the pentane-insoluble asphaltene fraction thereof into a pentane-soluble hydrocarbon oil. The process of the present invention is particularly adapted to the removal of nitrogen and sulfur and affords unexpected advantages relating to the removal of metallic contaminants from a petroleum oil containing pentane-insoluble asphaltenes.

Crude petroleum oils, as well as the heavier hydrocarbon fractions derived therefrom, generally contain metallic contaminants which have an adverse effect on catalysts utilized in various processes to which the crude oil, or heavy hydrocarbon fraction thereof, is ultimately subjected. The most common metallic contaminants are nickel and vanadium, although other metals including iron, copper, etc., are often present. These metals may occur in a variety of forms. They may exist as metal oxides or sulfides introduced into the crude oil as metallic scale or similar particles, or they may be present in the form of soluble salts of such metals. Usually, however, they exist in the form of stable organometallic compounds such as metal porphyrins and the various derivatives thereof. Although the metallic contaminants existing as oxide or sulfide scale may be removed, at least in part, by relatively simple filtering techniques, and the water-soluble salts are at least in part removable by washing and subsequent dehydration, a more severe treatment is required to remove the stable organometallic compounds, such as metal porphyrins, before the crude oil, or heavy hydrocarbon fraction thereof, is suitable for further processing. Notwithstanding that the concentration of these organometallic compounds is relatively small, for example, 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 3.0 p.p.m., is subjected to catalytic cracking, the metals become deposited upon the catalyst, altering the composition thereof to the extent that undesirable by-products are formed. That is to say, the composition of the catalyst composite, which is closely controlled with respect to the nature of the charge stock being processed and the quality and quantity of the product desired, is considerably changed as a result of the metal deposition thereon during the course of the cracking process. As a consequence, the liquid product recovery is reduced, and coke and hydrogen are formed in excessive amounts, the former producing relatively rapid catalyst deactivation. The presence of stable organometallic compounds, including metal porphyrins, adversely effects other processes including catalytic reforming, isomerization, hydrodealkylation, etc.

In addition, crude petroleum oils, and the heavier hydrocarbon fractions thereof, generally contain undesirable nitrogenous and sulfurous compounds in large quantities. For example, a Wyoming sour crude having a gravity of 23.2° API at 60° F., contains about 2.8 wt. percent sulfur and about 2700 p.p.m. of total nitrogen. The nitrogenous and sulfurous compounds may be removed from the petroleum oil by various treating processes wherein said compounds are converted to ammonia and hydrogen sulfide which are readily separated from the system in a gaseous phase. However, reduction in the concentration of the stable organometallic compounds, to the extent that the crude oil, or heavy hydrocarbon fraction thereof, becomes suitable for further processing, is not as readily achieved.

The crude oils and other heavy hydrocarbon fractions generally contain considerable quantities of pentane-insoluble materials present in the form of a colloidal suspension or dispersion, difficult of effective contact with conventional hydrorefining catalysts. These pentane-insoluble materials, described as asphaltenes, are a carbonaceous material considered as coke precursers having a tendency to become immediately deposited within the reaction zone and on the catalytic composite as a gummy hydrocarbonaceous residue. It is further considered that said asphaltenes contain the bulk of the difficulty removable metal contaminants as well as a considerable portion of the undesirable nitrogenous and sulfurous compounds.

It is an object of this invention to provide a process for hydrorefining heavier hydrocarbonaceous materials, particularly petroleum crude oils containing pentane-insoluble asphaltenes, said process involving the utilization of a novel catalyst in a unique manner. In other processes, the contaminating metals are removed from the petroleum oil by deposition of said metals on the particular catalyst composite employed. This practice greatly increases the catalytic element in a relatively short time, and precludes the use of the fixed-bed catalyst system commonly employed in present day refining operations. Slurry processes, employing catalytically active metals deposited upon silica and/or alumina, are very erosive and make plant upkeep difficult and expensive. The present invention teaches the utilization of a colloidally dispersed, unsupported catalyst particularly adapted to a slurry type process, and which catalyst will not effect extensive erosion of the reaction system. The present process yields a liquid hydrocarbon product suitable for further processing without experiencing the difficulties otherwise resulting from the presence of the foregoing described contaminants.

