

Description

This invention relates to a combination process for the catalytic dewaxing and catalytic desulfurization of gas oil.

Catalytic dewaxing of high pour point gas oils to low pour point No. 2 fuel over a shape-selective zeolite catalyst of the ZSM-5 family which selectively cracks long-chain normal paraffins, slightly-branched isoparaffins and long-chain cycloparaffins is known in the art (e.g., U.S. Patent No. 3,700,585 and its reissue, Re. 28,398). The catalytic dewaxing process disclosed in these patents (also known as Mobil Distillate Dewaxing or Distillate Dewaxing, MDDW and DDW, respectively), is often followed by a conventional hydrodesulfurization process (HDS) to remove substantially all sulfur from the product of the catalytic dewaxing process. The conventional hydrodesulfurization process is usually already present in a refinery; thus, the new catalytic dewaxing process may be incorporated into the refinery operations upstream or downstream of the HDS process, as required.

Prior to the development of the catalytic dewaxing process, high pour point oils were dewaxed by a conventional solvent dewaxing treatment. Although solvent dewaxing was also usually followed by the HDS process, it has been suggested in prior art to first subject the sulfur-containing high pour point gas oils to the HDS process and then to the conventional solvent dewaxing process (see, e.g., U.S. Patent Nos. 3,520,796 and 3,617,475). U.S. Patent No. 3,520,796 claims that this sequence of operations reduces the pour point of the product, and U.S. Patent No. 3,617,475 that it produces a product with better hazing characteristics. However, in the process sequence of both patents, the two unit operations (the HDS and the dewaxer) are used as physically and conceptually separate units connected only by the oil base stock entering the HDS unit and by the desulfurized product of the HDS unit entering the dewaxer. The only advantages claimed by these patents relate to the final product qualities.

US-A-4,394,249 discloses that substantial process and cost advantages can be attained if the conventional HDS unit is followed by the catalytic distillate dewaxing process unit (hereinafter DDW) and if a number of process streams flow between the units to maximize the utilization of compression and heat exchange capabilities between the two units.

The sequence of catalytic dewaxing of high pour point, high sulfur gas oils followed by hydrodesulfurization without intermediate product resolution is disclosed in U.S. Patent No. 3,894,938. The benefits disclosed for this sequence include longer cycle time between regenerations and longer total life for the dewaxing catalyst. As in U.S. Patent Nos. 3,520,796 and 3,617,475, the two operations of U.S. Patent 3,894,938 are employed as physically and conceptually separate units connected only by the pro-

duct from the dewaxing unit serving as the feed to the HDS unit. No common hydrogen compression or energy saving concepts are employed or suggested in the process of U.S. Patent No. 3,894,938.

The present invention provides a process for dewaxing and desulfurizing a gas oil which comprises:

(1) passing a gas oil boiling in the 204°C (400°F) to 482°C (900°F) range and having a pour point of above -12°C (+10°F) and a sulfur content of above 0.3 weight percent in indirect heat exchange relationship with the dewaxed and desulfurized product recovered in step (23) herein,

(2) passing a first gaseous stream comprising hydrogen in indirect heat exchange relationship with the first vapor phase from step (8) herein,

(3) passing the first gaseous stream comprising hydrogen from step (2) in indirect heat exchange relationship with the dewaxed effluent from step (7) herein,

(4) passing the gas oil from step (1) in indirect heat exchange relationship with the dewaxed effluent from step (3), the heat exchange of steps (3) and (4) being effective to provide, from the dewaxed effluent, a first liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a first vapor phase,

(5) combining the gas oil from step (4) with the first gaseous stream comprising hydrogen from step (3) to provide the first combined streams, the first gaseous stream being provided in an amount to furnish hydrogen effective to hydrodewax the gas oil under the conditions of step (7) herein,

(6) heating the first combined streams from step (5), the heat provided to the gas oil in steps (1) and (4), the first gaseous stream comprising hydrogen in steps (2) and (3) and the first combined streams in step (6) being effective to provide the first combined streams at the hydrodewaxing temperature of step (7) herein,

(7) contacting the first combined streams from step (6) with a ZSM-5 type zeolite catalyst under hydrodewaxing conditions effective to reduce the pour point of the gas oil to between -12 and -46°C (+10 and -50°F) and provide a dewaxed effluent,

(8) separating the dewaxed effluent from step (4) into a first liquid phase and a first vapor phase,

(9) passing the first vapor phase from step (2) in indirect heat exchange relationship with the second liquid phase from step (11) herein,

(10) cooling the first vapor phase from step (9), the heat exchange of steps (2), (9) and (10) being effective to provide, from the first vapor phase, a second liquid phase having a boiling range of from 38 to 332°C (100 to 630°F) and a second vapor phase,

(11) separating the first vapor phase from step (10) into a second liquid phase and a second vapor phase comprising hydrogen,

(12) recovering the second liquid phase from step (11) as wild naphtha,

(13) passing a second gaseous stream comprising hydrogen in indirect heat exchange relationship with the third vapor phase from step (19) herein,

(14) passing the second gaseous stream comprising hydrogen from step (13) in indirect heat exchange relationship with the desulfurized effluent from step (18) herein,

(15) passing the first liquid phase from step (8) in indirect heat exchange relationship with the desulfurized effluent from step (14), the heat exchange of steps (14) and (15) being effective to provide, from the desulfurized effluent, a third liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a third vapor phase,

(16) combining the first liquid phase from step (15) with the second gaseous stream comprising hydrogen from step (14), to provide the second combined streams, the second gaseous stream being provided in an amount to furnish hydrogen effective to hydrodesulfurize the first liquid phase under the conditions of step (18) herein,

(17) heating the second combined streams from step (16), the heat provided to the first liquid phase in step (15), the second gaseous stream comprising hydrogen in steps (13) and (14) and the second combined streams in step (17) being effective to provide the second combined streams at the hydrodesulfurization temperature of step (18) herein,

(18) contacting the second combined streams from step (17) with a hydrosulfurization catalyst under hydrodesulfurization conditions effective to reduce the sulfur content of the first liquid phase to from 0.05 to 0.5 wt.% and provide a desulfurized effluent,

(19) separating the desulfurized effluent from step (15) into a third liquid phase and a third vapor phase,

(20) passing the third vapor phase from step (13) in indirect heat exchange with the fourth liquid phase from step (22) herein,

(21) cooling the third vapor phase from step (20), the heat exchange of steps (13), (20) and (21) being effective to provide, from said third vapor phase, a fourth liquid phase having a boiling range of from 38 to 343°C (100 to 650°F) and a fourth vapor phase,

(22) separating the third vapor phase from step (21) into a fourth liquid phase and a fourth vapor phase comprising hydrogen and hydrogen sulfide, and

(23) recovering the third liquid phase as a dewaxed, and desulfurized gas oil product.

