

- [54] **PROCESS FOR THE CONVERSION OF
HYDROCARBONACEOUS BLACK OIL**
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- [58] Field of Search 208/48

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[57] **ABSTRACT**
A process for the conversion of a hydrocarbonaceous black oil, wherein a heated portion of the charge stock is recycled to the inlet of the charge heater, is disclosed.

4 Claims, No Drawings

PROCESS FOR THE CONVERSION OF HYDROCARBONACEOUS BLACK OIL

DISCLOSURE

The invention described herein is adaptable to a process for the conversion of petroleum crude oil into boiling hydrocarbon products. More specifically, the present invention is directed toward a process for converting atmospheric tower bottoms products, vacuum tower bottoms products, crude oil residuum, topped crude oils, crude oils extracted from tar sands, etc., which are sometimes referred to as "black oils," and which contain a significant quantity of asphaltic material.

Petroleum crude oils, particularly the heavy oils extracted from tar sands, topped or reduced crudes, and vacuum residuum, etc., contain high molecular weight sulfurous compounds in exceedingly large quantities. In addition, such crude, or black oils contain excessive quantities of nitrogenous compounds, high molecular weight organo-metallic complexes principally comprising nickel and vanadium, and asphaltic material. Currently, an abundant supply of such hydrocarbonaceous material exists, most of which has a gravity less than 20.0° API at 60°F., and a significant proportion of which has a gravity less than 10.0. This material is generally further characterized by a boiling range indicating that 10 percent or more, by volume boils above a temperature of about 1,050°F. The conversion of at least a portion of the material into distillable hydrocarbons—i.e., those boiling below about 1,050°F.—has hitherto been considered nonfeasible from an economic standpoint. Yet, the abundant supply thereof virtually demands such conversion, especially for the purpose of satisfying the ever-increasing need for greater volumes of the lower boiling distillables.

The present invention is particularly adaptable to the catalytic conversion of black oils into distillable hydrocarbons. Specific examples of the black oils to which the present scheme in uniquely applicable, include a vacuum tower bottoms product having a gravity of 7.1° API at 60°F. containing 4.05 percent by weight of sulfur and 23.7 percent by weight of asphaltics; a "topped" Middle East Kuwait crude oil, having a gravity of 11.0° API at 60°F., containing 10.1 percent by weight of asphaltenes and 5.20 percent by weight of sulfur; and a vacuum residuum having a gravity of 8.8° API at 60°F., containing 3.0 percent by weight of sulfur and 3,400 ppm. of nitrogen and having a 20.0 percent volumetric distillation point of 1,055°F. The principal difficulties, attendant the conversion of black oils, stem from the presence of the asphaltic material. This asphaltic material consists primarily of high molecular weight, non-distillable coke precursors, insoluble in light hydrocarbons such as pentane or heptane, and which are often found to be complexed with nitrogen, metals and especially sulfur. Generally, the asphaltic material is found to be colloiddally dispersed within the crude oil, and, when subjected to elevated temperatures, has the tendency to flocculate and polymerize whereby the conversion thereof to more valuable oil-soluble products becomes extremely difficult.

Not only does the flocculation and polymerization of the asphaltic material decrease the yield of valuable hydrocarbon products but when these coke precursors form coke during heating and prior to entering the catalytic reaction zone, the internal surfaces of the heaters

which contact the oil become coated with coke. Such coking or fouling of the heater's heat transfer surface causes less favorable heat transfer rates and in order to compensate for this lower heat transfer rate, the heater temperatures must be increased which only further aggravates the coking problem.

I have discovered that this problem can be alleviated by providing a recycle of previously heated black oil to the inlet of the heater to ensure adequate turbulence and ample mixing of the black oil being heated. This recycle will lessen the temperature gradient across the heat transfer area of the heater, and provide a more uniform oil temperature in the entire cross-section of the flowing black oil. Furthermore, this recycle will promote better heat transfer, thereby lowering the temperature of the heat transfer surface which, in turn, lessens the propensity of the black oil along with the asphaltenes contained therein to form coke and heavy polymers.