In one of its broad aspects the present invention embodies a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and a colloidally dispersed catalyst selected from the group consisting of a metal of Groups VB and VIB, an oxide of said metal, and a sulfide of said metal, reacting said mixture with hydrogen at a temperature in excess of about 225° C. and at a pressure in excess of about 500 p.s.i.g., and recovering a hydrorefined petroleum oil.

Other objects and embodiments of the present invention will become apparent in the following detailed specification thereof.

The asphaltene-containing petroleum hydrocarbon, selected for treatment in accordance with the process of the present invention, is initially admixed with a colloidally dispersed catalyst selected from the group consisting of a metal of Groups VB and VIB (Handbook of Physics and Chemistry, 43rd Ed.), an oxide of said metal, and a sulfide of said metal. The catalyst thus may be colliodally dispersed vanadium, niobium, tantalum, chromium, molybdenum, or tungsten, or a colloidally dispersed oxide of said metals, or a colloidally dispersed sulfide of said metals. It is also contemplated that the aforesaid catalyst may be a colloidally dispersed combination of any two or more of the aforesaid metals, metal oxides, and metal sulfides, for example, colloidally dispersed molybdenum in combination with colloidally dispersed molybdenum oxide and/or colloidally dispersed molybdenum

sulfide, colloidally dispersed molybdenum in combination with colloidally dispersed vanadium, etc.

The catalyst can be prepared as a colloidal dispersion in admixture with the petroleum hydrocarbon charge stock in any conventional or otherwise convenient manner. One preferred method comprises thermally decomposing a suitable organometallic complex in admixture with said petroleum hydrocarbon charge stock. A suitable organometallic complex would of course comprise a metal of Groups VB and VIB heretobefore enumerated, or an oxide or a sulfide thereof. Also, it is desirable to utilize an organometallic complex subject to thermal decomposition at a temperature below the initial cracking temperature of the particular petroleum hydrocarbon being treated, generally less than about 310° C. A suitable organometallic complex would include such as molybdyl acetylacetonate, molydenum ethylanthate, vanadium ethylanthate, molybdenum hexacarbonyl, tungsten hexacarbonyl, etc.

Another preferred method whereby the catalyst can be prepared as a colloidal dispersion in admixture with the petroleum hydrocarbon charge stock, comprises dissolving a soluble compound of vanadium, niobium, tantalum, chromium, molybdenum, or tungsten in a suitable solvent, admixing the resulting solution with at least a portion of the petroleum hydrocarbon at conditions whereby the aforesaid solvent is substantially immediately distilled, evaporated, or otherwise separated from the petroleum hydrocarbon charge stock. For example, phosphomolybdic acid can be prepared in aqueous, alcoholic, or ether solution. Said solution is added to the petroleum hydrocarbon and, in the case of an aqueous solution, the water can be immediately distilled from the petroleum hydrocarbon, for example, as an azeotropic mixture with benzene. Other methods of preparing the catalyst as a colloidal dispersion in the petroleum hydrocarbon charge stock will be apparent to one skilled in the art and it is not intended to limit the process of this invention to any particular method. The colloidally dispersed metal, metal oxide, or metal sulfide comprises from about 0.1 wt. percent to about 10.0 wt. percent of the initial charge stock, calculated as the elemental metal. As will hereinafter appear, the catalyst of this invention can be substantially self sustaining after the initial charge.

On admixture of the petroleum hydrocarbon containing pentane-insoluble asphaltenes, and the colloidally dispersed catalyst, said catalyst contacts the asphaltenes to form a suspension therewith in the petroleum hydrocarbon charge stock. It is considered that the presence of the asphaltenes in contact with the colloidally dispersed catalyst is essential to maintain the catalyst as a colloidal dispersion or suspension in the manner herein contemplated. The colloidally dispersed catalyst has proved to be somewhat less effective in the absence of asphaltenes, and, of course, asphaltenes per se are totally ineffective as a hydrorefining catalyst. The asphaltenes should comprise at least about 0.1 wt. percent of the petroleum hydrocarbon charge stock.

