

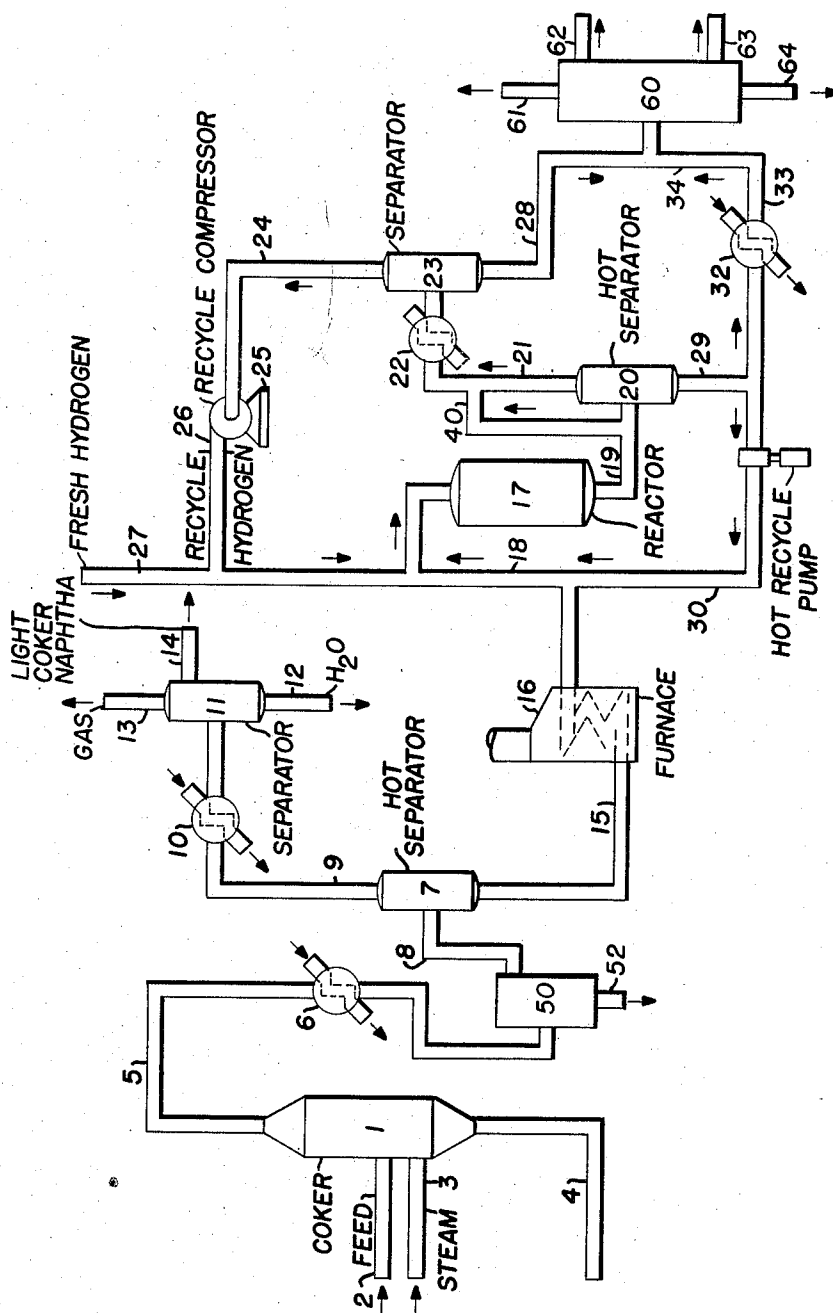
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PROCESS FOR HYDRODESULFURIZATION OF COKER PRODUCTS

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**PROCESS FOR HYDRODESULFURIZATION OF
COKER PRODUCTS**

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1 Claim. (Cl. 208—212)

The present invention is broadly concerned with an improved process for the manufacture of high quality petroleum products. The invention is more specifically concerned with the treatment of particular streams derived from heavy residual coking operations. In accordance with the present invention, high quality petroleum products secured from heavy residual coking operations are desulfurized in a hydrofining zone wherein the constituents boiling in the naphtha boiling range and the constituents boiling in the gas oil boiling range are processed together in a mixed liquid-gas phase operation. In the preferred adaption of this operation the hydrofined products are withdrawn from the hydrodesulfurization zone and passed to a hot separator wherein lower boiling constituents such as those boiling in the naphtha boiling range are removed in the vapor phase, and wherein the higher boiling constituents such as those boiling above the motor fuel boiling range are removed as a liquid phase, and wherein at least a portion of this liquid phase is recycled to the hydrodesulfurization zone in a manner to secure the desired time of contact.