According to the present invention, a catalytic distillate dewaxing process (DDW) is arranged in a cascade relationship with a catalytic hydrodesulfurization process (HDS) for the processing of high pour point, high sulfur gas oils to permit the use of a common hydrogen system and to integrate the two operations whereby substantial quantities of thermal energy are recovered and transferred from one unit to the other. The processing sequence also results in a longer life for the dewaxing catalyst than is obtained when the sequence is reversed.

In an additional embodiment, the gaseous effluents from the dewaxing step and the desulfurization step of the process may be recycled to

supply hydrogen to each step after removal of hydrogen sulfide generated during the desulfurization. In a further embodiment, the dewaxed and desulfurized gas oil is subjected to steam stripping.

The feed to the process of this invention is a petroleum distillate known as gas oil having both a pour point and a sulfur content which are too high for a satisfactory diesel fuel, heating oil or other fuel oil. Typically, the gas oils employed in this invention have a boiling range in the 204 to 482°C (400 to 900°F) boiling range, exhibit a pour point of above -12°C (+10°F) and sulfur content of above 0.5 weight percent. Those skilled in the art can appreciate that gas oils having properties differing somewhat from those described may be satisfactorily processed in accordance with the present invention by making appropriate adjustments to the operating conditions in the dewaxing process and the desulfurization process.

The dewaxing process used in the present invention is operated in the conventional manner of other catalytic dewaxing, such as that disclosed in U.S. Patent No. 3,700,585 and Reissue Patent 28,398. Thus, the catalyst used in the dewaxing process is a catalyst of the ZSM-5 type which includes the following specific zeolites: ZSM-5, ZSM-11, ZSM-23, ZSM-38 and ZSM-48 with ZSM-5 zeolite being particularly preferred.

ZSM-5 is more particularly described in U.S. Patent No. 3,702,886, ZSM-11 in U.S. Patent No. 3,709,979, ZSM-23 in U.S. Patent No. 4,076,842, ZSM-38 in U.S. Patent No. 4,046,859 and ZSM-48 in European Patent Application Publication No. 0 015 132, published September 3, 1980.

The conditions of the catalytic dewaxing are those of cracking or hydrocracking. Although the dewaxing may be practiced with or without hydrogen, it is preferred to employ hydrogen. Typical catalytic dewaxing conditions include a temperature of from 343 and 538°F (650 and 1000°F), pressure of from 791 kPa to 20786 kPa (100 to 3000 psig), preferably between 1480 and 4928 kPa (200 and 700 psig), liquid hourly space velocity (LHSV) between 0.1 and 10, preferably between 0.5 and 4 and a hydrogen rate of from 89 to 1781 1/1 (500 to 10,000 SCF/B), preferably between about 356 and about 1069 1/1 (2000 and about 6000 SCF/B). The feed introduced into the dewaxing portion of this process is modified by incorporating quantities of hydrogen in the catalytic dewaxing reactor. In one embodiment, this is accomplished by recycling a substantial amount of gaseous components from the low temperature separator associated with the dewaxing operation together with a quantity of fresh make-up hydrogen. These combined streams are added to the gas oil feed to the dewaxing reactor. The amount of gaseous components from the low temperature separator introduced into the catalytic reactor is such that the gases constitute from 50% to 100%, preferably 80% to 100% of the total feed in the catalytic reactor. Accordingly, higher operating temperatures can be sustained in the catalytic reactor

without a substantial increase in the amount of coke produced therein. Thus, the catalytic dewaxing reactor can be operated at a temperature of from 343°C to 538°C (650 to 1000°F) at hydrocracking process conditions with virtually no increase in coke production, as compared to the amount of coke produced at conventional hydrocracking conditions used in prior art catalytic dewaxing operations. Increased temperature of the catalytic dewaxing reactor produces a number of high temperature process streams exiting the reactor which, in turn, enables the operator of the process to recover a substantially higher proportion of thermal energy from such high temperature process streams in appropriate heat exchanging operations. In this connection, the gaseous components recycled into the catalytic dewaxing reactor are comprised of vapor from the DDW low temperature separator as well as make-up hydrogen.

The hydrodesulfurization process used in the present invention is any conventionally known hydrodesulfurization process (HDS) used in the art. For example, the catalyst used in the process could be any conventional hydrodesulfurization catalyst such as a catalyst comprising a Group VIB (chromium, molybdenum, or tungsten) metal, and a Group VIII metal or their oxides or sulfides. The HDS process is conducted with the catalyst under hydroprocessing conditions comprising a pressure of from 3549 kPa to 20786 kPa (500 to 3000 psig), preferably from 4238 kPa to 5617 kPa (600 to 800 psig); a temperature of from 345°C (650°F) to 445°C (850°F), preferably from 370°C to 440°C (700°F to 820°F); a liquid hourly space velocity of from 0.1 to 6.0, preferably 0.4 to 4.0. The hydrogen gas used during the process of hydrodesulfurization is passed through the hydrodesulfurization reactor at the rate of from 178 to 2672 1/1 (1000 to 15,000 SCF/B) of feed and preferably between 178 to 1425 1/1 (1000 and 8000 SCF/B). The hydrogen purity may vary from 60 to 100%. If the hydrogen is recycled, as is customary, it is desirable to provide means of bleeding off a portion of the recycled gas and to add makeup in order to maintain the hydrogen purity within the specified range. The recycled gas is usually washed with a chemical absorbent for hydrogen sulfide or otherwise treated in a known manner to reduce the hydrogen sulfide content thereof prior to recycling. A hydrogen sulfide scrubber employing a monoethanolamine or a diethanolamine solution and known in the art as the MEA or the DEA process may be conveniently employed. The HDS process removes from 50% to 99.5% by weight of the sulfur originally present in the feedstock. Feedstocks which can be used in the process are high-pour point gas oils such as straight run atmospheric and vacuum gas oils and cracked gas oils. Products of the process include gas oils, naphthas and light ends.

