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(54) Catalytic dewaxing process.

(57) A hydrocarbon feedstock is desulfurized in a conventional hydrodesulfurization process unit (HDS), and then conducted into a catalytic dewaxing process unit (DDW). The cascading relationship of the HDS/DDW units enables the operator of the plant to recover a substantial portion of thermal energy from a number of process streams and decreases the size of the compressor required in the plant.

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IMPROVED CATALYTIC DEWAXING PROCESS

This invention relates to an improved catalytic process of dewaxing and desulfurization of gas oils. In particular, it relates to a process wherein a feedstock is hydrodesulfurized and subsequently catalytically dewaxed through its contact with a highly siliceous ZSM-5 type porous catalyst.

Catalytic dewaxing of high-pour gas oils to low pour 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 from U.S. Patent No. 3,700,585 and its reissue, Re. 28,398. The catalytic dewaxing process disclosed in these patents is usually followed by a conventional hydrodesulfurization process (HDS) to remove substantially all sulfur from the product of the catalytic dewaxing process. As the conventional hydrodesulfurization process is usually already present in a refinery the new catalytic dewaxing unit is simply incorporated into the refinery operations upstream of the HDS process.

Prior to the development of the catalytic dewaxing process, high pour point gas 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 gas oils to the HDS process and then to the conventional solvent dewaxing process (U.S. Patents Nos. 3,520,796 and 3,617,475). It is there stated that this sequence of operations reduces pour point of the product, and produces a product with better hazing characteristics. However, in the process sequence disclosed in both patents 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 claimed advantages relate to the final product qualities.

In contrast, it has now been discovered that substantial process and cost advantages can be attained if the conventional HDS unit is followed by the catalytic distillate dewaxing process unit (herein- after 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 Figure is a flow chart of one exemplary embodiment of the invention.

According to the hydrodesulfurization process unit (HDS) is arranged in a cascading relationship with the catalytic distillate dewaxing process unit (DDW) so that a smaller booster compressor between the HDS and the DDW units is required than would have been needed if the dewaxing unit were placed upstream of the HDS unit. In addition, the cascading operation also reduces or eliminates coking in the DDW charge heater. The HDS and the DDW unit operations are completely integrated to recover a substantial amount of thermal energy from various process streams and transfer it from one unit operation to another.

The hydrodesulfurization process unit used in the present invention may be any conventionally known hydrodesulfurization process unit (HDS) used in the art. The catalyst used in the process may be any conventional hydrodesulfurization catalyst, such as a catalyst comprising a Group VIIA (chromium, molybdenum, or tungsten) metal, and a Group VIIIA metal or their oxides or sulfides. The HDS process is conducted with the catalyst under hydroprocessing conditions comprising: a hydrogen pressure of 4053 kPa (40 atmospheres) to 20772 kPa (205 atmospheres), preferably 10436 kPa (103 atmospheres) to 17327 kPa (171 atmospheres); a temperature of 345°C (650°F) to 455°C (850°F), preferably 370°C (700°F) to 440°C (820°F); a liquid hourly space velocity of 0.1 to 6.0, preferably 0.4 to 4.0. The hydrogen gas used during the process of hydrodesulfurization is circulated through the hydrodesulfurization reactor at the rate of between 178 and 2670 l/l of feed (1000 to 15,000 scf/bbl) and preferably between 178 and 1424 (1000 and 8000 scf/bbl). 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 hydrogen 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. The HDS process removes 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 gas oils, such as straight run atomospheric 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 unit operation of the process and a portion thereof is subsequently recycled, after compression, to the HDS unit operation. Only a portion, such as between 40% and 50%, of the hydrogen stream introduced into the catalytic dewaxing unit is subsequently recycled to the HDS unit, depending on the relative amounts of hydrogen required for the two units. Accordingly, the size of the booster compressor required to compress the makeup recycle gases is reduced because only half or less of the total stream of the recycle gases must be compressed to the higher pressure under which the HDS process is operating. In contrast, in an operation wherein the catalytic dewaxing process precedes the HDS process, the size of the compressor unit would have been at least double the size of that in the present process since the entire hydrogen makeup recycle stream would have to be compressed to the higher pressure of the HDS unit operation.