In order to secure a satisfactory hydrodesulfurization operation, normally the operating conditions employed for the hydrodesulfurization of constituents boiling in the motor fuel boiling range are appreciably different from the operating conditions employed in the hydrodesulfurization of constituents boiling above the motor fuel boiling range as, for example, boiling in the heating oil boiling range and gas oil boiling ranges. Typical temperatures employed for hydrodesulfurization of a heavy naphtha fraction boiling in the motor fuel boiling range are in the range from about 650° F. to 700° F. Pressures are in the range from about 200 lbs. per square inch to 400 lbs. per square inch. The feed rates are generally in the range from about 2 to 8 volumes of oil per volume of catalyst per hour. This heavy naphtha fraction boils in the range from about 250° F. to 430° F. On the other hand, when hydrodesulfurizing a gas oil boiling in the range from about 430° F. to 1050° F., the temperatures are usually in the range from about 675° F. to 800° F., preferably in the range from about 700° F. to 750° F. Pressures are about 200 lbs. per square inch to 1000 lbs. per square inch, preferably in the range from 200 lbs. per square inch to 400 lbs. per square inch. The feed rates are about 0.5 to 2.0 v./v./hr.

The catalyst for hydrodesulfurization operation may be any satisfactory hydrofining catalyst, as for example a mixture of cobalt oxide and molybdenum oxide. A preferred catalyst comprises 12% cobalt molybdate on alumina. Other satisfactory catalyst are sulfides of nickel and tungsten.

Also with respect to naphtha and gas oil fractions derived from the coking of heavy residual fractions as for example those residuals having gravities below about 15° A.P.I. a particular problem arises. While the processing of the coker fractions boiling above about 400° F. in a hydrodesulfurization can be satisfactorily controlled, the coker naphtha on the other hand due to the presence

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of a large quantity of mono-olefins and diolefins is extremely exothermic in the hydrodesulfurization operation. The heat liberated gives a marked temperature rise during the reaction with adverse results. While this temperature rise can be controlled it is difficult and expensive.

The heavy residual coking operation can be carried out by a number of processes as, for example, by a "fluid coking" or "fixed bed" operation. The fluid coking process employs no catalyst and depends upon a circulating stream of finely divided coke particles to furnish heat and a large amount of surface to accomplish the coking reaction. The operation requires the use of a burner vessel and a reaction vessel with the necessary standpipes and transfer lines to accomplish the circulation of fluidized coke between the two vessels. The fluidized coke is continually formed in the process and it is partly burned to supply heat. The bulk of the coke is withdrawn from the system as a by-product.

The feed to the coking operation is usually a bottoms stream from a vacuum distillation operation and may comprise from about 4% to 50% of the crude depending upon the source and character of the crude. The temperatures employed in the coking operation may vary appreciably but are generally in the range from about 850° F. to 1050° F. in the coking zone. The pressures in the coking zone are generally in the range from about 5 lbs. per square inch to 50 lbs. per square inch. The temperatures in the burning zone are in the range from about 1100° F. to 1200° F. while the pressures are in the range from about 15 lbs. per square inch to 50 lbs. per square inch.

The products secured from a fluid coking operation processing residual stock are high in sulfur and are relatively unstable. However, hydrogenation provides a satisfactory means of converting the raw unstable coker products into finished low sulfur products with good stability. Hydrodesulfurization of coker gas oil (boiling in the range from about 430° F. to 1050° F.) can be accomplished without difficulty. However, hydrodesulfurization of coker naphtha due to the presence of unsaturated constituents is extremely exothermic. The heat liberated tends to give a marked temperature rise during the reaction.

In accordance with the present invention a blend of coker naphtha and coker gas oil are hydrodesulfurized. When operating in this manner the temperature rise in the reactor is minimized by the high heat capacity of the liquid phase gas oil and by the tendency of this gas oil to vaporize further as the temperature tends to rise. An operation of this character is entirely satisfactory when loss of octane number of the naphtha is not of importance, as for example wherein the naphtha is used as feed to a hydroforming operation or as diesel fuel. However, hydrodesulfurization of the blend does have the typical disadvantage of treating a wide boiling range feed stock. The conditions required for the hydrodesulfurization of the gas oil are overly severe for the hydrodesulfurization of the naphtha to be blended in motor gasoline.

The process of the present invention may be fully understood by reference to the attached drawing illustrating one embodiment of the same. Referring specifically to the drawing a heavy residual fuel as, for example, one boiling above about 1000° F. and having a gravity in the range from about 16° A.P.I. to 20° A.P.I. is introduced into the coker reaction zone 1 by means of feed line 2. Steam is introduced into zone 1 by means of line 3 which maintains the small particles of coke in the fluidized state. Coke particles are withdrawn from the bottom of coking zone 1 by means of line 4 and

passed to a burner zone (not shown). In the burner zone portions of the coke particles are burned and a portion of said particles are returned by conventional means to coker zone 1.