In the present invention, the hydrogen makeup stream is preferably added to the catalytic dewaxing operation of the process and a portion thereof

is subsequently recycled, after compression, to the HDS operation. Only a portion, e.g., between 40% and 50%, of the hydrogen stream introduced into the catalytic dewaxing process is subsequently recycled to the HDS process, depending on the relative amounts of hydrogen required for the two operations.

In addition, a number of high temperature process streams in the dewaxing process and in the desulfurization process are passed through various heat exchanging means with cooler process streams from one or both processes to extract the thermal energy from the high temperature streams.

The improvements described herein can be illustrated by reference to Figure 1 which presents a flowplan of an embodiment of this invention. An atmospheric heavy gas oil having a boiling range of from 204 to 482°C (400 to 900°F) a pour point of 10°C (+50°F) and a sulfur content of 2 weight percent is the feed to the process. This fresh gas oil feed enters the process through line 2, is heated to about 93°C (200°F) in heat exchanger 4 by the gas oil product stream from the process. The feed then flows through line 6 to heat exchanger 8 where it is further heated to about 232°C (450°F) by the effluent stream from the dewaxing reactor. The gas oil passes through line 10 where it is combined with a preheated recycle hydrogen stream supplied through line 12 at a temperature of about 288°C (550°F). The combined stream, at a temperature of about 271°C (520°F), flows through line 14 to heater 16 where the temperature of the combined stream is increased to about 427°C (800°F). The mixture of gas oil and hydrogen passes through line 18 into MDDW reactor 20 which contains a bed of ZSM-5 catalyst. Dewaxing conditions in the reactor include a pressure of about 4790 kPa (680 psig) and a LHSV of about 2. During passage through MDDW reactor 20, the paraffins and other high pour points components of the gas oil are cracked, thereby substantially reducing the pour point of the gas oil. The dewaxed effluent at a temperature of about 410°C (770°F) exits from reactor 20 through line 22 and flows through heat exchangers 24 and 8 where it gives up some of its heat to preheat the recycle hydrogen stream and the gas oil feed, respectively. The effluent then passes into high temperature separation 26 which is operated at a temperature of about 277°C (530°F) thereby causing the effluent to separate into a first liquid phase boiling in the 166 to 482°C (330 to 900°F) range and a first vapor phase. The first vapor phase flows from high temperature separation 26 through line 28 and then through heat exchangers 30 and 32 and cooler 34 and into low temperature separator 36. The first vapor phase provides preheat to the recycle hydrogen stream as it passes through heat exchanger 30 and the vapor phase is cooled further by the liquid effluent from low temperature separator 36 in heat exchanger 32. Cooler 34 then cools the first vapor phase so that a phase separation may be made in low temperature separator 36 which is

operated at a temperature of about 38°C (100°F) and about 4514 kPa (640 psig). The first vapor phase is separated in separator 36 into a naphtha distillate boiling in the 38°C to 332°C (100 to 630°F) range and a second vapor phase which contains hydrogen and gaseous products from the dewaxing operation. The naphtha distillate is a wild naphtha which will usually require stabilization by known means before being added to the gasoline pool. The second vapor phase passes through lines 38 and 40 to the suction of compressor 42 for compression from about 4514 to about 5203 kPa (640 to about 740 psig) and recycle to the dewaxing reactor. Make-up hydrogen, as required, is introduced from line 44 into line 40 for use in the process. To maintain the desired hydrogen purity, quantities of the recycle stream are purged from the system for disposition (not shown). The recycle hydrogen stream flows from compressor 42 through line 46 to heat exchanger 30 where it is heated from 38 to 171°C (100 to 340°F) by the gaseous phase from high temperature separator 26 and then through line 48 to heat exchanger 24 wherein the dewaxed effluent from MDDW reactor 22 further heats it to about 288°C (550°F). The preheated recycle hydrogen stream then passes through line 12, as explained above, where it is combined with the gas oil feed.

Returning to high temperature separator 26, the dewaxed gas oil, now at a temperature of about 277°C (530°F), is passed to the desulfurization stage for further processing. The gas oil flows through line 50 to heat exchanger 52 where it is heated to about 316°C (600°F) by the partially cooled effluent from the desulfurization reactor. The preheated dewaxed gas oil passes through line 54 where it is combined with a preheated recycle hydrogen stream supplied through line 56 at a temperature of about 304°C (580°F). The combined stream, at a temperature of about 293°C (560°F), flows through line 58 to heater 60 where the temperature of the combined stream is increased to about 399°C (750°F). The mixture of dewaxed gas oil and hydrogen passes through line 62 into HDS reactor 64 which contains a catalyst bed of cobalt-molybdenum on alumina. Desulfurization conditions in the reactor include a pressure of about 4238 kPa (600 psig) and a LHSV of about 2. During passage through HDS reactor 64, the sulfur components of the gas oil are converted to hydrogen sulfide, thereby substantially reducing the sulfur content of the gas oil. The cascade principle utilized in the process of this invention is based on the use of a common hydrogen system so that the process streams pass from the MDDW reactor through the interconnecting pipes, heat exchangers, separators, etc. to the HDS reactor which operates at about a 446–791 kPa (50–100 psi) lower pressure than the MDDW reactor.