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

The dewaxing process unit is otherwise operated in the conventional manner of other catalytic dewaxing units such as that disclosed in U.S. Patent No. 3,700,585. Thus, the catalyst used in the dewaxing unit operation is the catalyst of the ZSM-5 type which includes the specific zeolites ZSM-5, ZSM-11, ZSM-23, ZSM-38 and ZSM-43, and is preferably ZSM-5.

The conditions of the catalytic dewaxing are those of cracking or hydrocracking operations. Typical cracking process conditions include: a liquid hourly space velocity between 0.5 and 200, a temperature between 288°C and 593°C (550°F and 1100°F), and a pressure between about subatmospheric and several hundred atmospheres. Conversely, typical hydrocracking operation conditions include: temperatures of between 343°C and 538°C (650°F and 1000°F), a pressure between 791 and 20786 kPa (100 and 3000 psig), and preferably between 1480 and 4826 kPa (200 and 700 psig), liquid hourly space velocity of between 0.1 and 10, preferably between 0.5 and 4, and the hydrogen to hydrocarbon mole ratio of between 1 and 20, preferably between 4.0 and 12. The feed introduced into the dewaxing unit reactor is modified by recycling a substantial amount of gaseous components from the low temperature separator into the catalytic dewaxing reactor. The amount of gaseous components from the low temperature separator introduced into the catalytic reactor is such that the gases constitute 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 260°C to 454°C (500°F to 850°F) under cracking process conditions, or at a temperature of 260°C to 538°C (500°F to 1000°F) at hydrocracking process conditions with virtually no increase in coke production, as compared to the amount of coke produced at conventional cracking and 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 HDS low temperature separator and, that from DDW low temperature separator, as well as make-up hydrogen.

The process will now be described in conjunction with a process flow chart of one embodiment thereof illustrated in the Figure.

The feedstock (atmospheric heavy gas oil) is received either from storage at the plant or through any other conventional transfer means, such as a direct pipeline from an unrelated unit operation in the plant or elsewhere, and is conducted at the rate of 8000 barrels per standard day (BPSD) to the feed surge and water knockout drum 101. The drum 101 is of a conventional construction known in the art and it removes substantially all of the water, if any, present in the feedstock as a residue stream R.

The feed stream, now substantially free of water, (containing not more than 300 ppm by weight of water) is pumped from the drum 101 into a heat exchanger 103, then through a 3-way valve 104, and subsequently through a heat exchanger 105 into a hydrodesulfurization charge heater 80. The heat exchanger 103 extracts heat from a stream 66 (a product stripper bottoms), while the heat exchanger 105 extracts heat from the stream 55, which is a stream obtained from the dewaxing catalytic reactor effluent. Before entering the HDS heater 80, the feed is mixed in line with preheated HDS recycle gas (stream 17). On the basis of the aforementioned feedstock flow rate, the heat exchanger 103 transfers 4.103×10^6 J/S (14 million BTU/hr) to the feed stream 51; the heat exchanger 105 transfers 6.741×10^6J/S (23 million BTU/hr), thus increasing the temperature of the stream from 182°C (360°F) immediately before the 3-way valve 104 to 371°C (700°F) immediately after exiting the heat exchanger 105. The temperature of the preheated HDS recycle gas stream 17) is 332°C (630°F). Accordingly, after this stream is mixed with the stream 52, the temperature of the combined stream is 338°C (640°F), as that combined stream enters the HDS charge heater 80. In the charge heater 80, 1.172×10^6J/S (4 million BTU/hr) are transferred to the combined oil feed and HDS recycle gas (stream 21). The charge heater 80 is also of a conventional construction, such as box-type with vertical tubes. The heated stream 23 exiting the charge heater has a temperature of 371°C (700°F). It is then conducted to a downflow fixed bed reactor 108 operating at the pressure of 4826 kPa (700 psig). The reactor 108 is also of a conventional construction for hydrodesulfurization units well known in the art.

