Oct. 14, 1952 P. W. CORNELL 2,614,066

HYDRODESULFURIZATION OF PETROLEUM HYDROCARBONS

Filed May 10, 1949 2 SHEETS—SHEET 1

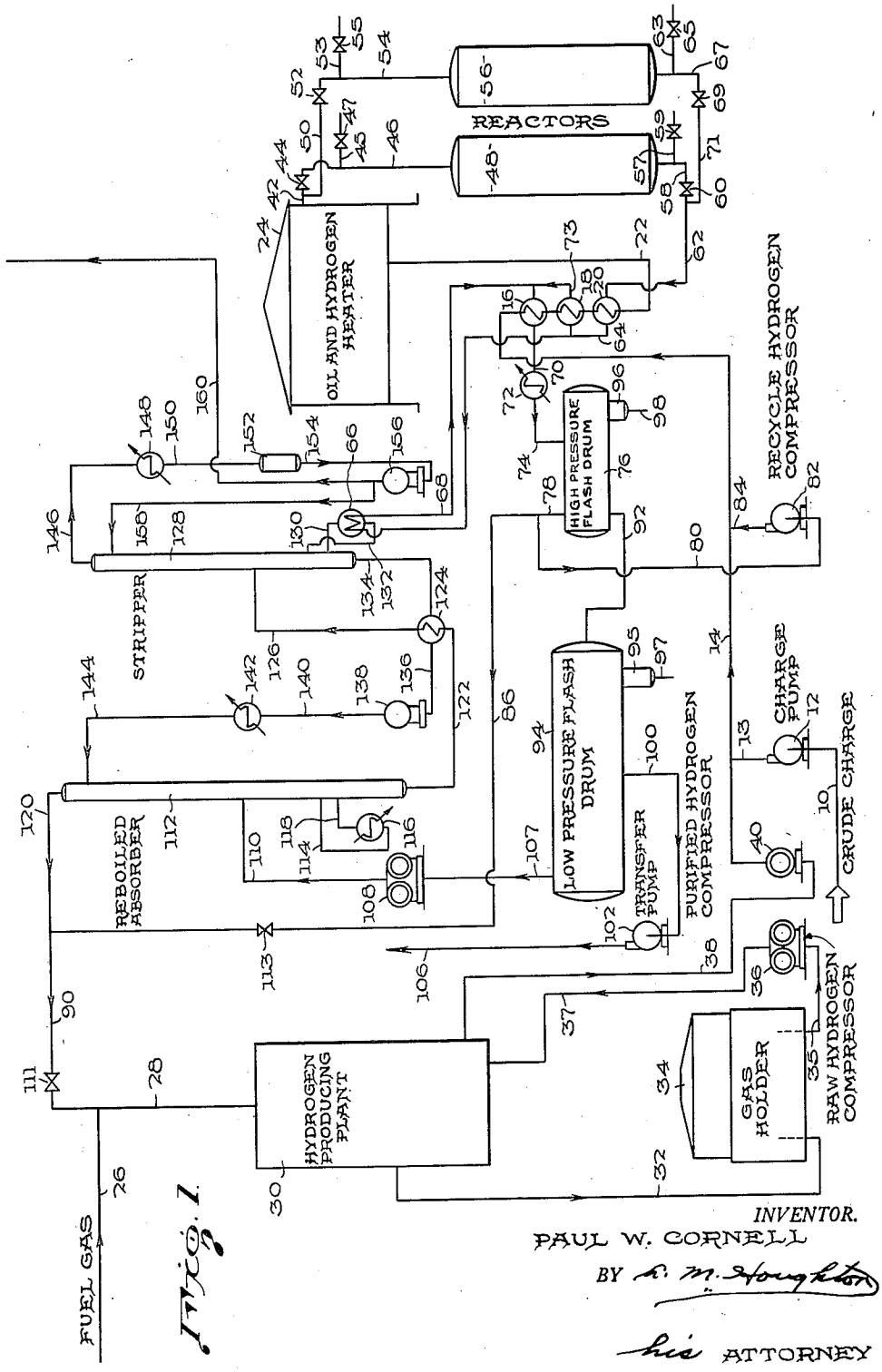


Fig. 1.