The coker zone 1 is operated at a temperature in the range from about 850° F. to 1100° F. and at a pressure in the range from about 15 to 50 lbs. per square inch.

Vaporized products are removed overhead from coker zone 1 by means of line 5 at a temperature in the range from about 850° F. to 1100° F. The products are passed through a cooling zone 6 operated to cool the products. The cooled products are introduced into a separation zone 7 by means of line 8. The separator is operated to remove overhead by means of line 9 hydrocarbon constituents boiling below about 250–275° F. These overhead constituents are passed through a cooling zone 10 and then introduced into a separator 11. In separation zone 11 water is removed by means of line 12, uncondensed gases by means of line 13 and a light coker naphtha by means of line 14.

A liquid stream comprising heavy naphtha constituents and constituents boiling above the motor fuel boiling range is removed from separator 7 by means of line 15, passed through furnace or equivalent means 16 and introduced into a hydrodesulfurization reactor 17 by means of line 18. The temperature of the stream removed from furnace 16 is in the range from about 500° F. to 700° F.

Hydrodesulfurization zone 17 is operated at a temperature in the range from about 500° F. to 800° F. and at a pressure in the range from about 100 to 1000 p.s.i.g. The feed rate is in the range from about 0.5 to 4.0 volumes of oil per volume of catalyst per hour. The catalyst comprises cobalt molybdate supported on alumina.

In accordance with the broad concept of the present invention the hydrodesulfurized blend of naphtha and gas oil constituents is removed from zone 17 by means of line 19 and by-passes the hot separator by means of line 40. This blend is cooled in zone 22 and passed to a separator zone 23 wherein the hydrogen is separated from hydrodesulfurized product.

However, the preferred adaptation is to remove the treated product from zone 17 by means of line 19 and introduce it into a hot separator 20. This zone is operated under temperature and pressure conditions to remove overhead by means of line 21 hydrogen and hydrocarbon constituents boiling below about 450–700° F. These hydrocarbon constituents are passed through a cooling zone 22 and introduced into a separator 23. Uncondensed hydrogen is removed overhead from separator 23 by means of line 24 compressed in zone 25 and recycled to hydrodesulfurization zone 17 by means of line 26.

Higher boiling hydrocarbon constituents such as those boiling in the gas oil boiling range are removed from hot separator 20 by means of line 29. These constituents boil above about 430° F., preferably above about 700 to 730° F.

In accordance with the preferred mode of operation at least a portion of these constituents is recycled to hydrodesulfurization zone 17 by means of line 30. The remainder of these constituents is passed through cooling zone 32 and then introduced into distillation zone 60 by means of line 34.

The quantity of gas oil constituents recycled is preferably of such magnitude that the quantity of hydrocarbon constituents boiling below about 430° F. and passed to hydrodesulfurization zone 17 is not greater than 25 volume percent based upon the total feed.

Under certain conditions the coker products withdrawn by means of line 5 is passed to a distillation zone 50 wherein a selected stream is removed by means of line 8 and handled as hereinbefore described. This stream will comprise hydrocarbon constituents boiling in the motor fuel boiling range and gas oil constituents boiling

up to about 1050° F. The heavier constituents are removed by means of line 52 and may be recycled to zone 1.

In accordance with the present invention the products segregated by means of line 28 and 33 are passed to a distillation zone 60 wherein a segregation of the desired products as, for example, motor fuels or heating oils are made. These streams may be withdrawn by means of lines 61, 62, 63, and 64.

The process of the present invention may be more fully understood by the following examples illustrating the same.

Example I

An operation at 700° F., 400 p.s.i.g., 3500 cubic feet per barrel of hydrogen, and a space velocity of 1 v./v./hr. was used to treat a blend of 17% coker naphtha and 83% coker gas oil. Sulfur in the naphtha was reduced from 1% to 0.01–0.02% and in the gas oil from 4% to 0.3–0.5%. The extent of desulfurization of the gas oil was in the range desired but the reduction of sulfur in the naphtha to such a low level was accomplished with an excessive amount of saturation of olefins and an excessive loss in octane number. On hydrogenation the bromine number was reduced from 130 to 8 and the clear research octane number from 75 to 55.

Example II

A naphtha fraction boiling in the range from 100–430° F. was cut from the products obtained from fluid coking of a West Texas residuum. The naphtha contained 0.9% sulfur and had a bromine number of 110. An attempt was made to hydrodesulfurize this naphtha in an isothermal pilot unit containing 500 cc. of a cobalt molybdate catalyst supported on alumina. Operating pressure was 400 p.s.i.g. and hydrogen rate was 4000 standard cubic feet per barrel. Feed rate was varied from 1 to 4 v./v./hr. Excessive temperature gradients were obtained in all attempts to operate with this feed stock in the range of conditions indicated. When the inlet end of the catalyst was held at 500° F. and all heat taken off the bottom and middle of the catalyst bed, the temperature at the outlet end of the catalyst could not be held below 800–900° F.