The HDS reactor effluent, stream 27, has a temperature of 366°C to 393°C (690°F to 740°F) and it is used to preheat its recycle gas in the heat exchanger 81 so that the stream 26 exiting the heat exchanger has a temperature of 332°C (630°F). This stream is then cooled in the low pressure steam boiler 84 to the temperature at which the high temperature separator 109 is operated. The heat exchanger 84 extracts 2.051 x 10^6J/S (7.0 million BTU/hr) from the stream 26. The cooled stream 26 is now conducted to the high temperature separator 109, operating at 288°C (550°F) and 4343.7 kPa (630 psig). The separater 109 separates the stream 26 into a stream 28, a liquid flowing at the rate of 7700 BPSD, and a stream 29, a gaseous stream, comprising essentially hydrogen and lower hydrocarbons, including alkanes and alkenes of C_1 to C_4 flowing at the rate of 10.0 million SCFD.

The liquid stream 28 is combined with a preheated recycle gas (stream 78) into a stream 3 which is introduced into the catalytic dewaxing process charge heater 111. The stream 3 has a temperature of 271°C (520°F). The catalytic dewaxing process charge heater 111 operates at 4275 kPa (620 psig) to add 8.792 x 10^6J/S (30 million BTU/hr) to the stream 3. The heated stream 11 exiting the heater 111 has a temperature of 438°C (820°F).

The HDS high temperature separator vapor, stream 29, is used to preheat low temperature separator vapor after it has gone through an amine scrubber 102 to remove hydrogen sulfide and ammonia. The high temperature separator vapor is further cooled to the temperature at which the low temperature separator 110 operates. Thus, the high temperature separator vapor stream 29 is conducted to the heat exchanger 82, wherein its temperature is decreased to 193°C (380°F), and then to a water cooler 83, wherein its temperature is reduced to

37.8°C (100°F). The heat exchanger 83 removes 1.172 x 10^6J/S (4.0 million BTU/hr) from the stream 29.

The low temperature separator 110 operates at 37.8°C (100°F) and 4137 kPa (600 psig). The HDS low temperature separator vapor (stream 32) is charged to an amine scrubber 102, while the liquid stream 31, an unstabilized naphtha, can be charged to any conventional stabilizer or stripper. The flow rate of the stream 31 is 500 BPSD.

The HDS low temperature separator vapor is conducted to a vessel 120 which is a knock-out drum, to remove any entrained amines in the vapor. From the vessel 120, the vapor is conducted through a heat exchanger 82, as discussed above, and then to a heat exchanger 104, where it is further heated by the catalytic dewaxing reactor bottoms effluent, stream 55. After leaving the heat exchanger 104 which is sized at 1.026 x 10^6J/S (3.5 million BTU/hr), the vapor has a temperature of 388°C (stream 41). Stream 41 is then combined in-line with the heated stream 11 from the catalytic dewaxing charge heater 111 and then to the catalytic dewaxing reactor 117. The stream 54 entering the reactor 117 has a temperature of 427°C (800°F) and it is introduced into the reactor 117 at 4137 kPa (600 psig). The reactor 117 is of a conventional construction used in prior art for such catalytic dewaxing unit operations. Thus, the reactor 117 is filled with a ZSM-5 type catalyst, and equipped with an appropriate distribution system for mixed phase (vapor and liquid) feeds.

Stream 54 is introduced into the reactor 117 at the rate of 7700 BPSD. Stream 41 flows at the rate of 9.0 million SCFD.

HDS high temperature separator liquid, stream 28, is mixed in-line with preheated recycle gas (stream 78) from the catalytic dewaxing unit before entering the catalytic dewaxing unit charge heater 111. The heater 111 is sized at 8.79 x 10^6J/S (30 million BTU/hr). The temperature of stream 11 exiting the heater is 437°C (820°F). Conversely, the temperature of the combined reactor charge (stream 3) before the introduction thereof into the heater 111 is 271°C (520°F).

