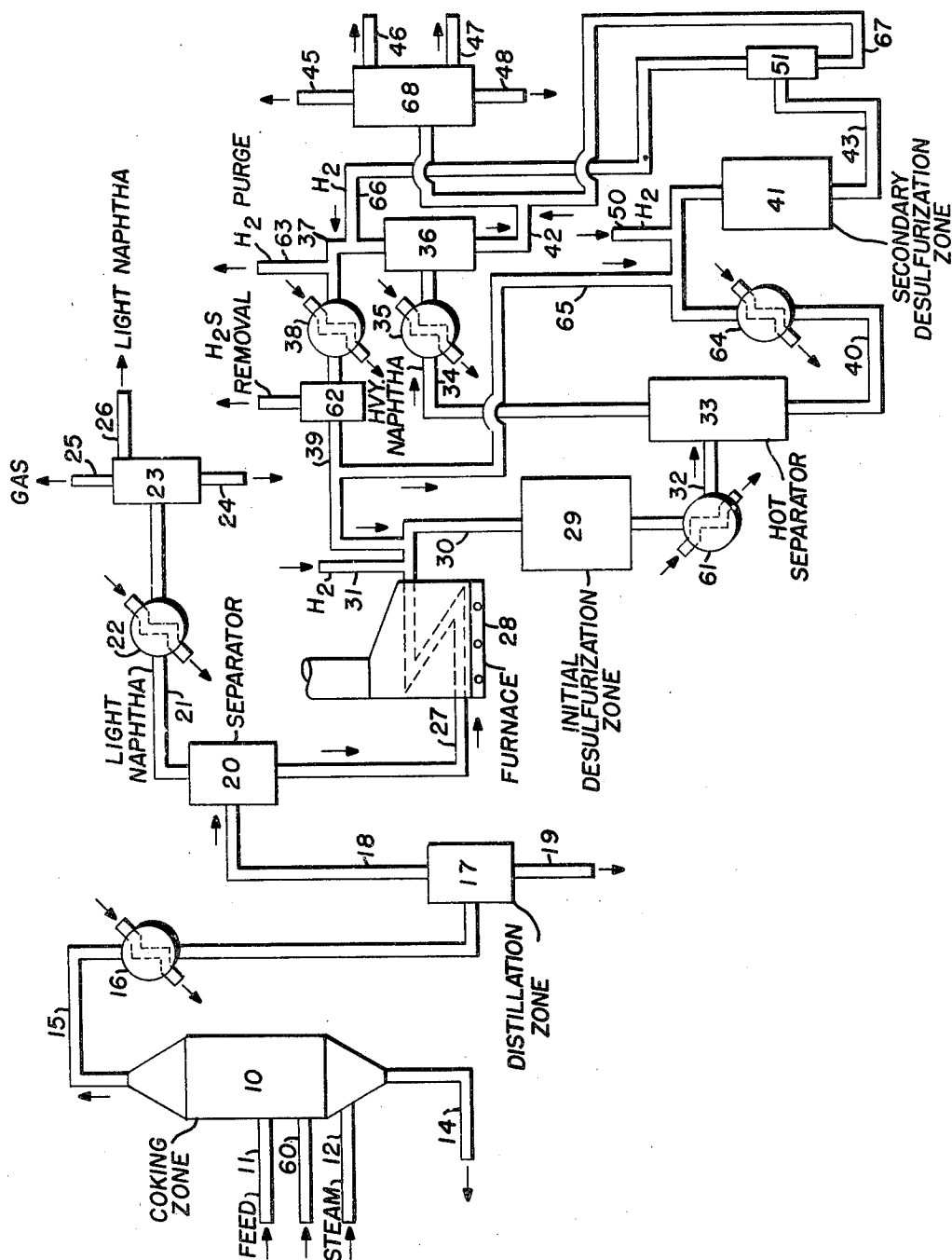


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PROCESS FOR HYDRODESULFURIZATION OF COKER PRODUCTS

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PROCESS FOR HYDRODESULFURIZATION OF COKER PRODUCTS

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This invention is concerned with an improved process for the manufacture of high quality petroleum oil products. The invention is more specifically concerned with the treatment of streams derived from heavy residual coking operations. In accordance with a specific adaptation of the present invention, petroleum oil products secured from heavy residual coking operations are desulfurized in a hydrogen treating zone wherein the constituents boiling in the motor fuel boiling range and the constituents boiling in the gas oil boiling range are processed together in a mixed liquid-gas phase operation. In a preferred adaption of this invention the hydrofined products are withdrawn from an initial hydrodesulfurization zone and passed to a hot separator zone wherein lower boiling constituents such as those boiling in the motor fuel and light gas oil boiling ranges are removed in the vapor phase, and wherein the higher boiling constituents such as those boiling above the light gas oil boiling range are removed as a liquid phase. This liquid phase is withdrawn and passed to a secondary hydrodesulfurization zone operated under operating conditions adapted to secure the desired degree of desulfurization.