A principal object of the present invention is to retard and inhibit the formation of undesirable coke and polymers on the heat transfer surfaces of the primary heater in a process for the conversion of hydrocarbonaceous black oil.

Another object is to promote better initial heat transfer rates in such a heater which will permit a lower temperature for the heat transfer surfaces which, in turn, will minimize coke-producing high temperatures.

Yet another object is to extend the length of time between maintenance of the heat exchange surfaces for the removal of accumulated coke and polymers.

In one embodiment, therefore, the present invention relates to a process for the conversion of a hydrocarbonaceous black oil, which process comprises the steps of: (a) admixing said black oil with hydrogen and heating the resulting mixture in a heater to a temperature above about 600°F.; (b) recycling at least a portion of the heated mixture to the inlet of said heater; (c) contacting at least a portion of the heated mixture with a catalytic composite in a conversion zone maintained at hydrocarbon conversion conditions; and, (d) recovering a converted hydrocarbon product.

A black oil is intended to connote a hydrocarbonaceous mixture of which at least about 10 percent boils above a temperature of about 1,050°F., and which has a gravity, °API at 60°F., of about 20 or less. As will be readily noted by those skilled in the art of petroleum refining techniques, the conversion conditions herein-after enumerated are well known and commercially employed. The conversion conditions include temperatures above about 600°F., with an upper limit of about 800°F., measured at the inlet to the catalytic reaction zone. Since the bulk of the reactions are exothermic, the reaction zone effluent will be at a higher temperature. In order to preserve catalyst stability, it is preferred to control the inlet temperature such that the effluent temperature does not exceed about 900°F. Hydrogen is admixed with the black oil charge stock by compressive means in an amount generally less than about 20,000 SCFB, at the selected pressure and preferably in an amount of from about 1,000 to about 10,000 SCFB. The operating pressure will be greater than 500 psig. and generally in the range of about 1,500 psig. to about 5,000 psig. It is not essential to my invention to employ a particular type of reaction zone. Up-flow, downflow or radial flow reaction zones may suitably be employed within the reaction zone in a fixed bed, moving bed, ebullating bed or a slurry system.

Likewise, the type, form or composition of the catalyst is not essential to my invention and any suitable black oil hydrocarbon conversion catalyst may be selected. The catalyst disposed within a fixed bed or moving bed reaction zone can be characterized as comprising a metallic component having hydrogenation activity, which component is composited with a refractory inorganic oxide carrier material of either synthetic or natural origin. The precise composition and method of manufacturing the carrier material is not considered essential to the present process, although a siliceous carrier, such as 88 percent alumina and 12 percent silica, or 63 percent alumina and 37 percent silica, or an all alumina carrier, are generally preferred. Suitable metallic components having hydrogenation activity are those selected from the group consisting of the metals of Group VI-B and VIII of the Periodic Table, as indicated in the Periodic Chart of the Elements, Fisher Scientific Company (1953). Thus the catalytic composite may comprise one or more metallic components from the group of molybdenum, tungsten, chromium, iron, cobalt, nickel, platinum, palladium, iridium, osmium, rhodium, ruthenium and mixtures thereof. The concentration of the catalytically active metallic component, or components, is primarily dependent upon the particular metal as well as the characteristics of the charge stock. For example, the metallic components of Group VI-B are preferably present in an amount within the range of about 1.0 percent to about 20.0 percent by weight, the iron-group metals in an amount within the range of about 0.2 percent to about 10.0 percent by weight, whereas the platinum-group metals are preferably present in an amount within the range of about 0.1 percent to about 5.0 percent by weight, all of which are calculated as if the components existed within the finished catalytic composite as the elemental metal.