The relative pressure levels of HDS low temperature separator vapor and the catalytic dewaxing reactor dictate that separator vapor cannot be charged through the heater 111 without a booster compressor. Therefore, it is preheated in the heat exchanger 104 which is sized at 1.026 x 10^6J/S (3.5 million BTU/hr) to 388°C (730°F).

The liquid/vapor mixture heated in the catalytic dewaxing unit charge heater must obtain high enough temperature in order to produce a reactor charge having a temperature of 427°C (800°F) at the end of the operating cycle. At the same time, however, the temperature in the charge heater is limited due to the tendency of the heated stock to form coke in the heater.

The tendency to form coke in the heater is either diminished or almost completely eliminated by supplying a relatively large volume of gaseous components (recycle gas-stream 78) into the heater.

The catalytic dewaxing unit reactor effluent (stream 55) is used to heat HDS low temperature separator vapor (stream 37) in the heat exchanger 104, and then is also used to preheat gas oil charge in the heat exchanger 105. The heat exchanger 105 is controlled by means of a cold feed bypass to maintain a constant temperature (260°C to 316°C) of the high temperature separator 130.

The liquid (stream 63) from the high temperature separator 130 is charged directly to product stripper 132. The vapor stream 56 from the high temperature separator 130 is utilized to preheat DDW recycle gas in the heat exchanger 113, which lowers the temperature of the vapor stream to 221°C (430°F). The vapor stream is then conducted to a heat exchanger 106 wherein it is cooled by liquid stream 44, obtained from the low temperature DDW separator 134, to 171°C (340°F), and it is subsequently cooled in a heat exchanger 106 to 37.8°C (100°F). The heat exchanger 106 extracts 2.931 x 10^6J/S (10 million BTU/hr) from the vapor stream, while the heat exchanger 136 is sized to 1.172 x 10^6J/S (4.0 million BTU/hr). The low temperature separator 134 operates at 37.8°C (100°F) and 3241 kPa (470 psig).

The heated low temperature separator liquid, stream 76, is charged to the product stripper 132. If necessary, low temperature separator vapor, stream 58, is charged to an amine scrubber to remove hydrogen sulfide and ammonia. After the optional scrubber, part of the vapor is sent to fuel gas system (stream 48) at the rate of 1,800,000 standard cubic feet per day (SCFD), and the remainder of the vapor is recycled through a compressor knock-out drum 137 into the HDS unit operation and the DDW unit operation.

Hydrogen makeup, stream 15, is added at the rate of 2,000,000 SCFD to the DDW recycle gas stream 59 to meet the process requirements for both HDS and DDW units. The combined stream of the hydrogen makeup and the recycle gas is conducted to a compressor knock out drum 137, wherein liquid is removed, and it then is conducted into a compressor unit 138 where its pressure is increased to 4482 kPa (650 psig). The compressor 138 is used only to raise the pressure for the DDW unit. Part of the compressed gas stream 81, (50%-60%) is recycled to the DDW unit, while the rest, stream 13, (40%-50%) is further compressed by compressor 140 to 5102 kPa (740 psig), the level required for the HDS unit operation. Knock-out drum 139 removes any liquids which may be present in the stream 13. Consequently, the amount of compression required for the entire HDS/DDW cascade process scheme is reduced, since only a portion of the recycle gas (40% to 50%) is compressed to the compression level required by the HDS unit operation.

Both the high temperature DDW separator liquid stream 63, and the heated DDW low temperature separator liquid, stream 76, are charged to the product stripper 132. The product stripper is of a conventional construction, comprising about 20 trays. The stripper is provided with an overhead condenser 107 which removes 2.345 x 10^6J/S (8.0 million BTU/hr) and with an accumulator 142, which operates at 37.8°C (100°F) and 586.1 kPa (85 psig). A steam stream 73 is injected into the bottom of the stripper. Stream 73 has a temperature of 288°C (550°F) and a pressure of 1241 kPa (180 psig). Overhead vapor (stream 67 flowing at the rate of 400,000 SCFD), if necessary, is charged to an amine unit to remove hydrogen sulfide and ammonia, and finally to a fuel gas system.

