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PROCESS FOR HYDROREFINING A HYDROCARBON CHARGE STOCK

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ABSTRACT OF THE DISCLOSURE

This invention relates to a process for the hydrorefining of petroleum crude oils, heavy vacuum gas oils, heavy cycle stocks, crude oil residuum, topped crude oil, tar sand oil, shale oil, liquefied coal, etc. More specifically the present invention involves a process for hydrorefining heavy hydrocarbon charge stocks to effect the removal of nitrogen and sulfur therefrom, and is advantageous when employed for the destructive removal of organometallic contaminants and particularly the conversion of pentane-insoluble hydrocarbonaceous material.

Petroleum crude oil, heavier hydrocarbon fractions and/or distillates obtained therefrom and other hydrocarbons derived from various solid mineral deposits contain nitrogenous and sulfurous compounds in large quantities. In addition the above-mentioned hydrocarbons generally contain detrimental quantities of organometallic contaminants which exert deleterious effects upon the catalyst utilized in various processes to which such hydrocarbons may ultimately be subjected. The more common of such metallic contaminants are nickel and vanadium, often existing in concentrations in excess of 50 p.p.m. although other metals including copper, iron, etc., may be present. An intensive treatment is required to effect the destructive removal of organo-metallic compounds, such as metal porphyrins, particularly to the degree necessary to produce a crude oil or heavy hydrocarbon fraction which is suitable for further processing.

The above-mentioned heavy hydrocarbons contain greater quantities of sulfurous and nitrogeneous compounds than are generally found in lighter hydrocarbon fractions such as naphtha, kerosene, etc. For example, a Wyoming sour crude, having a gravity of 23.2° API at 60° F., contains about 2.8% by weight of sulfur, 8.3 percent by weight pentane-insolubles, 3800 p.p.m. of nitrogen and 85 p.p.m. of metallic contaminants. The nitrogenous and sulfurous compounds are converted, upon being subjected to a catalytic hydrorefining process, into hydrocarbons, ammonia and hydrogen sulfide; 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, particularly in regard to further processing of the hydrocarbon oil. When a hydrocarbon charge stock containing metals in excess of about 3 p.p.m., is subjected to a fluid catalytic cracking process for the purpose of producing lower-boiling components, the metals become deposited upon the catalyst employed, steadily increasing in quantity until such time as the composition of the catalyst composite is changed to the extent that undesirable results are obtained.

However, in addition to the foregoing contaminating influences, crude oils and other heavier hydrocarbon fractions contain excessive quantities of pentane-insoluble material. For example, the Wyoming sour crude described above consists of about 8.3% by weight of pentane-insoluble asphaltenes. These are hydrocarbonaceous compounds having the tendency to become immediately deposited within the reaction zone, and onto the catalyst composite, in the form of an exceedingly high molecular

weight, gummy residue. Since this constitutes a large loss of charge stock, it is economically desirable to convert such asphaltenes into useful hydrocarbon oil fractions, thereby increasing the liquid yield based upon the quantity of oil charged to the process. Furthermore, the deposition of this heavy material onto the catalytic composite has the effect of shielding the active centers and surfaces thereof from the material being processed. The conversion of these pentane-insoluble asphaltenes is that function of the catalyst most difficult to achieve, and not withstanding an acceptable degree of elimination of the other contaminants, the liquid product effluent may contain a detrimental amount of this material.

When heavy hydrocarbons are produced and collected, many assorted and extraneous contaminants such as metallic oxide and sulfide scale, sand, crushed rock, grit, etc., are often present. Various techniques have been employed including filtering, centrifuging and settling to reduce the amount of extraneous contaminants but these separation techniques, when applied to heavy hydrocarbons, are slow, tedious and expensive. Since large volumes of heavy hydrocarbons must be processed in relatively short periods of time, the cost of the required equipment is prohibitive. The above-mentioned separation techniques are nicely suited for carefully controlled laboratory experiments or for the production of refined chemicals but not for the initial hydrorefining of heavy hydrocarbons.