The refractory inorganic oxide carrier material may comprise alumina, silica, zirconia, magnesia, titania, boria, strontia, hafnia, and mixtures of the two or more including silica-alumina, alumina-silica-boron phosphate, silica-zirconia, silica-magnesia, silica-titania, alumina zirconia, alumina-magnesia, alumina-titania, magnesia-zirconia, titania-zirconia, magnesia-titania, silica-alumina-zirconia, silica-alumina-magnesia, silica-alumina-titania, silica-magnesia-zirconia, silica-alumina-boria, etc. It is preferred to utilize a carrier material containing at least a portion of silica, and preferably a composite of alumina and silica with alumina being in the greater proportion. The catalysts utilized in a slurry system preferably contain at least one metal selected from the metals of Group VI-B, V-B and VIII. Slurry system catalysts usually are colloiddally dispersed in the hydrocarbonaceous charge stock and may be supported or unsupported.

The following examples are given to illustrate the process of the present invention and the effectiveness thereof in inhibiting and retarding the formation of undesirable coke and polymers of the heat transfer surfaces of the primary heater in a process for the conversion of hydrocarbonaceous black oil. In presenting these examples, it is not intended that the invention be limited to the specific illustrations, nor is it intended that the process be limited to particular operating conditions, catalytic composite, processing techniques, charge stocks, etc. It is understood, therefore, that the present invention is merely illustrated by the specifics hereinafter set forth.

EXAMPLE I

A topped Middle-East Kuwait crude containing 5.2 percent by weight sulfur and 10 percent by weight oil-insoluble asphaltenic material and having a gravity of 11° API at 60 °F. is selected for desulfurization in a catalytic reaction zone containing a desulfurization catalyst which contains 2 percent by weight nickel and 16 percent by weight molybdenum composited with a carrier material of 88 percent alumina and 12 percent silica. The desulfurization catalyst is loaded into fixed beds in a downflow catalytic reaction zone. The topped crude is admixed with sufficient hydrogen to achieve a hydrogen circulation rate of 6,000 SCFB. The admixture of topped crude and hydrogen is passed over the heat exchange surfaces of a primary heater and then into the catalytic reaction zone. A desulfurized hydrocarbonaceous black oil is recovered from the reaction zone effluent. A target 1 percent residual sulfur (the equivalent of 80 percent desulfurization) in the hydrocarbon product is maintained by periodically adjusting the outlet temperature of the primary heater. With a liquid hourly space velocity of 0.9 hr.⁻¹, the initial catalyst inlet temperature required to reach the 1 percent target is 725°F. The hereinabove processing scheme is continuously operated for 90 days and then is shut down. Inspection of the heat exchange surfaces shows that the carbon and polymer buildup on these surfaces amounts to 40 grams per square meter.

EXAMPLE II

The processing scheme in Example I is modified to permit a slipstream of heated black oil to be taken from the effluent of the primary heater and recycled to the inlet of said primary heater. The heat exchange surfaces are thoroughly cleaned to remove the accumulated carbon and polymers. A fresh batch of catalyst which is identical to that used in Example I is loaded into the catalytic reaction zone and fresh topped crude is desulfurized at the same operating conditions utilized in Example I except that 10 percent of the liquid effluent from the primary heater is recycled to the inlet of the primary heater. The processing scheme is also continuously operated for 90 days and is then shut down. Inspection of the heat exchange surfaces shows that the carbon and polymer buildup on these surfaces amounts to 30 grams per square meter which is considerably less than that produced in Example I.

The foregoing specification and illustrative examples clearly indicate the means by which the present invention is effected, and the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the conversion of a hydrocarbonaceous black oil, which process comprises the steps of:
 - a. admixing said black oil with hydrogen and heating the resulting mixture in a heater to a temperature above about 600°F.;
 - b. recycling at least a portion of the heated mixture to the inlet of said heater;
 - c. contacting at least a portion of the heated mixture with a catalytic composite in a conversion zone maintained at hydrocarbon conversion conditions; and,
 - d. recovering a converted hydrocarbon product.
2. The process of claim 1 further characterized in that said heater is a direct fired heater.

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3. The process of claim 1 further characterized in that said black oil is derived from tar sand, shale or any other inorganic oil-bearing substance.

4. The process of claim 1 further characterized in that said hydrocarbon conversion conditions comprise

a pressure of from about 500 psig. to about 5,000 psig., a temperature of from about 600°F. to about 900°F., a hydrogen gas circulation rate from about 1,000 SCFB to about 20,000 SCFB.

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