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HYDRODESULFURIZATION OF PETROLEUM HYDROCARBONS

Filed May 10, 1949 2 SHEETS—SHEET 2

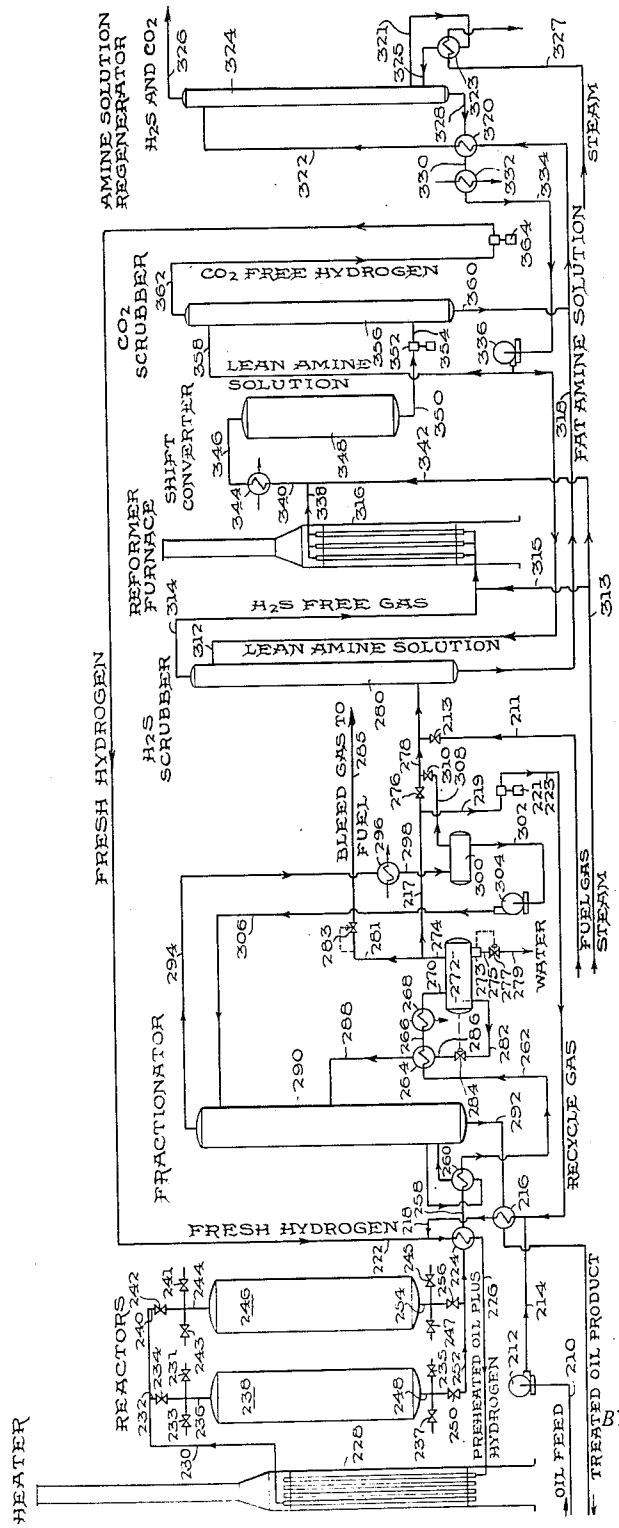


Fig. 2.

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UNITED STATES PATENT OFFICE

2,614,066

HYDRODESULFURIZATION OF PETROLEUM HYDROCARBONS

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Application May 10, 1949, Serial No. 92,436

4 Claims. (Cl. 196—28)

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This invention relates to the hydrodesulfurization of petroleum hydrocarbons, and more particularly to a continuous method of hydrodesulfurization in which the hydrogen utilized in the process is largely obtained from contaminant produced concomitant with the hydrodesulfurization process.

The hydrodesulfurization process has proved to be of marked value in the treatment of petroleum hydrocarbons containing sulfur, especially high boiling petroleum hydrocarbons such as high sulfur crudes. The hydrodesulfurization methods may be classified into two major type processes, namely the catalytic hydrodesulfurization method, and the contact hydrodesulfurization method. The former comprises contacting the sulfur-bearing petroleum hydrocarbon with a contact material having hydrogenating characteristics at a temperature of the order of 700° to 900° F. The sulfur present in the crude is converted into a gaseous form such as hydrogen sulfide, and in this manner removed from the hydrocarbon.