The desulfurized effluent, at a temperature of 800°F, exits from HDS reactor 64 through line 66 and flows through heat exchangers 68 and 52 where it gives up some of its heat to preheat the HDS recycle hydrogen stream and the dewaxed

gas oil feed, respectively. The effluent then passes into high temperature separator 70 which is operated at a temperature of about 277°C (530°F) thereby causing the effluent to separate into a third liquid phase boiling in the 166 to 482°C (330 to 900°F) range and a third vapor phase. The third vapor phase flows from high temperature separator 70 through line 72 and then through heat exchangers 74 and 76 and cooler 78 and into low temperature separator 80. The third vapor phase provides preheat to the HDS recycle hydrogen stream as it passes through heat exchanger 74 and the vapor phase is cooled further by the liquid effluent from low temperature separator 80 in heat exchanger 76. Cooler 78 then cools the third vapor phase so that a phase separation may be made in low temperature separator 80 which is operated at about 38°C (100°F) and about 3962 kPa (560 psig). The third vapor phase is separated in separator 80 into a naphtha distillate boiling in the 38 to 343°C (100–650°F) range and a fourth vapor phase which contains hydrogen and hydrogen sulfide. The fourth vapor phase passes through line 82 to H₂S scrubber 84 where a solution of monoethanolamine or diethanolamine contacts the fourth vapor phase removing sufficient hydrogen sulfide to permit the fourth vapor phase to be recycled to the HDS reactor for reuse. The fourth vapor phase then passes through line 86 and 88 to the suction of compressor 90 for compression from about 3893 to about 4514 kPa (550 to 640 psig). As required to maintain the desired hydrogen purity, a purge stream of gas is removed through line 92 for disposal in the fuel gas system. The recycle hydrogen stream flows from compressor 90 through lines 94 and 96 to heat exchanger 74 where it is heated from about 38°C (100) to about 121°C (250°F) by the gaseous phase from high temperature separator 70 and then through line 98 to heat exchanger 68 where the desulfurized effluent from HDS reactor 64 further heats it to about 304°C (580°F). The preheated recycle hydrogen stream then passes through line 56, as explained above, where it is combined with the dewaxed gas oil feed.

The naphtha distillate from low temperature separator 80 flows through line 100 and heat exchanger 76 where it obtains some preheat from the third vapor phase. The heated naphtha passes through line 102 and is introduced into product stripper 104. The dewaxed and desulfurized gas oil, which is also referred to as the third liquid phase, flows from high temperature separator 70 through line 106 and is also introduced into product stripper 104. Stripping stream is introduced into the bottom of the stripper through line 108 to strip both the naphtha and the gas oil. The stripper operates at a tower top pressure of about 687 kPa (85 psig) and a bottom pressure of about 860 kPa (110 psig). Wild naphtha at about 38°C (100°F) is recovered from the top of stripper 104 through line 110 for further processing prior to its addition to the gasoline pool. The product gas oil having a pour point of about -18°C (0°F) and a sulfur content of about 0.08 weight percent is

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removed from product stripper 104 at a temperature of about 249°C (480°F) through line 112. The gas oil flows to heat exchanger 4 where it provides some preheat to the gas oil feed to the process. The dewaxed and desulfurized gas oil then passes through line 114 to cooler 116 where it is cooled to the desired temperature before passing to product storage and further processing, as required.

Claims

1. A process for dewaxing and desulfurizing a gas oil which comprises:

(1) passing a gas oil boiling in the 204 to 482°C (400 to 900°F) range and having a pour point of above -12°C (+10°F) and a sulfur content of above 0.3 weight percent in indirect heat exchange relationship with the dewaxed and desulfurized product recovered in step (23) herein,

(2) passing a first gaseous stream comprising hydrogen in indirect heat exchange relationship with the first vapor phase from step (8) herein,

(3) passing the first gaseous stream comprising hydrogen from step (2) in indirect heat exchange relationship with the dewaxed effluent from step (7) herein,

(4) passing the gas oil from step (1) in indirect heat exchange relationship with the dewaxed effluent from step (3), the heat exchange of steps (3) and (4) being effective to provide, from the dewaxed effluent, a first liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a first vapor phase,

(5) combining the gas oil from step (4) with the first gaseous stream comprising hydrogen from step (3) to provide the first combined streams, the first gaseous stream being provided in an amount to furnish hydrogen effective to hydrodewax the gas oil under the conditions of step (7) herein,

(6) heating the first combined streams from step (5), the heat provided to the gas oil in steps (1) and (4), the first gaseous stream comprising hydrogen in steps (2) and (3) and the first combined streams in step (6) being effective to provide the first combined streams at the hydrodewaxing temperature of step (7) herein,

(7) contacting the first combined streams from step (6) with a ZSM-5 type zeolite catalyst under hydrodewaxing conditions effective to reduce the pour point of the gas oil to between -12°C (+10) and -46°C (-50°F) and provide a dewaxed effluent,

(8) separating the dewaxed effluent from step (4) into a first liquid phase and a first vapor phase,

(9) passing the first vapor phase from step (2) in indirect heat exchange relationship with the second liquid phase from step (11) herein,

(10) cooling the first vapor phase from step (9), the heat exchange of steps (2), (9) and (10) being effective to provide, from the first vapor phase, a second liquid phase having a boiling range of from 38°C to 332°C (100 to 630°F) and a second vapor phase,

(11) separating the first vapor phase from step

(10) into a second liquid phase and a second vapor phase comprising hydrogen,

(12) recovering the second liquid phase from step (11) as wild naphtha,

(13) passing a second gaseous stream comprising hydrogen indirect heat exchange relationship with the third vapor phase from step (19) herein,

(14) passing the second gaseous stream comprising hydrogen from step (13) in indirect heat exchange relationship with the desulfurized effluent from step (18) herein,

(15) passing the first liquid phase from step (8) in indirect heat exchange relationship with the desulfurized effluent from step (14), the heat exchange of steps (14) and (15) being effective to provide, from the desulfurized effluent, a third liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a third vapor phase,

(16) combining the first liquid phase from step (15) with the second gaseous stream comprising hydrogen from step (14), to provide the second combined streams, the second gaseous stream being provided in an amount to furnish hydrogen effective to hydrodesulfurize the first liquid phase under the conditions of step (18) herein;

(17) heating the second combined streams from step (16), the heat provided to the first liquid phase in step (15), the second gaseous stream comprising hydrogen in steps (13) and (14) and the second combined streams in step (17) being effective to provide the second combined streams at the hydrodesulfurization temperature of step (18) herein,

(18) contacting the second combined streams from step (17) with a hydrodesulfurization catalyst under hydrodesulfurizing conditions effective to reduce the sulfur content of the first liquid phase to from 0.05 to 0.5 wt.% and provide a desulfurized effluent,

(19) separating the desulfurized effluent from step (15) into a third liquid phase and a third vapor phase,

(20) passing the third vapor phase from step (13) in indirect heat exchange with the fourth liquid phase from step (22) herein,

(21) cooling the third vapor phase from step (20), the heat exchange of steps (13), (20) and (21) being effective to provide, from said third vapor phase, a fourth liquid phase having a boiling range of from 38°C to 343°C (100 to 650°F) and a fourth vapor phase,

(22) separating the third vapor phase from step (21) into a fourth liquid phase and a fourth vapor phase comprising hydrogen and hydrogen sulfide, and

(23) recovering the third liquid phase as a dewaxed, and desulfurized gas oil product.