The public as well as the hydrocarbon producing companies have recently become acutely aware of a potential energy crises. The increasing cost of producing conventional oil reserves and the depletion of the easily available sources of oil have made the recovery of hydrocarbons from tar sand and shale much more attractive.

Large deposits of bituminous sands are found in various localities throughout the world. The term "bituminous sand" is used herein to include those materials commonly referred to as oil sands, tar sands, and the like. One of the most extensive deposits of bituminous sands occurs for instance in the Athabasca district of the Province of Alberta, Canada, and extends for many thousands of square miles in thickness ranging in up to more than two hundred feet.

Since the crude oil obtained from this type of bituminous sand is relatively viscous material having high tar content and relatively low commercial value in comparison with other crude oils, a successful commercial process must involve relatively little expense in the separation of the crude oil from the bituminous sands. Operating costs of previously conceived methods for separating the oil have been sufficiently high so as to discourage commercial exploitation.

In attempting to separate crude oil from bituminous sands, considerable difficulty has been experienced due to the fact that the solids content of bituminous sands consists of particles of varying size and includes substantial amounts of silt in the form of clay and other very fine solid particles. In attempting to effect a complete separation of the crude oil from the bituminous sands previous processes have attempted to retain the silt with the remainder of the solids content of the sands and as a result have usually discarded considerable quantities of crude oil along with such slit and sand. Entrapped particles ranging in size from 1 to about 100 microns appear to be the most difficult to remove.

Therefore, it is highly desirable that an initial hydrorefining process be capable of processing heavy hydrocarbons which contain finely divided particles of sand, silt, metallic sulfide and oxide scale, etc.

An object of the present invention is to provide a more efficient process for hydrorefining heavy hydrocarbonaceous material, and particularly tar sand oil and

shale oil, utilizing an unsupported catalyst. The term "hydrorefining" as employed herein, connotes the catalytic treatment, in an atmosphere, of hydrogen of a petroleum crude oil, or a hydrocarbon fraction or distillate for the purpose of eliminating and/or reducing the concentration of the various contaminating influences previously described. As hereinabove set forth, metals are generally removed from the charge stock by deposition of the same on the catalyst employed. This increases the amount of catalyst, actively shields the catalytically active surfaces and centers from the material being processed, and thereby virtually precludes the utilization of a fixed-bed catalyst system for processing such contaminated crude oil. Various moving-bed processes, employing catalytically active metals deposited upon a carrier material consisting, for example, of silica and/or alumina, or other refractory inorganic oxide materials, are extremely erosive, causing plant maintenance to become difficult and expensive. The present invention teaches the preparation of a colloidally dispersed, unsupported catalytic material useful in a slurry process, which catalytic material will not effect extensive erosion or corrosion of the reaction 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 process of the present invention is particularly advantageous for effecting the conversion of sulfurous, nitrogenous and the organo-metallic contaminants without significant product yield loss, while simultaneously converting a substantial quantity of pentane-insoluble material into pentane-soluble liquid hydrocarbons.

It is another object of the present invention to provide an improved process for the production of distillable hydrocarbons from heavy hydrocarbonaceous material which contains finely divided particles of sand, silt, metallic sulfide and oxide scale, etc.

It is a further object of the invention to provide for a suitable and economical fuel to supply the heat and power requirements of the production facility or any other facility.

In a broad embodiment, the present invention relates to a process for hydrorefining a hydrocarbon charge stock which comprises: a process for hydrorefining a hydrocarbon charge stock which comprises the steps of: (a) reacting said charge stock with hydrogen at hydrorefining conditions utilizing a catalyst comprising a heteropoly acid containing a Group V–B metal component or a Group VI–B metal component having an atomic number greater than 24; (b) separating the hydrorefining reaction effluent to recover a distillable hydrocarbon fraction and a non-distillable fraction which contains said metal component; (c) oxidizing said non-distillable fraction to provide energy and to produce an oxide of said metal component; (d) contacting the resulting metal oxide with a liquid solution of an acid selected from phosphoric acid and silicic acid to produce a liquid solution of a heteropoly acid containing said metal component; and, (e) passing said heteropoly acid to reaction Step (a).