The contact method of hydrodesulfurization comprises contacting a sulfur-bearing petroleum hydrocarbon with a contact material having hydrogenating characteristics such as an iron group metal, metal oxide or combinations thereof on a carrier, and which causes the sulfur in the crude to become combined with the contact as metallic sulfide, and continuing said process until regeneration of the contact proves necessary. The contact agent is then regenerated and the process is continued as before.

One of the problems encountered with the aforementioned processes is the maintenance of adequate amounts of hydrogen in the system. This problem arises due to the fact that in these processes significant amounts of gaseous hydrocarbons such as methane are formed, thereby causing a reduction of the hydrogen purity in the recycle stream, as well as the consumption of hydrogen involved in the manufacture of these gaseous hydrocarbons. Furthermore, appreciable amounts of hydrogen are lost to the system by virtue of being dissolved in the liquid hydrocarbon product, either in the form of hydrogen per se or as gaseous hydrocarbon contaminants.

Various methods have been proposed for combating this problem, such as processing the recycle stream through an absorption system to remove the gaseops hydrocarbon, and thereby producing a stream having a higher hydrogen concentration. However, such methods have not proved satisfactory in that the substantial

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amounts of elemental hydrogen, and hydrogen compounds such as gaseous hydrocarbons dissolved in the product are lost to the system.

An object of the present invention is to provide a method whereby the hydrogen concentration of the recycle stream in a hydrodesulfurization process is maintained at sufficient purity to meet the requirements of the process.

A further object of this invention is to provide a method whereby hydrogen is manufactured from the contaminants of the hydrodesulfurization process.

These and other objects are achieved by the process of the present invention which comprises removing sulfur from petroleum hydrocarbons by contacting petroleum hydrocarbons containing sulfurous material at an elevated temperature with a hydrogen-containing gas in the presence of a contact material having hydrogenating characteristics, cooling the effluent to obtain a first gas portion, and a hydrocarbon liquid portion containing dissolved gases, separating said hydrocarbon liquid portion and removing the dissolved gases from said hydrocarbon liquid to form a second gas portion. Substantial amounts of the hydrocarbon portion of this second gas portion are then converted into hydrogen and this hydrogen is utilized for the hydrodesulfurization of petroleum hydrocarbons.

The present process is applicable to hydrodesulfurization processes in general. Such processes may be conducted over a wide range of temperatures and pressures although the temperature range that has been found most applicable for these processes is usually of the order of 600° to 950° F. Petroleum hydrocarbons having a wide range of specification characteristics may be utilized, although these methods are most widely used with high boiling crudes having a high sulfur content.

In accordance with my invention I utilize the fact that the hydrocarbon liquids emanating from the hydrodesulfurization reaction chamber preferentially absorb the hydrocarbon gases produced in the process, and that upon releasing these dissolved gases from the hydrocarbon liquids a gas having a high concentration of hydrocarbon gas is obtained. By converting the hydrocarbon portion of this gas into hydrogen and returning this manufactured hydrogen to the recycle stream, there is a marked benefit in the ease and facilities in which the process may be conducted.

The procedure for carrying out the contact hydrodesulfurization type of process has been

described in U. S. application Ser. Nos. 699,671 and 699,672, filed September 27, 1946, by W. A. Horne and J. F. Junge, now Patents 2,516,876 and 2,516,877 respectively. As disclosed in these copending Horne and Junge applications optimum results are obtained in contact hydrodesulfurization processes when the contact contains a substantial amount of the oxide of an iron group metal and especially nickel oxide, and these materials can be used in accordance with my invention. While contacts containing free metals of the iron group such as elemental nickel cause cracking of hydrocarbons to gas and excessive amounts of carbon to be deposited upon the contact, my invention permits an improvement with this type of contact as well as with the oxide type, and hence is to be regarded as equally applicable to both types of contacts. Whichever type contact is utilized it should be deposited upon a carrier such as kieselguhr, silica gel, alumina, aluminum silicates, silica-aluminas, Alfrax, Magnesol, Porocel, bauxite, diatomaceous earth, etc. Other contact materials having hydrogenating characteristics may be utilized but the aforementioned and particularly nickel oxide constitute the preferred contact material.