2. A process according to Claim 1 wherein

(a) a portion of the second vapor phase from step (11) together with fresh make-up hydrogen is compressed to provide the effective dewaxing pressure and to serve as the first gaseous stream of step (2), and

(b) hydrogen sulfide is removed from a portion of the fourth vapor stream from step (22), the

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removed from product stripper 104 at a temperature of about 249°C (480°F) through line 112. The gas oil flows to heat exchanger 4 where it provides some preheat to the gas oil feed to the process. The dewaxed and desulfurized gas oil then passes through line 114 to cooler 116 where it is cooled to the desired temperature before passing to product storage and further processing, as required.

Claims

1. A process for dewaxing and desulfurizing a gas oil which comprises:

(1) passing a gas oil boiling in the 204 to 482°C (400 to 900°F) range and having a pour point of above -12°C (+10°F) and a sulfur content of above 0.3 weight percent in indirect heat exchange relationship with the dewaxed and desulfurized product recovered in step (23) herein,

(2) passing a first gaseous stream comprising hydrogen in indirect heat exchange relationship with the first vapor phase from step (8) herein,

(3) passing the first gaseous stream comprising hydrogen from step (2) in indirect heat exchange relationship with the dewaxed effluent from step (7) herein,

(4) passing the gas oil from step (1) in indirect heat exchange relationship with the dewaxed effluent from step (3), the heat exchange of steps (3) and (4) being effective to provide, from the dewaxed effluent, a first liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a first vapor phase,

(5) combining the gas oil from step (4) with the first gaseous stream comprising hydrogen from step (3) to provide the first combined streams, the first gaseous stream being provided in an amount to furnish hydrogen effective to hydrodewax the gas oil under the conditions of step (7) herein,

(6) heating the first combined streams from step (5), the heat provided to the gas oil in steps (1) and (4), the first gaseous stream comprising hydrogen in steps (2) and (3) and the first combined streams in step (6) being effective to provide the first combined streams at the hydrodewaxing temperature of step (7) herein,

(7) contacting the first combined streams from step (6) with a ZSM-5 type zeolite catalyst under hydrodewaxing conditions effective to reduce the pour point of the gas oil to between -12°C (+10) and -46°C (-50°F) and provide a dewaxed effluent,

(8) separating the dewaxed effluent from step (4) into a first liquid phase and a first vapor phase,

(9) passing the first vapor phase from step (2) in indirect heat exchange relationship with the second liquid phase from step (11) herein,

(10) cooling the first vapor phase from step (9), the heat exchange of steps (2), (9) and (10) being effective to provide, from the first vapor phase, a second liquid phase having a boiling range of from 38°C to 332°C (100 to 630°F) and a second vapor phase,

(11) separating the first vapor phase from step

(10) into a second liquid phase and a second vapor phase comprising hydrogen,

(12) recovering the second liquid phase from step (11) as wild naphtha,

(13) passing a second gaseous stream comprising hydrogen indirect heat exchange relationship with the third vapor phase from step (19) herein,

(14) passing the second gaseous stream comprising hydrogen from step (13) in indirect heat exchange relationship with the desulfurized effluent from step (18) herein,

(15) passing the first liquid phase from step (8) in indirect heat exchange relationship with the desulfurized effluent from step (14), the heat exchange of steps (14) and (15) being effective to provide, from the desulfurized effluent, a third liquid phase having a boiling range of from 166 to 482°C (330 to 900°F) and a third vapor phase,

(16) combining the first liquid phase from step (15) with the second gaseous stream comprising hydrogen from step (14), to provide the second combined streams, the second gaseous stream being provided in an amount to furnish hydrogen effective to hydrodesulfurize the first liquid phase under the conditions of step (18) herein;

(17) heating the second combined streams from step (16), the heat provided to the first liquid phase in step (15), the second gaseous stream comprising hydrogen in steps (13) and (14) and the second combined streams in step (17) being effective to provide the second combined streams at the hydrodesulfurization temperature of step (18) herein,

(18) contacting the second combined streams from step (17) with a hydrodesulfurization catalyst under hydrodesulfurizing conditions effective to reduce the sulfur content of the first liquid phase to from 0.05 to 0.5 wt.% and provide a desulfurized effluent,

(19) separating the desulfurized effluent from step (15) into a third liquid phase and a third vapor phase,

(20) passing the third vapor phase from step (13) in indirect heat exchange with the fourth liquid phase from step (22) herein,

(21) cooling the third vapor phase from step (20), the heat exchange of steps (13), (20) and (21) being effective to provide, from said third vapor phase, a fourth liquid phase having a boiling range of from 38°C to 343°C (100 to 650°F) and a fourth vapor phase,

(22) separating the third vapor phase from step (21) into a fourth liquid phase and a fourth vapor phase comprising hydrogen and hydrogen sulfide, and

(23) recovering the third liquid phase as a dewaxed, and desulfurized gas oil product.

2. A process according to Claim 1 wherein

(a) a portion of the second vapor phase from step (11) together with fresh make-up hydrogen is compressed to provide the effective dewaxing pressure and to serve as the first gaseous stream of step (2), and

(b) hydrogen sulfide is removed from a portion of the fourth vapor stream from step (22), the



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fourth vapor stream is then compressed to provide the effective hydrosulfurization pressure and, together with a portion of the second vapor phase from step (11), serves as the second gaseous stream of step (13), the dewaxing pressure being from 345 to 689 kPa (50 to 100 psi) higher than the desulfurization pressure.