A more limited embodiment of the present invention involves a process for hydrorefining a hydrocarbon charge stock which comprises combining said charge stock with phosphomolybdic acid, heating the resulting mixture at a temperature less than about 310° C. and for a time sufficient to produce a colloidal dispersion of said phosphomolybdic acid, reacting said colloidal dispersion with hydrogen at a temperature within the range of from about 225° C. to about 500° C. and at a pressure of about 500 to about 5000 p.s.i.g., separating the hydrorefining reaction effluent to recover a distillable hydrocarbon fraction and a non-distillable fraction which contains said phosphomolybdic acid, oxidizing said non-distillable fraction to provide energy for the production facility or any other facility and to produce molybdenum oxide, treating the resulting molybdenum oxide with phosphoric acid to form said phosphomolybdic acid and recycling the newly formed phosphomolybdic acid.

From the foregoing embodiments, it is noted that the method of the present invention involves the preparation of a catalyst utilizing metals selected from Group V–B and Group VI–B of the Periodic Table. Reference is herein made to the Periodic Chart of the Elements, pages 448 and 449, 43rd edition of Handbook of Chemistry and Physics. It is further noted that the metals for Group VI–B namely molybdenum and/or tungsten, have an atomic number greater than 24. It has been found that heteropoly acids of chromium, in addition to other chromium complexes, upon decomposition within the hydrocarbon charge stock, do not yield acceptable economical results and particularly with respect to the conversion of the pentane-insoluble fraction and the organo-metallic compounds such as the nickel and/or vanadium porphyrins. Furthermore, the decomposition of such chromium complexes is effected above about 310° C., resulting in premature thermal cracking of the crude oil. Briefly, the catalyst is preferably prepared by dissolving heteropoly acids of molybdenum, tungsten or vanadium, such as phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, silicotungstic acid, phosphovanadic acid and silicovanadic acid in an appropriate solvent such as alcohols containing up to and including about ten carbon atoms per molecule. Although alcohols are the preferred solvents, additional solvents may be used such as water, acetone, ethyl acetate, etc. The solution is added to the petroleum crude oil and the mixture distilled with stirring, at a temperature less than about 310° C., to remove the solvent and form a colloidally dispersed catalyst suspended within the petroleum crude oil. The quantity of the heteropoly acid employed is such that the colloidal suspension, or dispersion, which results upon removal of the solvent, comprises from about 1.0% to about 10.0% by weight, calculated, however, as the elemental metal. The heteropoly acids may be used in combination of two or more of the acids described above.

When the heteropoly acid is initially dissolved in an alcohol containing up to and including about ten carbon atoms per molecule, the contaminating influences, with the exception of asphaltenes, contained within the petroleum crude oil are removed to the extent that the future processing of such crude oil no longer incurs the detrimental effects otherwise resulting from the presence of these contaminating influences. As previously set forth, the conversion of asphaltenes is most difficult to achieve; further, as the concentrations of the other contaminants increases, the degree of conversion of the asphaltenes is lessened. Typical of the alcohols suitable for use in preparing the solution of the desired heteropoly metallic acid include isopropyl alcohol, isopentyl alcohol, methyl alcohol, amyl alcohol, mixtures thereof, etc. The mixture of the alcohol solution of the heteropoly acid and the petroleum crude oil is heated at a temperature below about 310° C. for the purpose of distilling the alcohol, leaving the heteropoly acid as a colloidal dispersion within the crude oil. Temperatures above about 310° C. tend to result in premature cracking reactions whereby the effectiveness to convert pentane-insoluble asphaltenes becomes adversely affected.

The 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 hydrgen pressure within the range of about 500 to about 5000 p.s.i.g. The process may be conducted in a batch-type procedure or in an enclosed vessel through which the colloidal suspension is passed; when effected in a continuous manner, the process may be conducted in either upward flow or downward flow.

As hereinabove set forth, the hydrorefining catalyst utilized in the process of the present invention, exists as a colloidal dispersion within the hydrocarbonaceous charge stock being subjected to reaction with hydrogen. Thus the

catalyst is a colloidally dispersed heteropoly acid selected from the group which has been previously described.