The total amount of metal in the contact may be varied considerably. Minor amounts of other chemical substances may be added for special purposes or present as impurities. In those cases in which a metal oxide is employed, the contact agent may be prepared by coprecipitation of metal oxide and carrier, or the precipitation of the metal oxide in the presence of a support. Also, impregnation may be employed as a method of preparing contacts such as by absorbing soluble salts of the metal on the support followed by decomposition of the salt at elevated temperatures. The final contact agent may be prepared by either single or multiple impregnation to attain any suitable concentration of metal oxide. Other methods of preparation will be obvious to those versed in the art.

Where a metal or mixture of metal and metal oxide is to be used as contact agent, any of the above mentioned methods may be utilized and then followed by treatment with a reducing medium such as a hydrogen-containing gas. In the case of a metal-metal oxide contact this will consist of only a partial reduction.

The reaction takes place at varying temperatures, pressures and space velocities with the optimum conditions depending on the type charge stock that is used. For example, with low boiling hydrocarbons such as those normally liquid petroleum fractions having an ASTM end point below 600° F., such as straight run or cracked gasolines and naphtha, the temperature will usually lie between 600° and 800° F. I have found that at temperatures below 600° F., the desulfurization activity of the contact diminshes whereas with temperatures higher than 800° F. excessive cracking reactions result in decreased product recovery and rapid coke formation which deactivates the contact. I have further found that the optimum pressures lie between 100 and 500 p. s. i. g. At pressures below 100 p. s. i. g. the partial pressure of hydrogen is not sufficient to maintain desulfurization activity nor to suppress cracking reactions which result in coke formation. Increasing the pressure above 500 p. s. i. g. results in only a slight incremental gain in desulfurization, and a decrease in the bromine number of the end product gasoline and is thus not commercially desirable. The preferred space velocities lie, between 1.0 and 6.0 liquid volumes of charge per hour per volume of contact agent. Space velocities below 1.0 result in excessive cracking and olefin saturation reactions caused by the long contact time whereas at space velocities above 6.0 the contact time is too short to provide sufficient desulfurization.

This invention can be applied with exceptional success to high boiling petroleum hydrocarbon oils such as total crude as well as topped or reduced crude. These terms may be defined as follows: "total crude" is defined as naturally occurring petroleum oil which has not been processed in any manner but has been or preferably should be separated from water or sediment and desalted. "Topped or reduced crude" is defined as the residual pertoleum oil resulting from removal of all or some of the straight run fractions such as gas, gasoline, kerosene, naphtha, furnace oil, gas oil, etc., which are normally removed from the above defined total crude by the process of atmospheric and/or vacuum topping or distillation. Charge stocks such as total crude which has been diluted or admixed with lower boiling straight run or cracked petroleum fractions including gases are also included. Diluents of this kind may be required in processing low gravity crudes such as some of those from Mississippi as well as those from Kuwait. Diluents may also be necessary and preferred in desulfurizing topped or reduced crudes. The purpose of this diluent is to assist vaporization of the heavier constituents of the charge stock. I nsome cases it may be desirable to admix steam with the charge stock to asist vaporization. Preferred operating conditions for the aforementioned high boiling petroleum hydrocarbons may vary within certain ranges depending upon the charge stock.

I have found the optimum temperature range to be from 750° to 950° F. for high boiling petroleum hydrocarbons. At temperatures below 750° F. the desulfurizing activity of the contact diminishes whereas at temperatures greater than 950° F. excessive cracking actions result in decreased product recovery and rapid coke formation which deactivates the contact. I have further ascertained the preferred pressure range to be between 100 and 1000 p. s. i. g. With pressures below 100 p. s. i. g. it appears that the partial pressure of hydrogen is not sufficient to maintain desulfurizing activity nor to suppress cracking reactions which result in coke formation. Increasing the pressure above 1000 p. s. i. g. results in only a slight incremental gain in desulfurization and is thus not commercially desirable. The space velocity range which I prefer to employ is 0.2 to 6.0 volumes of charge per hour per volume of contact agent. A space velocity below the former causes excessive cracking reactions due to the long contact time, while space velocities above 6.0 are too short in duration to allow sufficient desulfurization. The hydrogen-containing gas to oil ratio should be greater than 300 S. C. F./bbl. of petroleum hydrocarbons. The throughput should be in the range of 1 to 50.