In the hydrodesulfurization of petroleum streams it is very desirable that the operating conditions employed for the hydrodesulfurization of constituents boiling in the motor fuel boiling range be appreciably different from the operating conditions employed for the hydrodesulfurization of constituents boiling above the motor fuel boiling range as, for example, boiling in the heating oil and gas oil boiling ranges. Typical temperatures employed for the 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 generally are in the range from about 200 lbs. per square inch to 400 lbs. per square inch. The feed rates are usually in the range from about 2 to 8 volumes of oil per volume of catalyst per hour. This typical 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 usually are about 0.5 to 2.0 volumes of oil per volume of catalyst per hour.

The catalyst may comprise a mixture of cobalt oxide and molybdenum oxide on alumina. A preferred catalyst comprises about 12% cobalt molybdate on alumina. Other satisfactory catalysts are sulfides of nickel and tungsten alone or on an alumina support.

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 these coker fractions boiling above about 400° F. in a hydrodesulfurization can be satisfactorily

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controlled, the coker naphtha on the other hand due to the presence 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 high sulfur residual stock are high in sulfur and are relatively unstable. However, hydrodesulfurization 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 as mentioned heretofore, hydrodesulfurization of coker constituents boiling in the motor fuel range due to the presence of unsaturated constituents is highly exothermic. The heat liberated tends to give a marked temperature rise during the reaction, making the operation difficult to control.

In accordance with the broad aspect of the present invention a blend of coker naphtha and coker gas oil are hydrodesulfurized in a mixed vapor-liquid phase process. 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. However, one disadvantage is that the octane number of motor fuel is impaired. This is not a disadvantage when loss of octane number of the naphtha is not of importance, as for example when the naphtha is used as feed to a hydroforming operation or as diesel fuel. As mentioned, the 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. In accordance with the specific concept of the present invention these disadvantages are overcome.

The process of the present invention may be fully understood by reference to the attached drawing illustrating one embodiment of the same wherein a coker product stream is processed. 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

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about 0° A. P. I. to 20° A. P. I. is introduced into the coker reaction zone 10 by means of feed line 11. Steam is introduced into zone 10 by means of line 12 which maintains the particles of coke in a fluidized state. Coke particles are withdrawn from the bottom of coking zone 10 by means of line 14 and passed to a burner zone (not shown). In the burner zone portions of the coke particles are burned and a portion of the heated coke particles are returned by conventional means of line 60 to coker zone 10. The coker zone 10 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 10 by means of line 15 at a temperature in the range from about 850° F. to 1100° F. These products are passed through a partial condenser zone 16. These cooled products are passed to distillation zone 17 wherein a stream comprising hydrocarbons boiling in the motor fuel range and in the gas oil range are segregated by means of line 18. Higher boiling hydrocarbons are removed by means of line 19 and may be recycled to coker zone 10.

The products removed by means of line 18 are introduced into a separation or distillation zone 20. The separator is operated to remove overhead by means of line 21 light hydrocarbon constituents boiling below about 250–275° F. These overhead constituents are passed through a cooling zone 22 and then introduced into a separator zone or distillation zone 23. In separation zone 23 water is removed by means of line 24, uncondensed gases by means of line 25 and a light coker naphtha by means of line 26.

A liquid stream comprising heavy naphtha constituents and constituents boiling above the motor fuel boiling range is removed from separator 20 by means of line 27, passed through furnace or equivalent means 28 and introduced into an initial hydrodesulfurization reactor 29 by means of line 30. The temperature of the stream removed from furnace 28 is in the range from about 500° F. to 800° F. Fresh hydrogen may be introduced by means of line 31 while recycle hydrogen may be introduced by means of line 39.

Hydrodesulfurization zone 29 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 preferably comprises cobalt molybdate supported on alumina.

The treated product is removed from the initial hydrodesulfurization zone 20 by means of line 32 and passed through partial condenser zone 61 and into a hot separator zone 33. This zone is operated under temperature and pressure conditions to remove overhead by means of line 34 hydrocarbon constituents boiling below about 450–800° F. These hydrocarbon constituents are passed through a cooling zone 35 and introduced into a separator or distillation zone 36. Hydrogen is removed overhead from separator 36 by means of line 37 and compressed in zone 38. Hydrogen sulfide is removed in zone 62 prior to recycling the hydrogen by means of line 39. Hydrogen may be purged from the system by means of line 63. Hydrocarbon constituents boiling in the motor fuel and heating oil boiling ranges are removed from zone 36 by means of line 42.

