

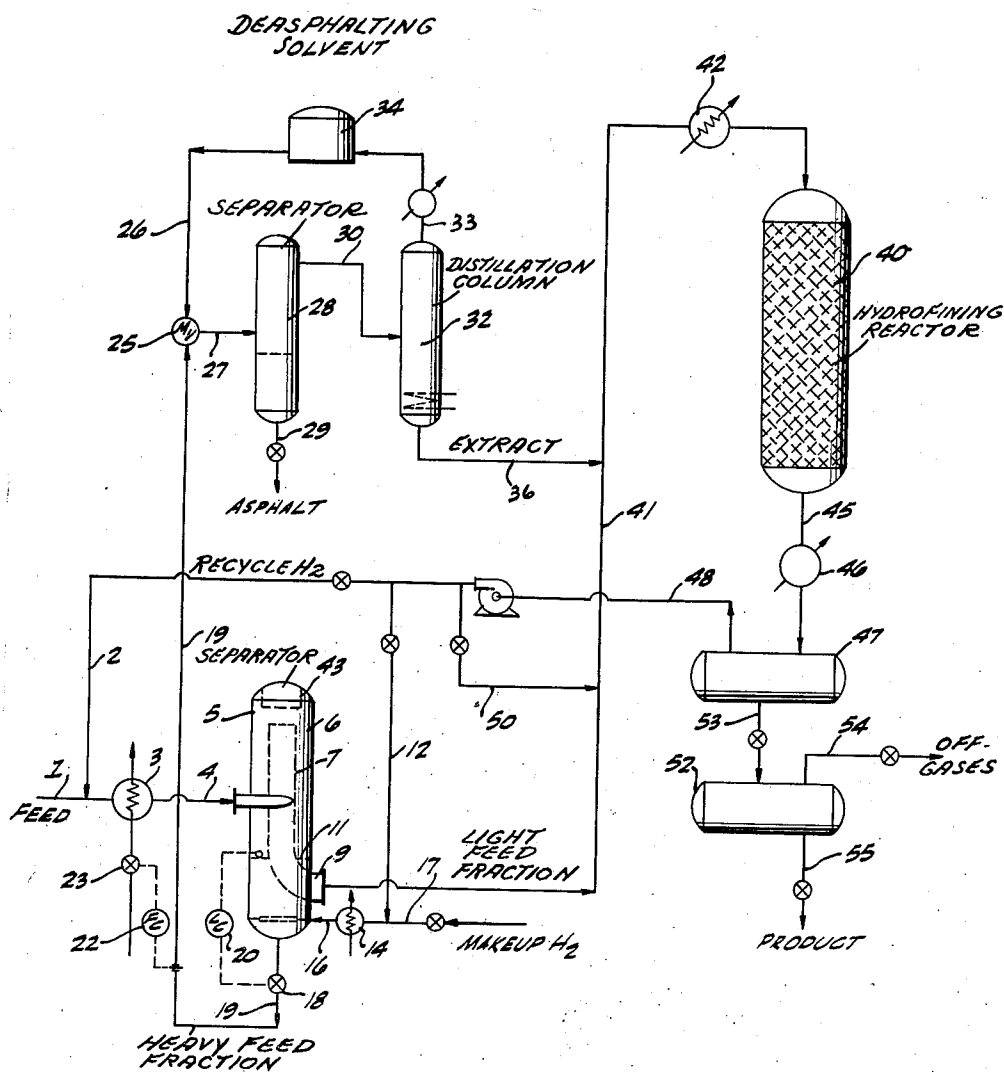
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HYDROREFINING OF HEAVY MINERAL OILS

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HYDROREFINING OF HEAVY MINERAL OILS

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This invention relates to methods for pretreating heavy oils, and especially crude oils, whereby they may be subsequently treated in a catalytic hydrorefining operation with a minimum deposition of deactivating deposits upon the catalyst. In broad aspect, the invention consists in first subjecting the feed oil to a combined vaporization-deasphalting step in the presence of the hydrogen-containing recycle gas from the hydrorefiner, and at substantially the pressure prevailing in the hydrorefiner. The asphaltic residue from the vaporization step is then subjected to a conventional liquid phase deasphalting procedure, using preferably a lower paraffin hydrocarbon to extract from said residue an additional quantity of oil which is then subjected to hydrorefining along with the gaseous mixture derived from the vaporization step.