The contact absorption hydrodesulfurization process can best be explained by examination of Figure 1. Crude charge enters the system through line **10** and is pumped by charge pump **12** through line **13** and line **14** into heat exchangers **16**, **18** and **20**. The charge then passes by means of line **22** into oil and hydrogen heater **24**.

The initial hydrogen is prepared from fuel gas

which enters the system in line 26 through line 28, into hydrogen producing plant 30. The hydrogen may be most advantageously produced by means of the conventional reforming and shift reactions, in which the fuel gas is burned in the presence of steam, and the carbon monoxide formed in the reaction is converted to carbon dioxide. The hydrogen plus carbon dioxide produced in plant 30 is passed by means of line 32 into gas holder 34 where it may be stored before returning to plant 30 by passing it through line 35, raw hydrogen compressor 36 and line 37. In hydrogen producing plant 30 the carbon dioxide is removed by conventional means and purified and compressed hydrogen is then removed from hydrogen producing plant 30 by means of line 38 and passed through compressor pump 40 to line 14 where it joins the crude petroleum charge coming from line 13. The hydrogen plus charge likewise passes from line 14 through heat exchangers 16, 18 and 20 into line 22 and then into oil and hydrogen heater 24. In oil and hydrogen heater 24 the charge and hydrogen are heated to reaction temperature. At this temperature the charge stock is substantially in the vapor phase, although small droplets of liquid may be present. The charge stock mixture is then passed by means of line 42 to valve 44 and line 46 into reactor 48. Alternatively, valve 44 may be closed and the oil and hydrogen mixture passed from heater 24 to line 42, into line 50, valve 52, line 54 and thence into reactor 56. By alternating, one reactor may always be kept on-stream while the other is being purged or regenerated. While only two reactors are shown, a greater number may be provided so that one or more may be in the processing stage, while the remaining reactors are at other stages in their reaction cycle. In the reactors the petroleum hydrocarbons are hydrodesulfurized by passing over the contact agent which may contain any of the iron group metal oxides, metals or combinations thereof on a carrier although as has heretofore been mentioned the preferred contact agent is nickel oxide.

The sulfur is removed from the charge stock by combining as sulfide with the contact agent. The desulfurized product is passed from reactor 48 into line 58, valve 60 and into line 62. If reactor 56 is on-stream desulfurized product from reactor 56 is passed by means of line 67, valve 69 and line 71 into line 62. The desulfurized product in line 62 is passed in heat exchanger relationship through heat exchanger 20 and into line 64 where a portion is diverted through heat exchanger 66 while the remainder is passed through heat exchanger 18 into line 73. The portion that was diverted through heat exchanger 66 is passed through line 68, heat exchanger 16 and into line 70. The remainder in line 73 likewise passes through heat exchanger 16 and enters line 70. The product from the heat exchangers passes through line 70, condenser 72, line 74, into high pressure flash drum 76.

In high pressure flash drum 76 the non-dissolved gaseous portion of the hydrodesulfurization products is separated from the liquid portion. Any water in high pressure flash drum 76 is removed by water separator 96 and line 98. This liquid portion passes from high pressure flash drum 76 to line 92, and then into low pressure flash drum 94. The gaseous portion is removed from high pressure flash drum 76 by line 78 where it may be recycled into the system by passing through line 80, recycle compressor 82, line 84 into line 14. If desired, a portion of the gases from high pressure flash drum 76 may be passed from line 78 through line 86 valve 113 into line 90. From line 90 these gases are passed through valve 111 and line 28 into hydrogen-producing plant 30 where they are converted, as has heretofore been explained, into hydrogen. It will be suitable in most cases to recirculate all of the gases from high pressure flash drum 76 and in these cases valve 113 may be closed and all the gases recirculated through line 80.

The liquid product in low pressure flash drum 94 is removed by means of line 100, transfer pump 102 to line 106. From line 106 the product is removed from the system. Any water present in low pressure flash drum 94 is removed by means of water separator 95 and line 97.