3. A process according to Claim 1 wherein the desulfurization catalyst comprises a Group VIB metal and a Group VIII metal or their oxides or sulfides.

4. A process according to Claim 2 wherein the hydrogen sulfide removal is effected in a MEA process or a DEA process.

5. A process according to Claim 1 including the following additional step:

(24) stream stripping the dewaxed and desulfurized gas oil product.

6. A process according to Claim 2 wherein the hydrodewaxing conditions of step (7) comprise a temperature of from 343 to 538°C (650° to 1000°F), a pressure of from 1480 to 4928 kPa (200 to 700 psig), a LHSV from 0.5 to 4 and a hydrogen rate of from 356 to 1069 1/1 (2000 to 6000 SCF/B), and the hydrodesulfurization conditions of step (18) comprise a temperature of from 371 to 438°C (700° to 820°F), a pressure of from 4238 to 5617 kPa (600 to 800 psig), a LHSV of from 0.4 to 4 and a hydrogen rate of from 178 to 1425 1/1 (1000 to 8000 SCF/B), the hydrodewaxing pressure being between 345 to 689 kPa (50 to 100 psi) higher than the desulfurization pressure.

Patentansprüche

1. Verfahren zum Entwachsen und Entschwefeln eines Gasöles, welches umfaßt:

(1) Leiten eines Gasöles, das im Bereich von 204 bis 482°C (400 bis 900°F) siedet und einen Pourpoint von etwa -12°C (+10°F) und einen Schwefelgehalt von über 0,3 Gew.% hat im Verhältnis des indirekten Wärmeaustausches mit dem entwachsensten und entschwefeltem Produkt, das in Stufe (23) zurückgewonnen wird;

(2) Leiten eines ersten gasförmigen Stromes, der Wasserstoff umfaßt, im Verhältnis des indirekten Wärmeaustausches mit der ersten Dampfphase aus Stufe (8);

(3) Leiten des ersten gasförmigen Stromes, der Wasserstoff umfaßt, aus Stufe (2) im Verhältnis des direkten Wärmeaustausches mit dem entwachsensten ausströmenden Mittel aus Stufe (7);

(4) Leiten des Gasöles aus Stufe (1) im Verhältnis des indirekten Wärmeaustausches mit dem entwachsensten ausströmenden Mittel aus Stufe (3), wobei der Wärmeaustausch der Stufen (3) und (4) effektiv ist, um aus dem entwachsensten ausströmenden Mittel eine erste flüssige Phase mit einem Siedebereich von 166 bis 482°C (330 bis 900°F) und eine erste Dampfphase zu schaffen;

(5) Kombinieren des Gasöles aus Stufe (4) mit dem ersten gasförmigen Strom aus Stufe (3), der Wasserstoff umfaßt, um die ersten kombinierten Ströme zu schaffen, wobei der erste gasförmige Strom in einer Menge geschaffen wird, um den

Wasserstoff effektiv für das Hydroentwachsen des Gasöles unter den Bedingungen der Stufe (7) zu machen;

(6) Erwärmen der ersten kombinierten Ströme aus Stufe (5), die Wärme, die für das Gasöl in den Stufen (1) und (4), den ersten gasförmigen Strom, der Wasserstoff umfaßt, in den Stufen (2) und (3) und und die ersten kombinierten Ströme in Stufe (6) geschaffen wird, ist effektiv, um die ersten kombinierten Ströme auf die Entwachstungs-temperatur von Stufe (7) zu bringen;

(7) Kontaktieren, der ersten kombinierten Ströme aus der Stufe (6) mit einem Zeolith-Katalysator vom Typ ZSM-5 unter Entwachstungsbedingungen, die effektiv sind, um den Pourpoint des Gasöles auf zwischen -12°C (+10°F) und -46°C (-50°F) zu verringern und ein entwachsenstes ausströmendes Mittel zu schaffen;

(8) Trennen des entwachsensten ausströmenden Mittels aus Stufe (4) in eine erste flüssigen Phase und eine erste Dampfphase;

(9) Leiten der ersten Dampfphase aus der Stufe (2) im Verhältnis des indirekten Wärmeaustausches mit der zweiten flüssigen Phase aus der Stufe (11);

(10) Abkühlen der ersten Dampfphase aus der Stufe (9), wobei der Wärmeaustausch der Stufen (2), (9) und (10) effektiv ist, um aus der ersten Dampfphase eine zweite flüssige Phase mit einem Siedebereich von 38 bis 332°C (100 bis 630°F) und eine zweite Dampfphase zu schaffen;

(11) Trennen der ersten Dampfphase aus der Stufe (10) in eine zweite flüssige Phase und eine zweite Dampfphase, die Wasserstoff umfaßt;

(12) Rückgewinnung der zweiten flüssigen Phase aus der Stufe (11) als ungeordnetes Benzin;

(13) Leiten eines zweiten gasförmigen Stromes, der Wasserstoff umfaßt, im Verhältnis des indirekten Wärmeaustausches mit der dritten Dampfphase aus der Stufe (19);

(14) Leiten des zweiten gasförmigen Stromes, der Wasserstoff umfaßt, aus der Stufe (13) im Verhältnis des indirekten Wärmeaustausches mit den entschwefelten, ausströmenden Mittel aus der Stufe (18);

(15) Leiten der ersten flüssigen Phase aus der Stufe (8) im Verhältnis des indirekten Wärmeaustausches mit dem entschwefelten, ausströmenden Mittel aus der Stufe (14), wobei der Wärmeaustausch der Stufen (14) und (15) effektiv ist, um aus dem entschwefelten, ausströmenden Mittel eine dritte flüssige Phase mit einem Siedebereich von 166 bis 482°C (330 bis 900°F) und eine dritte Dampfphase zu schaffen;

(16) Kombinieren der ersten flüssigen Phase aus der Stufe (15) mit dem zweiten gasförmigen Strom, der Wasserstoff umfaßt, aus der Stufe (14), um diese zweiten, kombinierten Ströme zu schaffen, wobei der zweite gasförmige Strom in einer Menge geschaffen ist, um den Wasserstoff effektiv für die Hydroentschwefelung der ersten flüssigen Phase unter den Bedingungen der Stufe (18) zu machen;