The principal objective of the invention is to provide means for hydrorefining crude oils, or heavy fractions thereof, while avoiding to a maximum extent the normally occurring deposition of coke and other deactivating deposits upon the catalyst. Another objective is to provide methods for removing the precursors of such deactivating deposits from the feed oil, while maintaining maximum over-all liquid yields. Still another object is to achieve maximum vaporization of the feed oil by pressure stripping with the hydrorefiner recycle gas in such manner as to minimize utility costs. Specifically, it is desired to avoid the expensive depressuring and repressuring of recycle gas. Other objects will be apparent from the more detailed description which follows.

The process of this invention is adapted mainly for the treatment of total crude oils, or reduced crude oils. It is especially adapted for the treatment of crude shale oils, i.e. the full-range oil produced directly from the retorting of shale rock. Crude shale oils present difficult problems in refining in that they contain a high proportion of asphaltenes and carboids and up to about 4% of nitrogen in the form of organic nitrogen compounds. In addition, metals may be present in the form of porphyrin-metal complexes or other organometallic compounds. Crude shale oils also possess an unusually high pour point. For example, the crude oil from Colorado shale is normally a solid at room temperature, and its pour point may be in excess of 100° F.

From the standpoint of refining flexibility, the most desirable initial treatment for such oils consists of catalytic hydrorefining to decompose nitrogenous compounds and sulfur compounds, to hydrogenate asphaltenes and carboids, to decompose organo-metallic compounds, and in general to improve the color and handleability of the oil for subsequent refining procedures such as cracking, reforming and the like. The first major difficulty encountered in attempting to hydrorefine such oils consists in the tendency of the oil to deposit deactivating solids upon hot catalytic surfaces when the feedstock is brought into contact therewith. The exact nature of the deposit-forming constituents is not known, but they may comprise any of the above-noted organo-metallic compo-

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nents, asphaltenes, carboids, and/or nitrogenous compounds.

It has been found that conventional pretreatment steps such as vacuum distillation, thermal coking, or liquid phase deasphalting using lower paraffins, do not entirely solve the problem of removing such deposit-forming materials, unless severe pretreating conditions are employed entailing sacrificial yields. While the light fractions from thermal coking do not cause difficulty, the heavier coker distillates still tend to form deposits, as does the raffinate from conventional deasphalting of the total crude oil, using for example n-pentane as the deasphalting agent. As a corollary to the above, thermal coking and liquid phase deasphalting are subject to the disadvantage that relatively low liquid yields are obtained if those treatments are made sufficiently severe or exhaustive to give a nondeposit-forming distillate or raffinate. It is hence highly desirable to provide a more selective method for removing the deposit-forming constituents without removing all of the heavier components, some of which do not tend to form deposits.

In the case of vacuum distillation, it has been found that only about 40–50% by volume of nondeposit-forming distillate can be economically produced without employing cracking temperatures. The residue, constituting the vacuum distillation bottoms, must then be subjected to coking or deasphalting with attendant disadvantages above noted. By going to extremely high vacuum, higher distillate yields may be obtained, but such distillates then will include some of the heavier, deposit-forming bodies. The process of this invention is designed to overcome the major disadvantages of each of the foregoing processes.

While as above indicated, conventional liquid phase deasphalting of the total crude oil is ineffective for removing all deposit-forming components unless exhaustive deasphalting conditions are employed, resulting in low raffinate yields, it has now been found that the asphaltic concentrate produced in the vaporization step of this invention may be subjected to such deasphalting to recover as much as 50–75% thereof as suitable feed to the hydrorefining step. Since the hydrocarbons recovered in the deasphalting step are extremely high boiling, their recovery in the vaporization step is impractical, and moreover the withdrawal of some liquid phase from the vaporization step is a mechanical convenience in that it functions as a vehicle for the asphaltic materials which would normally be solid or semisolid. It is hence preferred to remove from about 1–25% by volume of the initial feedstock as bottoms from the vaporization step, and to effect further recovery of nondeposit-forming hydrocarbons therefrom by liquid phase deasphalting.