Higher boiling hydrocarbon constituents such as those boiling in the gas oil boiling range are removed from hot separator 33 by means of line 40. These constituents boil above about 430° F., preferably above about 700° F. to 730° F.

In accordance with the present invention these constituents are passed through heat exchange zone 64 and are then passed to a secondary hydrodesulfurization zone 41. Zone 41 is preferably operated at a temperature between about 675° F. and 800° F. and at a feed rate of 0.5 to 2.0 volumes of oil per volume of catalyst per hour. The

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temperature of the stream in zone 64 is raised or lowered depending on the inlet temperature desired in hydrodesulfurization zone 41. Fresh hydrogen is added by means of line 50 while recycle hydrogen may be added by means of line 65. It is preferred to add all the fresh hydrogen to the process through line 50 and to employ only recycle hydrogen in the initial desulfurization zone 29. The hydrodesulfurized higher boiling hydrocarbons are removed from zone 41 by means of line 43, cooled by means not shown and introduced into zone 51. Hydrogen is removed by means of line 66 while the hydrodesulfurized heavy product is removed from zone 51 by means of line 67.

In accordance with the present invention the hydrocarbon products segregated by means of lines 42 and 67 are passed to a distillation zone 68, wherein a segregation of the desired products as, for example, motor fuels and heating oils are made. Hydrocarbon constituents boiling below the motor fuel boiling range and hydrogen sulfide are removed by means of line 45, hydrocarbon constituents boiling in the motor fuel boiling range are removed by means of line 46, hydrocarbons boiling in the gas oil boiling range are removed by means of line 47 while higher boiling hydrocarbon constituents are segregated by means of line 48.

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.) in a mixed vapor-liquid operation. In this operation it is preferred to pass a heavy naphtha fraction and gas oil fraction boiling up to about 1050° F. through an initial hydrodesulfurization zone. The hydrodesulfurized product is removed from the initial hydrodesulfurization zone, passed through a partial condenser and into a hot separator zone wherein hydrocarbon constituents boiling below about 450° F. to 800° F. are removed overhead as a vapor stream. The higher boiling constituents are removed as a liquid stream and passed through a secondary hydrodesulfurization zone.

The latter liquid stream comprises constituents boiling above about 700° F. to 730° F. and is passed to the secondary hydrodesulfurization zone wherein conditions are adapted to secure efficient hydrodesulfurization of the high boiling stock. In general, the temperature is in the range of about 675° F. to 800° F., preferably in the range from about 700° F. to 750° F. Pressures are in the range of from about 200 to 1000 lbs. per square inch gauge while the feed rate is preferably in the range from 0.5 to 2.0 volumes of oil per volume of catalyst per hour. The hydrodesulfurized products from both zones are preferably passed to a distillation zone wherein the desired final product streams are segregated as desired.

What is claimed is:

1. Process for the hydrodesulfurization of hydrocarbon constituents boiling in the motor fuel boiling range and hydrocarbon constituents boiling in the gas oil boiling range, both of which are derived by the coking of heavy residual petroleum fractions, which comprises passing a combined stream of these constituents and added hydrogen through an initial hydrodesulfurization zone in a mixed liquid-gas phase operation, maintaining said initial zone at a temperature in the range of from about 650° to 700° F., withdrawing the product from said initial zone and passing the same to a hot separation zone wherein hydrocarbon constituents boiling below about 400° to 750° F. are segregated as a vapor phase, passing said vapor phase to a separator and removing hydrogen therefrom, removing from said hot separation zone a liquid phase comprising hydrocarbon constituents boiling above about 400° to 750° F., and passing said liquid phase by itself, together with added hydrogen, through a secondary hydrodesulfurization zone, maintaining said secondary zone at a temperature in the range of

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from about 700° to 750° F., removing the product from said secondary hydrodesulfurization zone, separating hydrogen therefrom, combining the respective hydrodesulfurized streams and segregating a fraction boiling in the motor fuel boiling range and a fraction boiling in the gas oil boiling range.

2. Process as defined by claim 1 wherein said hydrocarbon constituents boiling in the motor fuel boiling range boil in the range from about 250° to 430° F.

3. Process as defined by claim 1 wherein said stream segregated as a vapor phase in said hot separator has a final boiling point in the range from about 600° to 700° F.

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