The following example is 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, the conversion of nitrogenous and sulfurous compounds to nitrogen-free and sulfur-free hydrocarbons and the satisfactory disposal of indigenous particulate matter. It is not intended that said example 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, is a Wyoming sour crude with a gravity of 23.2 API at 60° F., a 10% boiling point of 641° F. and a 50% boiling point of 934° F. The crude oil contains 8.3 weight percent pentane-insoluble asphaltenes, 2.8 weight percent sulfur as sulfurous compounds, 27 p.p.m. of nickel, 71 p.p.m. of vanadium and 2.5 weight percent of indigenous particulate matter. Both the nickel and vanadium are present 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 and the disposal of said indigenous particulate matter 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

A colloidal dispersion of phosphomolybdic acid is prepared by initially dissolving 30 grams of the phosphomolybdic acid in 400 grams of isopropyl alcohol. One thousand grams of the crude, as hereinbefore described, is placed in a two-liter reaction flask containing a stirrer, and the isopropyl alcohol solution is added thereto in drop-wise fashion. The temperature of the contents of the two-liter flask is maintained at 130° C. such that the alcohol is distilled while the solution is added to the crude.

An 1800 milliliter, rocker-type autoclave is selected and 200 grams of the colloidal dispersion is placed therein. The autoclave is pressured to 1500 p.s.i.g. with hydrogen and is heated to a temperature of 390° C. After five hours at these conditions, the contents of the autoclave is cooled to room temperature, removed therefrom and subjected to fractionation thereby recovering a distillable fraction and a non-distillable fraction. Said distillable fraction is free from metals, asphaltenes and particulate matter and contains substantially reduced quantities of sulfur and nitrogen which fraction is then suitable for further processing in conventional refining processes. Said non-distillable fraction which contains said phosphomolybdic acid and reduced quantities of asphaltenes and organo-metallic compounds is oxidized to supply energy and to produce molybdenum oxide. The molybendum oxide is recovered and treated with phosphoric acid solution to form phosphomolybdic acid which is then used again in the early stages of the process.

I claim as my invention:

1. A process for hydrorefining a hydrocarbon charge stock which comprises the steps of:
   (a) reacting said charge stock with hydrogen at hydrorefining conditions utilizing a catalyst comprising a heteropoly acid containing a Group V–B metal component or a Group VI–B metal component having an atomic number greater than 24;
   (b) separating the hydrorefining reaction effluent to recover a distillable hydrocarbon fraction and a non-distillable fraction which contains said metal component;
   (c) oxidizing said non-distillable fraction to provide energy and to produce an oxide of said metal components;
   (d) contacting the resulting metal oxide with a liquid solution of an acid selected from phosphoric acid and silicic acid to produce a liquid solution of a heteropoly acid containing said metal component; and,
   (e) passing said heteropoly acid to reaction Step (a).

2. The process of claim 1 further characterized in that said heteropoly acid is commingled with said hydrocarbon charge stock and the resulting mixture is heated at a temperature less than 310° F. for a time sufficient to form a colloidal dispersion of said heteropoly acid prior to reacting said charge stock with said hydrogen.

3. The process of claim 1 further characterized in that said metallic component is selected from molybdenum, tungsten and vanadium.

4. The process of claim 1 further characterized in that said heteropoly acids are selected from phosphomolybdic acid, silicomolybdic acid, phosphotungstic acid, silicotungstic acid, phosphovanadic acid and silcovanadic acid.

5. The process of claim 1 further characterized in that said hydrocarbon charge stock is reacting with hydrogen at a temperature within the range of about 225° C. to about 500° C. and under a pressure of from about 500 p.s.i.g. to about 5000 p.s.i.g.

6. The process of claim 1 further characterized in that said hydrocarbon charge stock is selected from tar sand oil and shale oil.

References Cited

UNITED STATES PATENTS

3,432,442	3/1969	Gleim	208—253
3,232,887	2/1966	Pessimisis	252—435
3,617,528	11/1971	Hilfman	208—216
3,755,150	8/1973	Mickelson	208—216

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