While it has been indicated that crude oils, and especially shale oils, are the feeds of major concern herein, it is not intended to preclude the use of heavier distillate fractions, some of which present similar problems in catalytic hydrorefining, though to a decidedly lesser extent. In general, any crude oil, heavy distillate, or other heavy fraction having an end boiling point in excess of about 700° F. may be employed. It is also contemplated that mixtures of crude oils and distillate fractions may be employed, as well as mixtures of petroleum crudes and crude shale oil.

The crude shale oil described herein may be produced for example by the retorting procedures described in U.S. Patents 2,501,153, 2,640,015, and 2,640,019. In general, the retorting procedure consists in initiating combustion in a body of moving shale rock, and utilizing the hot combustion gases to educt the oil from uncombusted shale rock upstreamwardly.

The process of this invention will now be described in more detail in connection with the attached flow sheet,

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which is intended merely to illustrate the principal modifications, but is not intended to be limiting in scope. The initial feedstock is brought in through line 1, wherein it is mingled with the major portion of hydrorefiner recycle gas from line 2. This combined stream is then preheated to a temperature sufficient to achieve the desired vaporization of oil in preheater 3. This temperature may range anywhere between about 200° and 850° F. but is preferably within about 100° F. of the temperature to be employed in the subsequent hydrorefining step.

The mixed phase effluent from preheater 3 is then transferred via line 4 to a centrifugal separator 5, which may be of the Webre cyclone type. This unit consists of an outer cylindrical shell 6 enclosing an axially positioned open-ended vapor outlet conduit 7 which extends upwardly to near the top of shell 6, and terminates at its lower end in vapor outlet port 9, located below the center portion of shell 6. The feed inlet line 4 enters shell 6 tangentially thereto at a point approximately midway between the top of vapor outlet conduit 7 and the vapor outlet port 9. The liquid portion of entering feed spirals downwardly inside shell 6 by centrifugal force, and forms a liquid level indicated approximately at 11. The entering gas phase spirals upwardly around vapor outlet conduit 7 and enters the top thereof and thence flows downwardly and out through vapor outlet port 9. In this manner, the liquid and gas phases are rapidly and effectively separated, and maximum vaporization is obtained. An additional stream of recycle gas may if desired be diverted through line 12, preheated in heater 14 to a temperature 50° to 100° F. in excess of that prevailing in separator 5, and then admitted via line 16 into the lower extremity of separator 5. By this means, additional vaporization by stripping is obtained. Any fresh makeup hydrogen required in the hydrorefining operation is preferably admitted via line 17 at this point in order to utilize to a maximum extent its stripping capacity.

The pressure in separator 5 is preferably maintained at substantially that prevailing in the hydrorefiner 40, hereinafter described. Specifically, in order to obtain a maximum recovery of oil free from deposit-forming constituents, it is preferred that the pressure should be within about 300 p.s.i.g. above or below the hydrorefiner pressure. However, other pressures may be used to somewhat less over-all advantage.

The liquid phase accumulating in separator 5 is withdrawn via valve 18 and line 19 more or less continuously in response to liquid level controller 20. The proportion of feed which is vaporized in separator 5 may be controlled in response to any desired process variable such as temperature, or relative recycle gas volume admitted thereto. In the modification illustrated, feed temperature is the controlling variable; when the flow of liquid in line 19 becomes too great, indicating insufficient vaporization, flow-controller 22 opens valve 23 to admit additional heating agent to feed preheater 3. Too small a flow rate in line 19, indicating excessive vaporization, is corrected by a reduction in temperature.

Ordinarily, the liquid stream removed in line 19 will comprise only about 1-25% by volume of the total liquid feed. It is an important feature of this invention that the 75-99% vapor phase fraction removed from separator 5 is produced under deasphalting conditions substantially identical to those prevailing in the hydrorefiner, hence totally excluding therefrom any deposit-forming constituents. To the best of our knowledge this objective cannot be achieved by other methods such as vacuum distillation, coking, or conventional liquid phase deasphalting. An overhead or raffinate of analogous proportions from such conventional procedures still may contain deposit-forming constituents which would rapidly deactivate the catalyst in the hydrorefiner. This result is achieved moreover with a minimum of utility requirements in that the major heat input is utilized in the sub-

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sequent hydrorefining step, and there is little pressure drop in the system.