Unstabilized naphtha is produced as overhead liquid product stream 68 at the rate of 1300 BPSD and it is charged to a stabilizer. Water is drained from the boot of the accumulator 142 as stream 74 and is sent to the sour water system. The dewaxed product is withdrawn from the bottom of the stripper as the stream 66 at 249°C (480°F). This stream is first used to preheat the feedstock in the heat exchanger 103 and it is then further cooled in a heat exchanger 108 to 43.3°C (110°F). The heat exchanger 108 removes 1.026 x 10^6J/S (3.5 million BTU/hr) from the stream 69, a cooled stream 66.

CLAIMS:

1. A process for dewaxing at least one petroleum feedstock, comprising hydrodesulfurizing the feedstock and subsequently conducting the desulfurized feedstock to a catalytic dewaxing unit, wherein it is contacted with a highly siliceous ZSM-5 type porous crystalline material.

2. A process according to claim 1 wherein the petroleum feedstock has a boiling point of at least 176.7°C (350°F).

3. A process according to Claim 2 wherein the highly siliceous porous crystalline material is ZSM-5.

4. A process according to Claim 2 wherein a make-up hydrogen stream is introduced into the process downstream of the point of contacting the desulfurized feedstock with the highly siliceous porous crystalline material of the zeolite ZSM-5 type.

5. A process according to Claim 4 wherein the hydrodesulfurizing step is conducted at a temperature of 343°C to 454°C (650°F to 850°F) and at a pressure of 4137 to 20684 kPa (600 to 3000 psig), and the step of contacting the desulfurized feedstock with the crystalline material, is conducted under cracking process conditions, is carried out at a temperature of 288°C to 538°C (550°F to 1000°F), at a pressure of 689.5 to 20684 kPa (100 to 3000 psig), and at liquid hourly space velocity of 0.5 to 200, and, if conducted under hydrocracking process conditions, it is carried out at a temperature of 343°C to 538°C (650°F to 1000°F), a pressure of 689.5 to 20684 kPa (100 psig) to 3000 psig, liquid hourly space velocity of 0.1 to 10, and hydrogen to hydrocarbon mole ratio of 1 to 20.