(17) Erwärmen der zweiten kombinierten Ströme aus der Stufe (16), die Wärme, die für die erste



flüssige Phase in Stufe (15), den zweiten gasförmigen Strom, der Wasserstoff umfaßt; in den Stufen (13) und (14) und die zweiten kombinierten Ströme in Stufe (17) geschaffen wird, ist effektiv, um die zweiten kombinierten Ströme auf die Hydroentschwefelungs-Temperatur der Stufe (18) zu bringen;

(18) Kontaktieren der zweiten kombinierten Ströme aus der Stufe (17) mit einem Hydroentschwefelungs-Katalysator unter Hydroentschwefelungsbedingungen, die effektiv sind, um den Schwefelgehalt der ersten flüssigen Phase auf 0,05 bis 0,5 Gew.% zu reduzieren und ein entschwefeltes, ausströmendes Mittel zu schaffen;

(19) Trennen des entschwefelten, ausströmenden Mittels aus der Stufe (15) in eine dritte flüssige Phase und eine dritte Dampfphase;

(20) Leiten der dritten Dampfphase aus der Stufe (13) in indirektem Wärmeaustausch mit der vierten flüssigen Phase aus der Stufe (22);

(21) Abkühlen der dritten Dampfphase aus der Stufe (20), wobei der Wärmeaustausch der Stufen (13), (20) und (21) effektiv ist, um aus der dritten Dampfphase eine vierte flüssige Phase mit einem Siedebereich von 38 bis 343°C (100 bis 650°F) und eine vierte Dampfphase zu schaffen;

(22) Trennen der dritten Dampfphase aus der Stufe (21) in eine vierte flüssige Phase und eine vierte Dampfphase, die Wasserstoff und Schwefelwasserstoff umfaßt;

(23) Rückgewinnung der dritten flüssigen Phase als ein entwachstes und entschwefeltes Gasölprodukt.

2. Verfahren nach Anspruch 1, worin

(a) ein Teil der zweiten Dampfphase aus der Stufe (11) zusammen mit der frischen Wasserstoffzufuhr unter Druck gesetzt wird, um den effektiven Entwachstungsdruck zu schaffen und als erster gasförmiger Strom der Stufe (2) zu dienen, und

(b) der Schwefelwasserstoff aus einem Teil des vierten Dampfstromes aus der Stufe (22) entfernt wird, der vierte Dampfstrom dann unter Druck gesetzt wird, um den effektiven Hydroentschwefelungsdruck zu schaffen und zusammen mit einem Teil der zweiten Dampfphase aus der Stufe (11) als zweiter gasförmiger Strom der Stufe (13) zu dienen, wobei der Entwachstungsdruck von 345 bis 689 kPa (50 bis 100 psi) mehr als der Entschwefelungsdruck beträgt.

3. Verfahren nach Anspruch 1, worin der Entschwefelungskatalysator ein Metall der Gruppe VIB und ein Metall der Gruppe VIII oder ihre Oxide oder Sulfide umfaßt.

4. Verfahren nach Anspruch 2, worin die Entfernung des Schwefelwasserstoffes in einem MEA (Monoethanolamin)-Verfahren oder einem DEA (Diethanolamin)-Verfahren durchgeführt wird.

5. Verfahren nach Anspruch 1, welches die folgende zusätzliche Stufe einschließt:

(24) Dampfabbstreifen des entwachsten und entschwefelten Gasölproduktes.

6. Verfahren nach Anspruch 2, worin die Hydro-

entschwefelungsbedingungen der Stufe (7) umfassen:

Eine Temperatur von 343 bis 538°C (650 bis 1000°F), einen Druck von 1480 bis 4928 kPa (200 bis 700 psig), eine LHSV von 0,5 bis 4 und eine Wasserstoffgeschwindigkeit von 356 bis 1069 l/h (2000 bis 6000 SCF/B), und die Hydroentschwefelungsbedingungen der Stufe (18) umfassen:

Eine Temperatur von 371 bis 438°C (700 bis 820°F), einen Druck von 4238 bis 5617 kPa (600 bis 800 psig) eine LHSV von 0,4 bis 4 und eine Wasserstoffgeschwindigkeit von 178 bis 1425 l/h (100 bis 8000 SCF/B), wobei der Hydroentschwefelungsdruck zwischen 345 bis 689 kPa (50 bis 100 psig) mehr als der Entschwefelungsdruck beträgt.

Revendications

1. Procédé de déparaffinage et de désulfuration d'un gasoil qui consiste à:

(1) à faire passer un courant de gasoil dont le point d'ébullition est compris entre 204°C (400°F) et 482°C (900°F), dont le point d'écoulement est supérieur à -12°C (+10°F) et dont la teneur en soufre est supérieure à 0,3% en poids, dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec le produit déparaffiné et désulfuré récupéré dans la présente étape (23);

(2) à faire passer un premier courant gazeux comprenant de l'hydrogène dans un échangeur de chaleur par l'intermédiaire duquel est en contact indirect avec la première phase vapeur de la présente étape (8);

(3) à faire passer le premier courant gazeux comprenant de l'hydrogène provenant de l'étape (2) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec l'effluent déparaffiné provenant de la présente étape (7);

(4) à faire passer le courant de gasoil provenant de l'étape (1) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec l'effluent déparaffiné provenant de l'étape (3), les échanges de chaleur des étapes (3) et (4) étant capables de donner, à partir de l'effluent déparaffiné, une première phase liquide dont le point d'ébullition est compris entre 166 et 482°C (330 et 900°F) et une première phase vapeur;

(5) à combiner le courant de gasoil provenant de l'étape (4) avec le premier courant gazeux comprenant de l'hydrogène provenant de l'étape (3) pour former un premier courant résultant, le premier courant gazeux étant admis en quantité suffisante pour fournir de l'hydrogène apte à déparaffiner par hydrogénation le gasoil dans les conditions de la présente étape (7);