The liquid phase withdrawn through line 19 will normally consist of viscous heavy ends together with suspended asphaltene and carboids precipitated by the deasphalting action of the gas phase in separator 5. This liquid phase is then transferred via line 19 to mixing valve 25, wherein it is mingled with the desired solvent from line 26. The solvent may comprise any relatively low-boiling paraffin hydrocarbon as for example propane, butane, pentane, hexane, heptane, octane, and the like. Either the straight-chain or branched-chain paraffins may be employed, and mixtures of one or more of such components of the same or different boiling points may be used. The amount of solvent to be used may vary between about 0.5 and 20 volumes per volume of oil admitted to mixing valve 25. Normally when n-pentane is used for example, suitable proportions range between about 1 and 5 volumes per volume of oil. Atmospheric temperatures and pressures may be utilized, but preferably somewhat elevated temperatures are desirable in order to keep the heavy oil in liquid phase. Temperatures between about 50° and 300° F. may be employed. The preferred boiling range for the solvent lies within the limits of about -50° and +450° F.

The mixture of solvent and oil is then transferred via line 27 to liquid-liquid phase separator 28, wherein the solvent forms a supernatant phase. The lower phase, consisting of heavy asphaltic oil is withdrawn via line 29, and may be blended with fuel oil, or put to any conventional use.

The supernatant solvent phase in separator 28 is withdrawn via line 30 and transferred to distillation column 32 wherein the solvent is removed overhead via line 33, and recycled to mixing valve 25 via storage tank 34 and line 26. The bottoms from column 32 is withdrawn via line 36, and is utilized in the hydrorefining operation to be subsequently described.

Returning to separator 5, the gaseous portion of the feed is introduced therein at a considerable velocity, and tends to spiral upwardly around outlet conduit 7, entering the top thereof and flowing downwardly and out through vapor outlet port 9, and thence into hydrorefiner 40 via line 41 and preheater 42, along with the bottoms from column 32. In order to prevent entrainment of liquid in the gas phase from separator 5, a depending cylindrical drip ring 43 is provided in the top of separator 5.

In hydrorefiner 40 the pretreated mixed feed is contacted with a suitable sulfative hydrorefining catalyst under conditions of hydrorefining. The catalyst may be disposed in a fixed stationary bed, or the various moving bed, or fluidized bed techniques may be employed. Generally, the fixed bed technique is most satisfactory. The catalyst may comprise any of the oxides and/or sulfides of the transitional metals, and especially an oxide or sulfide of a group VIII metal (particularly iron, cobalt or nickel) mixed with an oxide or sulfide of a group VIB metal (preferably molybdenum or tungsten). Such catalysts may be employed in undiluted form, but preferably are distended and supported on an adsorbent carrier in proportions ranging between about 2% and 25% by weight. Suitable carriers include in general the difficultly reducible inorganic oxides, e.g. alumina, silica, zirconia, titania, clays such as bauxite, bentonite, etc. Preferably the carrier should display little or no cracking activity, and hence highly acidic carriers are generally to be avoided. The preferred carrier is activated alumina, and especially activated alumina containing about 3-15% by weight of coprecipitated silica gel.

The preferred hydrorefining catalyst consists of cobalt oxide plus molybdenum oxide supported on silica-stabilized alumina. Compositions containing between about 2% and 8% of CoO, 4% and 20% of MoO₃, 3% and 15% of SiO₂, and the balance Al₂O₃, and wherein the

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mole-ratio of CoO/MoO_3 is between about 0.2 and 4, are specifically preferred. These catalysts are preferably prepared by alternate impregnation with aqueous solutions of ammonium molybdate and cobalt nitrate, as described in U.S. Patent No. 2,687,381.