The mixture of the petroleum hydrocarbon and the colloidally dispersed catalyst is reacted with hydrogen at a temperature in excess of about 225° C., preferably from about 225° C. to about 500° C., and at a hydrogen pressure in excess of about 500 p.s.i.g., preferably from about 500 to about 5000 p.s.i.g. This last mentioned treatment with hydrogen results in the conversion of a substantial portion of the pentane-insoluble asphaltenes to pentane-soluble hydrocarbons. In addition there is further formed what is herein referred to as a catalyst sludge which is readily separated from the hydrorefined petroleum oil product. Said catalyst sludge comprises any unconverted asphaltenes, catalyst, and pentane-soluble hydrocarbons as well as the metal portion of the petroleum hydrocarbon charge stock separated therefrom.

One preferred embodiment of the present invention relates to a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and colloidally dispersed molybdenum, and reacting said mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

Another preferred embodiment is in a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and a colloidally dispersed oxide of molybdenum, and reacting said mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

Still another preferred embodiment of this invention is in a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and colloidally dispersed vanadium, and reacting said mixture with hydrogen at a temperature from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

Another preferred embodiment of this invention relates to a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and a colloidally dispersed oxide of vanadium, and reacting said mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

Yet another preferred embodiment of the present invention relates to a process for hydrorefining a petroleum hydrocarbon containing pentane-insoluble asphaltenes which comprises forming a mixture of said petroleum hydrocarbon and a colloidally dispersed sulfide of vanadium, and reacting said mixture with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

The process of this invention may be effected in any suitable manner and may comprise either a batch or a continuous type of operation. For example, when a batch type of of operation is employed, the petroleum hydrocarbon charge stock is admixed with the colloidally dispersed catalyst in a suitable reaction vessel, such as a high pressure autoclave, and sealed therein. The vessel is charged with hydrogen to the desired pressure and the vessel contents are stirred at the desired temperature. After a suitable period the hydrorefined product is recovered from the reaction mixture by any suitable means, for example, by means of centrifuge, the resulting catalyst sludge being recovered for subsequent re-use as catalyst. The ammonia and hydrogen sulfide, resulting from the conversion of nitrogenous and sulfurous compounds, may be removed in a gaseous phase along with any light paraffinic hydrocarbons such as methane, ethane, and the like.

A continuous type of operation is preferred. In this type of operation the starting materials, comprising hydrogen and the colloidally dispersed catalyst in admixture with the petroleum oil containing asphaltenes, are continuously charged to a suitable high-pressure reactor maintained at the proper conditions of temperature and pressure. The reaction mixture is continuously withdrawn from the reactor at a rate which will insure an adequate residence time therein. The hydrorefined product may be recovered from the catalyst sludge by means of a centrifuge, or by means of a settling tank, and the catalyst sludge recycled as a portion of the charge to the aforesaid reactor. The catalyst sludge embodies certain metals, separated from the hydrocarbon charge

by means of the hydrorefining process, which are suitable for use as colloidally dispersed catalysts in accordance with the present invention. Thus, the recycled catalyst sludge is supplemented with catalytic material so that in most cases only small amounts of make-up catalyst will be required, and in some cases the catalyst can be substantially self sustaining.

The following examples are presented as a further illustration of the process of this invention and the advantages to be derived therefrom with respect to the conversion of pentane-insoluble asphaltenes, removal of metallic contaminants, and the conversion of nitrogenous and sulfurous compounds to nitrogen-free and sulfur-free hydrocarbons. It is not intended that said examples be construed as a limitation on the generally broad scope of this invention.

The petroleum hydrocarbon charge stock employed to illustrate the process of this invention and the particular advantages derived therefrom, was a Wyoming sour crude with a gravity of 23.2° API at 60° F. The crude oil contained 8.3 wt. percent pentane-insoluble asphaltenes, and also 2.8 wt. percent sulfur and approximately 2700 p.p.m. of nitrogen as sulfurous and nitrogenous compounds, and 18 p.p.m. of nickel and 71 p.p.m. of vanadium as metal porphyrins, calculated as the elemental metal. As hereinafter illustrated, the process of this invention effects the conversion of a substantial portion of said asphaltenes while substantially simultaneously effecting the conversion of the metallic contaminants and nitrogenous and sulfurous compounds to the extent that the same no longer exert an adverse effect on subsequent processing procedures.