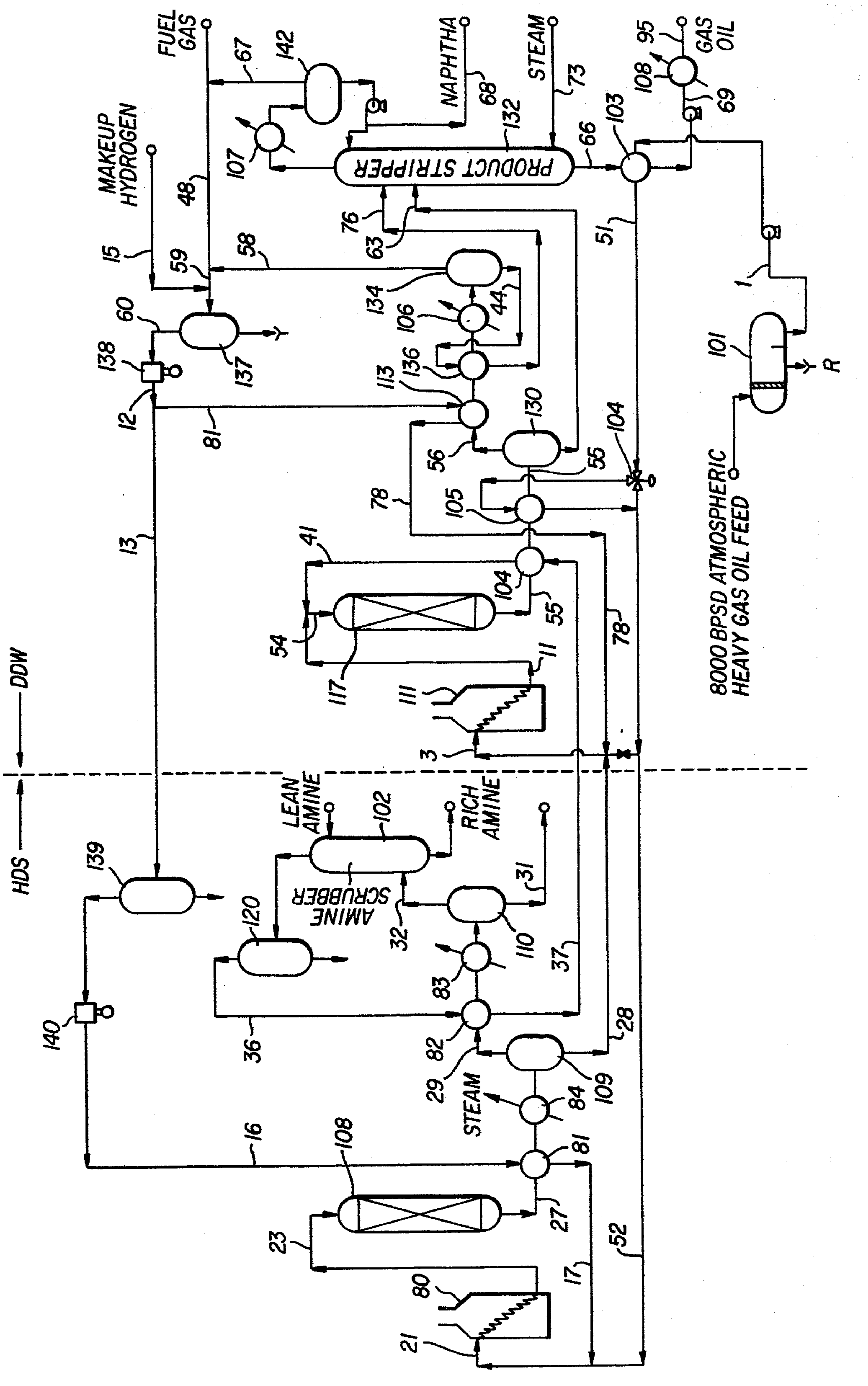
6. A process according to Claim 5 wherein at least 40% by volume of the total hydrogen stream is conducted from the catalytic dewaxing step to the hydrodesulfurizing step.

7. A process according to Claim 6 wherein 50% by volume of the total hydrogen stream is conducted from the catalytic dewaxing step to the hydrodesulfurization step.

8. In a catalytic process for dewaxing at least one petroleum feedstock comprising contacting the petroleum feedstock with a highly siliceous ZSM-5 type zeolite porous crystalline material at a temperature of 288°C to 593°C (550°F to 1100°F) and at a pressure of 103 to 20684 kPa (15 psig to 3000 psig), the improvement which comprises desulfurizing the petroleum feedstock prior to the introduction thereof into the catalytic process so that the feed of the catalytic process contains less than 3% by weight of sulfur.

9. A process according to Claim 8 wherein the petroleum feedstock is desulfurized by contacting the feedstock with a hydrodesulfurization catalyst and hydrogen at hydrogen pressure of 6895 to 20684 kPa (1000 to 3000 psig), at a temperature of 343°C to 454°C (650°F to 850°F), thereby removing 50% to 99.5% by weight of sulfur originally present in the feedstock.

10. A process according to claim 9 wherein the feedstock subjected to desulfurization is a high pour gas oil.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EUROPEAN SEARCH REPORT

0128250

Application number

EP 83 30 3307

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
X,Y	EP-A-0 028 062 (MOBIL OIL) * Claims 1-7 *	1-10	C 10 G 65/04
Y	FR-A-2 184 684 (U.O.P.) * Figure; claims 1-6 *	6,7	
Y	DE-A-1 470 533 (ESSO RESEARCH) * Figure; claims 1-7 *	6,7	
A	US-A-4 100 056 (REYNOLDS) * Figure; column 1, line 54 - column 2, line 53 *	1	
D,A	US-A-3 700 585 (CHEN et al.) * Claims 1-11 *		
A	FR-A-2 233 384 (MOBIL OIL) * Claims 1-6 *		

TECHNICAL FIELDS SEARCHED (Int. Cl. ³)

C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-03-1984	MICHIELS P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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