Suitable hydrorefining conditions are as follows:

	Operative	Preferred
Temperature, ° F.	600-875	650-800
Pressure, p.s.i.g.	100-5,000	400-2,000
Liquid hourly space velocity	0.5-15	1-10
Hydrogen ratio, s.c.f./bbl.	300-8,000	500-5,000

Within the above operating conditions, the specific hydrorefining conditions selected should be such as to meet required product specifications.

The product from hydrorefiner 40 is withdrawn via line 45, condensed in cooler 46 and transferred to high-pressure separator 47. Hydrogen-rich recycle gas, containing minor amounts of light hydrocarbon gases, is withdrawn via line 48, and sufficient thereof is diverted through lines 2 and 12 to separator 5 to achieve the ends above described. Any remaining portion of recycle gas not utilized in separator 5 may be recycled directly via lines 50 and 41.

The liquid product accumulating in separator 47 may then be flashed into low-pressure separator 52 via line 53. Low-pressure off-gas is withdrawn via line 54, and liquid product via line 55. This liquid product is then suitable for use in conventional refining units as for example distillation columns, catalytic cracking units, catalytic reforming units, catalytic hydrocracking, and the like.

The following example is cited to illustrate one practical application of the process to a typical Colorado crude shale oil, but manifestly it is not intended that this should be limiting in scope.

Example

Feed characteristics.—Gravity, ° API, 20.4; total nitrogen, 1.84 wt. percent; sulfur, 0.72 wt. percent; Ramsbottom carbon residue, 3 wt. percent; pour point, 90° F.; initial boiling point, 346° F.; 60% boiling point, 700° F.

Hydrorefining catalyst.—3% CoO plus 9% MoO_3 supported on $\frac{1}{4}$ " pellets of silica-stabilized alumina (5% SiO_2 -95% Al_2O_3), prepared by impregnating pelleted carrier first with aqueous ammonium molybdate, then with aqueous cobalt nitrate, drying and calcining.

The total feed is blended with 3,000 s.c.f./bbl. of hydrogen-rich recycle gas, and introduced into cyclone separator 5 at a temperature of 825° F. and pressure 2,200 p.s.i.g. An additional stream of fresh makeup hydrogen is introduced via line 16 at 850° F., and at the rate of 1,000 s.c.f./bbl. of initial feed. Liquid bottoms product is withdrawn at the rate of 15 barrels per 100 barrels of fresh feed.

The bottoms product is subjected to pentane deasphalting at 75° F. using 2 volumes of pentane per volume of feed thereto. Upon distilling off pentane from the resulting extract phase, 85% by volume of the separator bottoms is recovered for hydrorefining. The asphalt phase amounts to about 2% of the fresh feed.

The vapor phase from separator 5 is then blended with the solvent-free extract from the deasphalting step. The blend is then preheated to about 700° F. and subjected to hydrorefining at an average bed temperature of 800° F., pressure 2000 p.s.i.g., hydrogen ratio 5,000 s.c.f./bbl., and liquid hourly space velocity 1.0. The product is recovered in 106% yield, contains about 0.11% nitrogen and 0.037% sulfur, and has a gravity of 37.3° API.

Operation under the above conditions can be continued for several weeks without shutdown for catalyst regeneration, and without substantial decline in product quality. When the raw crude oil is used directly in the hydrorefiner, plugging of the reactor and catalyst deactivation require shutdown within a few hours, or days at the most. When

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the feed to the hydrorefiner consists of a 98% fraction of the crude oil, obtained by vacuum distillation with pentane deasphalting of the bottoms, the catalyst life is improved as compared to using the crude oil, but not to the extent obtained when using the 98% feed fraction prepared as described in the foregoing example.

The foregoing description of specific methods and materials for use in this invention is not intended to be limiting in scope except where indicated. Many variations will occur to those skilled in the art and all such variations which yield essentially the same result are intended to be included. The true scope of the invention is intended to be embraced within the following claims.