The vapors from low pressure flash drum 94 are passed through line 107, absorber gas compressor 108, line 110 into reboiled absorber column 112. Reboiled absorber column 112 is kept under proper distillation conditions by means of line 114, vaporizer 116 and line 118.

In reboiled absorber column 112 the low boiling contaminants, such as the low boiling hydrocarbon gases from low pressure flash drum 94 and the unreacted hydrogen-containing gas, are removed as overhead, passed into line 120 and thence into line 90, valve 111 and line 28 into hydrogen-producing plant 30. In hydrogen-producing plant 30 it is converted, as heretofore indicated, into hydrogen and reutilized in the process. Depending upon the mechanical leakage, and the degree of purity of hydrogen required in the system, more or less quantities of fuel gas may be added from time to time by means of line 26 to supplement the source materials for the production of hydrogen.

The desirable hydrocarbon products present in the vapors from low pressure flash drum 94, such as the normally liquefiable hydrocarbons, are removed as bottoms by means of line 122 and passed through heat exchanger 124, line 126 into stripper 128. The distilling conditions in stripper 128 are maintained by means of line 130, heat exchanger 66 and line 132. The lean oil bottoms from stripper 128 are removed by means of line 134, pass in heat exchanger relationship through heat exchanger 124, line 136, pump 138, line 140, cooler 142, line 144 into reboiled absorber 112 for use as absorption oil. The overhead vapors, from stripper 128 which comprise the valuable hydrocarbon products, are discharged through line 146, condenser 148 and then passed through line 150, reflux drum 152, line 154 into stripper reflux pump 156 where a portion is returned as reflux to stripper 128 by means of line 158. The remainder of the overhead from stripper 128 is removed from the system by means of line 160, and may be combined with the products that were removed from the system through line 106.

The on-stream cycle is terminated at the completion of the hydrodesulfurization process and the contact is regenerated. The time of termination of the on-stream cycle may be varied depending upon the nature of the charge stock as well as the results to be achieved. In instances where hydrogen sulfide cannot be tolerated in the product from the hydrodesulfurization reactors, the on-stream cycle must be concluded when substantial amounts of hydrogen sulfide appear in the product.

Another method for determining the point at which the on-stream cycle should be consummated is by the empirical method of concluding the on-stream cycle when the contact has been 30 to 60% sulfided, e. g., when between about 30

to 60% of the iron group metal content of the contact has been converted into metallic sulfide.

In those cases in which small amounts of hydrogen sulfide may be tolerated in the product, or means for removing hydrogen sulfide from the product are available, the hydrosulfurization process may be continued until the iron group metal content of the contact has been substantially converted into metal sulfide, e. g., the contact has become saturated with sulfur.

At the completion of the on-stream cycle the on-stream cycle is stopped by closing valves **44** or **52**. The contact beds are then regenerated by depressuring and purging the reactors with an inert substance such as steam. The purpose of the purge is to recover valuable hydrocarbons which remain in the contact bed. An inert substance is introduced into reactor **48** by means of valve **47**, lines **45** and **46** and may leave the reactor through line **58**, valve **60** and line **62**, or through line **58** and a valve, condenser and lines (not shown) to low pressure flash drum **94**. The inert substance for reactor **56** is introduced by means of valve **55**, lines **53** and **54** and leaves the reactor by means of line **67**, valve **69**, line **71** and line **62** or through line **67** and a valve, condenser and lines (not shown) to drum **94**.

Following the purge, valves **60** or **69** are closed and regenerating gas such as oxygen, or an oxygen-containing gas such as air is introduced into reactors **48** or **56** from lines **45** and **46**, or **53** and **54** by opening valves **47** or **55**. In reactor **48** or **56** the contact bed is oxidized and the sulfur on the contact surface is removed as sulfur dioxide. This regeneration product gas is removed from reactors **48** or **56** by their corresponding lines **57** and **63**, and valves **59** and **65**. The sulfur dioxide in this gas may be recovered in a conventional manner such as by solvent absorption and stripping. The regeneration off-gas, which has been freed from sulfur dioxide, may then serve to dilute the first regeneration gas admitted to the reactors. Alternatively, the sulfur dioxide gas containing regeneration off-gas may serve to dilute the fresh regeneration gas. After regeneration is complete, which may readily be determined by the fact that the contact agent is substantially free of sulfur and is once again in the oxide form, the oxidizing gas is shut off and the reactor steamed to remove any oxygen present.