Example 1

The above described sour crude oil was prepared in admixture with a colloidally dispersed molybdenum by heating a mixture of about 200 gms. of said crude oil and about 23 gms. of molybdenum hexacarbonyl at a temperature of about 250° C. for a period of about three hours. Carbon monoxide, resulting from the decomposition of the hexacarbonyl, was separated from the mixture which was thereafter sealed in an 850 cc. autoclave and the autoclave pressured to 100 atms. with hydrogen. The autoclave contents were stirred at a temperature of about 400° F. for a period of about 8 hours. The hydrorefined product, consisting of the normally liquid hydrocarbons, was separated from the catalyst sludge and found to contain about 0.10 wt. percent pentane-insoluble asphaltenes, less than about 0.02 p.p.m. of nickel, less than about 0.02 p.p.m. of vanadium, and about 0.2 weight percent sulfur, and only 7.1 p.p.m. of nitrogen.

Example 2

A mixture of the Wyoming sour crude and colloidally dispersed vanadium and/or sulfide of vanadium, was prepared by adding a solution of about 42 gms. of vanadyl acetylacetonate in 500 gms. of n-amyl alcohol dropwise to about 250 gms. of the sour crude which was stirred at a temperature of about 160–165° C. The alcohol solvent was recovered in an overhead condenser. Thereafter, hydrogen sulfide was bubbled through the stirred mixture at a temperature of about 180° C. 100 gms. of the mixture was then sealed in an 850 cc. autoclave and the autoclave pressured to 100 atms. with hydrogen. The autoclave contents were stirred at a temperature of about 400° C. for a period of about 8 hours. The hydrorefined product, consisting of normally liquid hydrocarbons, was separated from the catalyst sludge and found to contain about 0.308 wt. percent pentane-insoluble asphaltenes, less than about 0.03 p.p.m. of nickel, less than about 0.6 p.p.m. of vanadium, 139 p.p.m. of nitrogen, and 0.19 wt. percent sulfur.

Example 3

A mixture of the Wyoming sour crude and a colloidally dispersed molybdenum was prepared by adding a solution of about 6.34 gms. of phosphomolybdic acid in 100 gms. of isoamyl alcohol dropwise to about 250 gms. of the sour crude, the isoamyl alcohol being immediately distilled therefrom. This mixture was thereafter sealed in an 850 cc. autoclave and said autoclave was pressured to about 200 atms. with hydrogen. The autoclave contents were stirred at a temperature of about 400° C. for a period of about 8 hours. The hydrorefined product, consisting of normally liquid hydrocarbons, was separated from the catalyst sludge and found to contain about 0.318 wt. percent pentane-insoluble asphaltenes, less than about 0.06 p.p.m. of nickel, less than about 0.07 p.p.m. of vanadium, 112 p.p.m. of nitrogen, and 0.09 wt. percent sulfur.

We claim as our invention:

1. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing in said petroleum oil a catalyst selected from the group consisting of a metal of Groups VB and VIB, an oxide of said metal, and a sulfide of said metal, reacting the resultant dispersion with hydrogen at a temperature in excess of about 225° C. and a pressure in excess of about 500 p.s.i.g., and recovering a hydrorefined petroleum oil.

2. The process of claim 1 further characterized in that said colloidally dispersed catalyst is a metal of Groups VB and VIB.

3. The process of claim 1 further characterized in that said colloidally dispersed catalyst is an oxide of a metal of Groups VB and VIB.

4. The process of claim 1 further characterized in that said colloidally dispersed catalyst is a sulfide of a metal of Groups VB and VIB.

5. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing molybdenum in said petroleum oil, reacting the resultant dispersion with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

6. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing an oxide of molybdenum in said petroleum oil, reacting the resultant dispersion with hydrogen at a temperature of about from 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

7. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing vanadium in said petroleum oil, reacting the resultant dispersion with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

8. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing an oxide of vanadium in said petroleum oil reacting the resultant dispersion with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

9. A process for hydrorefining a petroleum oil containing pentane-insoluble asphaltenes which comprises colloidally dispersing a sulfide of vanadium in said petroleum oil, reacting the resultant dispersion with hydrogen at a temperature of from about 225° C. to about 500° C. and at a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g., and recovering a hydrorefined petroleum oil.

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