We claim:

1. In a process for the catalytic hydrorefining of a high-boiling mineral oil feedstock, wherein the conditions of hydrorefining and the feedstock are such that said catalyst would normally be rapidly deactivated by the deposition of solid materials on the catalytic surfaces, the improved method of pretreatment to avoid such deactivation which comprises subjecting said feedstock to partial vaporization in equilibrium with hydrogen-rich recycle gas from said hydrorefining, the conditions of temperature, pressure and hydrogen ratio in said partial vaporization step being adjusted so as to vaporize between about 75% and 99% of said feedstock, subjecting the liquid residue from said partial vaporization to liquid-liquid extraction with a paraffinic solvent to produce a highly asphaltic raffinate and a nonasphaltic extract, separating said extract from said raffinate, recovering dissolved oil from said extract, blending said recovered oil with the vapor phase from said partial vaporization step and subjecting the resulting blend to said catalytic hydrorefining.

2. A process as defined in claim 1 wherein said feedstock is essentially a crude oil.

3. A process as defined in claim 1 wherein said feedstock is essentially a crude shale oil.

4. A process for hydrorefining a feedstock which is essentially a full-range crude oil, which comprises first subjecting said feedstock to partial vaporization in equilibrium with hydrogen-rich recycle gas derived from the hydrorefining step hereinafter defined, said partial vaporization being carried out at a temperature within about 100° F., and at a pressure within about 300 p.s.i.g. of the temperature and pressure prevailing in the hydrorefining step hereinafter defined, thereby producing a gas phase comprising between about 75% and 99% of said feed oil and a liquid phase comprising about 1% to 25% thereof, separating said liquid phase and subjecting the same to liquid-liquid extraction with a lower paraffinic solvent to produce a highly asphaltic raffinate and a nonasphaltic extract, recovering dissolved oil from said extract, blending said recovered oil with said gas phase, and then subjecting the resulting blend to hydrorefining at a temperature between about 600° and 875° F., a pressure between about 100 and 5000 p.s.i.g. and a hydrogen ratio between about 300 and 8,000 standard cubic feet per barrel of liquid feed, and in the presence of a hydrorefining catalyst, cooling the product from said hydrorefining step and condensing the major portion thereof at substantially the pressure prevailing in said hydrorefining zone, thereby producing a supernatant hydrogen-rich recycle gas phase, and contacting at least a portion of said recycle gas phase with said initial feed to effect partial vaporization as above described.

5. A process as defined in claim 4 wherein said hydrorefining catalyst consists essentially of a minor proportion of cobalt oxide plus molybdenum oxide supported on a carrier which is predominantly activated alumina.

6. A process as defined in claim 4 wherein said solvent boils between about -50° and 450° F.

7. A process as defined in claim 4 wherein said feedstock is essentially a crude shale oil.

8. A process for hydrorefining a feedstock which is essentially a full-range crude oil, which comprises first

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subjecting said feedstock to partial vaporization in equilibrium with (1) hydrogen-rich recycle gas derived from the hydrorefining step hereinafter defined, and (2) fresh makeup hydrogen required for said hydrorefining step, said partial vaporization being carried out at a temperature within about 100° F., and at a pressure within about 300 p.s.i.g. of the temperature and pressure prevailing in the hydrorefining step hereinafter defined, thereby producing a gas phase comprising between about 75% and 99% of said feed oil and a liquid phase comprising about 1% to 25% thereof, separating said liquid phase and subjecting the same to liquid-liquid extraction with a lower paraffinic solvent to produce a highly asphaltic raffinate and a nonasphaltic extract, recovering dissolved oil from said extract, blending said recovered oil with said gas phase, and then subjecting the resulting blend to hydrorefining at a temperature between about 600° and 875° F., a pressure between about 100 and 5000 p.s.i.g. and a hydrogen ratio between about 300 and 8000 standard cubic feet per barrel of liquid feed, and in the pres-

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ence of a hydrorefining catalyst, cooling the product from said hydrorefining step and condensing the major portion thereof at substantially the pressure prevailing in said hydrorefining zone, thereby producing a supernatant hydrogen-rich recycle gas phase, and contacting at least a portion of said recycle gas phase with said initial feed to effect partial vaporization as above described.

9. A process as defined in claim 8 wherein the feedstock in said partial vaporization step is first equilibrated with said recycle gas and the resulting liquid phase is then stripped with said fresh makeup hydrogen.

10. A process as defined in claim 9 wherein the rate of injection of fresh makeup hydrogen in said stripping operation is the same as the rate of hydrogen consumption in said hydrorefining step.

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