Example III

The naphtha used in Example II was blended with gas oil having a boiling range of 430–1050° F. and obtained from the same fluid coking operation as the naphtha. The volume ratio of naphtha to gas oil was 24/76. This blend was hydrodesulfurized in the same reactor used in Example I. Operating conditions were 1 v./v./hr. feed rate, 400 p.s.i.g. pressure, 1000 standard cubic feet per barrel fresh hydrogen rate, 2500 standard cubic feet per barrel recycle hydrogen rate and 700° F. temperature. The operation proceeded with no temperature gradient across the catalyst. The hydrodesulfurized products were separated into an initial to 430° F. and a 430° F.+ bottoms fraction. The naphtha product contained .011% sulfur compared to 0.89% on the feed and the gas oil product contained .46% sulfur compared to 4.0% on the feed.

Example IV

A blend of 18% naphtha boiling in the range from 250–430° F. and 82% gas oil boiling in the range from 430–1050° F. was hydrodesulfurized in the same isothermal reactor used in Examples I and II. Both naphtha and gas oil fractions were obtained from a fluid coking operation on a West Texas residuum. The catalyst was cobalt molybdate on alumina. The operating conditions were 700° F. temperature, 400 p.s.i.g., pressure, 1 v./v./hr. feed rate, 800 standard cubic feet per barrel fresh hydrogen rate and 2000 standard cubic feet per barrel recycle hydrogen rate. The operation was conducted with no appreciable temperature gradient across the catalyst. The hydrodesulfurized product was sepa-

rated into naphtha and gas oil fractions. The naphtha contained 0.008% sulfur compared to 1.1% on the feed and the gas oil contained 0.31% sulfur compared to 4.0% on the feed.

Example V

The same blend used as feed stock in Example IV was hydrodesulfurized in an adiabatic reactor. The catalyst was cobalt molybdate on alumina. Operating conditions were 400 p.s.i.g. pressure, 1 v./v./hr. feed rate, 910 standard cubic feet per barrel fresh hydrogen rate and 2180 standard cubic feet per barrel recycle hydrogen rate. Catalyst temperatures were 574 at the inlet, 731 at the middle and 760° F. at the outlet giving a temperature gradient of 186° F. The hydrodesulfurized products were cut to give a 430° F. end point naphtha and a 430° F.+bottoms gas oil. The naphtha contained 0.019% sulfur and the gas oil contained 0.47% sulfur.

The present process is broadly concerned with an operation wherein hydrocarbon constituents boiling in the motor fuel boiling range (100° F. to 430° F.) are hydrodesulfurized with gas oil constituents boiling above the motor fuel boiling range (430° F. to 1050° F.). A preferred adaptation of the operation is to utilize a hot recycle step. In this operation it is preferred to pass a heavy naphtha fraction and gas oil constituents boiling up to about 1050° F. into a hot separator wherein hydrocarbon constituents boiling below about 450° F. to 800° F. are removed overhead as a vapor and higher boiling constituents are removed as a bottom liquid stream. At least a portion of this bottoms liquid stream is recycled to the hydrodesulfurization reactor. A very satisfactory method of operation is to remove overhead in the hot separator hydrocarbons boiling below about 700° F. to 730° F. The entire hydrodesulfurized product is preferably passed to a distillation zone wherein the desired product streams are segregated as, for example, a heavy naphtha fraction and various gas oil and heating oil streams.

What is claimed is:

The process for the hydrodesulfurization of cracked highly unsaturated hydrocarbon constituents boiling in the motor fuel boiling range from 100° F. to 430° F. and hydrocarbon constituents boiling in the gas oil boiling range which comprises passing a combined stream consisting of about 18 to about 25% of constituents boiling in said motor fuel boiling range along with fresh and recycled constituents boiling in the gas oil boiling range with hydrogen through a hydrodesulfurization zone maintained under conditions to obtain at least a 75 wt. % reduction in sulfur of the constituents boiling in both the motor fuel and the gas oil boiling ranges, withdrawing the combined stream from said hydrodesulfurization zone and passing the same to a hot separator maintained under pressure and temperature conditions to separate a vapor stream comprising the hydrocarbon constituents boiling below about 450°-750° F., withdrawing as a liquid stream from said hot separator hydrocarbon constituents boiling above about 450°-750° F. and recycling at least a part of said liquid constituents boiling above about 450°-750° F. directly to the hydrodesulfurization zone.

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