(6) à chauffer le premier courant résultant provenant de l'étape (5), la chaleur fournie au gasoil dans les étapes (1) et (4), au premier courant gazeux comprenant de l'hydrogène dans les étapes (2) et (3) et au premier courant résultant dans l'étape (6) pouvant porter le premier courant



résultant à la température de déparaffinage par hydrogénation de la présente étape (7);

(7) à mettre le premier courant résultant provenant de l'étape (6) en contact avec un catalyseur à base de zéolite du type ZSM-5 dans les conditions de déparaffinage par hydrogénation propres à réduire le point d'écoulement du gasoil à une valeur comprise entre -12 et -46°C ($+10$ et -50°F) et à fournir en effluent déparaffiné;

(8) à séparer l'effluent déparaffiné provenant de l'étape (4) en une première phase liquide et en une première phase vapeur;

(9) à faire passer la première phase vapeur provenant de l'étape (2) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec la seconde phase liquide provenant de la présente étape (11);

(10) à refroidir la première phase vapeur provenant de l'étape (9), les échanges de chaleur des étapes (2), (9) et (10) étant capable de donner, à partir de la première phase vapeur, une seconde phase liquide dont le point d'ébullition est compris entre 38 et 332°C (100 et 630°F) et une seconde phase vapeur;

(11) à séparer la première phase vapeur provenant de l'étape (10) en une seconde phase liquide et en une seconde phase vapeur comprenant de l'hydrogène;

(12) à récupérer la seconde phase liquide provenant de l'étape (11) sous la forme de naphta brut;

(13) à faire passer un second courant gazeux comprenant de l'hydrogène dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec la troisième phase vapeur provenant de la présente étape (11);

(14) à faire passer le second courant de vapeur comprenant de l'hydrogène provenant de l'étape (11) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec l'effluent désulfuré provenant de la présente étape (18);

(15) à faire passer la première phase liquide provenant de l'étape (8) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec l'effluent désulfuré provenant de l'étape (14), les échanges de chaleur des étapes (14) et (15) pouvant donner, à partir de l'effluent désulfuré, une troisième phase liquide dont le point d'ébullition est compris entre 166 et 482°C (330 et 900°F) et une troisième phase vapeur;

(16) à combiner la première phase liquide provenant de l'étape (15) avec le second courant gazeux comprenant de l'hydrogène provenant de l'étape (14) pour réaliser le second courant résultant, le second courant gazeux étant admis en quantité suffisante pour fournir de l'hydrogène capable de désulfurer la première phase liquide dans les conditions de la présente étape (18);

(17) à chauffer le second courant résultant provenant de l'étape (16), la chaleur procurée à la première phase liquide dans l'étape (15), au second courant gazeux comprenant de l'hydrogène dans les étapes (13) et (14) et au second courant résultant dans l'étape (17) pouvant porter le second courant résultant à la température de

désulfuration par hydrogénation de la présente étape (18);

(18) à mettre en contact le second courant résultant provenant de l'étape (17) avec un catalyseur de désulfuration par hydrogénation dans les conditions de désulfuration par hydrogénation propres à réduire la teneur en soufre de la première phase liquide à une valeur comprise entre $0,05$ et $0,5\%$ en poids et à donner un effluent désulfuré;

(19) à séparer l'effluent désulfuré provenant de l'étape (15) en une troisième phase liquide et une troisième phase vapeur;

(20) à faire passer la troisième phase vapeur provenant de l'étape (13) dans un échangeur de chaleur par l'intermédiaire duquel il est en contact indirect avec la quatrième phase liquide provenant de la présente étape (22);

(21) à refroidir la troisième phase vapeur provenant de l'étape (20), l'échange de chaleur des étapes (13), (20) et (21) étant capable de donner, à partir de la troisième phase vapeur, une quatrième phase liquide dont le point d'ébullition est compris entre 38 et 343°C (100 et 650°F) et une quatrième phase vapeur;

(22) à séparer la troisième phase vapeur provenant de l'étape (21) en une quatrième phase liquide et une quatrième phase vapeur comprenant de l'hydrogène et du sulfure d'hydrogène; et

(23) à récupérer la troisième phase liquide sous la forme d'un produit de gasoil déparaffiné et désulfuré.

2. Procédé selon la revendication 1, dans lequel:

(a) on comprime une portion de la seconde phase vapeur provenant de l'étape (11) en même temps que de l'hydrogène neuf de complément pour réaliser la pression effective de déparaffinage et servir de premier courant gazeux de l'étape (2); et

(b) on élimine de l'hydrogène sulfuré provenant d'une portion du quatrième courant de vapeur provenant de l'étape (22), on comprime alors le quatrième courant de gaz pour réaliser la pression effective de désulfuration par hydrogénation et ce courant sert de second courant gazeux de l'étape (13), la pression de déparaffinage étant de 345 à 689 kPa (50 à 100 psi) supérieur à la pression de désulfuration.

3. Procédé selon la revendication 1, dans lequel le catalyseur de désulfuration comprend un métal du groupe VIB et un métal du groupe VIII ou leurs oxydes ou leurs sulfures.

4. Procédé selon la revendication 2, dans lequel l'élimination de l'hydrogène sulfuré s'effectue dans un procédé à la MEA ou un procédé à la DEA.

5. Procédé selon la revendication 1, comprenant l'étape additionnelle suivante:

(24) extraction par entraînement à la vapeur du gasoil produit déparaffiné et désulfuré.

6. Procédé selon la revendication 2, dans lequel les conditions de déparaffinage par hydrogénation de l'étape (7) comprennent une température de 343 à 538°C (650 à $1\ 000^{\circ}\text{F}$), une pression de



1 480 à 4 928 kPa (200 à 700 psig), une VSHL de 0,5 à 4 et un débit d'hydrogène de 356 à 1 069 l/1 (2 000 à 6 000 SCF/B), et les conditions de désulfuration par hydrogénation de l'étape (18) comprennent une température de 371 à 438°C (700 à 820°F), un pressin de 4 238 à 5 617 kPa (600 à 800

psig), une VSHL de 0,4 à 4 et un débit d'hydrogène de 178 à 1 425 l/1 (1 000 à 8 000 SCF/B), la pression de déparaffinage par hydrogénation étant de 345 à 689 kPa (50 à 100 psi) supérieur à la pression de désulfuration.

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