Depending upon the nature of the contact, it may be tested with a reducing gas following regeneration treatment. In the case of oxide contact agents this step is usually omitted. However, in those cases where free metal such as nickel, or a mixture of metal-metal oxide such as nickel-nickel oxide is employed as the contact, it is desirable to reduce or partially reduce the contact agent with a reducing gas such as a hydrogen-containing gas. This is accomplished by passing hydrogen-containing gas through valve **47**, line **45**, and line **46** into reactor **48** or through valve **55**, line **53** and line **54** into reactor **56**. The reducing gas is vented through line **57** and valve **59** or line **63** and valve **65**. This hydrogen-containing gas is recovered and may be used again, or may be purified in hydrogen-producing plant **30**.

The reactor is then blocked off by closing valves **47** or **55**. Also, valves **59** or **65** are likewise closed. At this point reactor **48** or **56** is brought on-stream by opening valves **44** or **52** and valves **60** and **69** and permitting the charge to enter the reactor. Then the process is continued as before.

I have found that when using a ratio of 5000 cubic feet of hydrogen rich gas per barrel of West Texas crude, a hydrogen purity of about 85% is desirable. As a practical matter, I have found that an average of 300–350 cubic feet of hydrogen are lost to the operation for each barrel of crude oil fed to it, and further, that a quantity of light gases such as methane, ethane and propane are produced in a quantity in excess of 250 cubic feet per barrel. In addition to a major portion of these contaminants, about 120 cubic feet per barrel of hydrogen are dissolved in the desulfurized product that is removed from the high pressure flash drum **76**. Thus, the hydrogen lost by solution in the product constitutes about one-third of the requirements of the process. If all of the light gases produced by the process together with the impurities introduced with the makeup or fresh hydrogen could be dissolved in the desulfurized product removed from flash drum **76**, then a recycle gas of 83–84% purity in the amount of 4625 or 4650 cubic feet per barrel would be removed overhead in line **78** from flash drum **76**. The hydrogen convertor may then be regulated to produce sufficient amounts of hydrogen of a purity of 93–96% to raise the average purity of the recycle stream to 85% and restore its rate to 5000 cubic feet per barrel.

If operating conditions are such that the liquid product does not dissolve quite all of the light gases produced, the purity of the recycle stream in equilibrium with the liquid and leaving the top of flash drum **76** will fall below 83–84%, and when the fresh hydrogen is added in the amount required the purity of 85% will not be obtained.

Since this net gas make escaping into the recycle gas must be withdrawn from the system, line **86** and valve **113** have been provided. In this manner, I have found it possible to keep the system operating in an economical manner without permitting the purity of the hydrogen in line **80** to fall below 80% and still achieve the desired overall purity of 85%.

As has heretofore been indicated my invention is equally applicable to catalytic hydrodesulfurization methods. In these methods the sulfur present in the hydrocarbons is converted into a gaseous form, usually hydrogen sulfide, and the hydrogen sulfide gas is removed from the product. The conditions for this type of process are somewhat similar to those for the contact method. The prime difference between these processes being the fact that in the contact method, the process is not permitted to continue beyond the point at which the contact has become completely sulfided, that is when the entire metal content of the contact has been converted into metal sulfide. The catalytic method contemplates longer on-stream cycle periods since it is not necessary to regenerate the catalyst after it has been completely sulfided. In addition to the oxide and free-metal type materials contemplated as useful contacts for the contact method, other compounds such as sulfide compounds may be used in the catalytic method. In fact, it appears that any material having hydrogenating characteristics may be utilized as a catalyst in the catalytic type method.

I have found that the optimum temperature conditions for this type process will be of the order of 700° to 900° F., with the higher temperature ranges being utilized for heavier charge stock materials. The optimum pressures will usually lie between 100 and 1,000 pounds per square inch and the space velocities should be of the order of 0.5 to 2.0. The hydrogen to oil ratio may be

varied over a wide range such as from 500 to 10,000 S. C. F./bbl. I have found that the throughput may also be varied between the range of about 2 to about 12.

The process of the present invention as applied to the catalytic hydrodesulfurization method is best understood by an examination of accompanying Figure 2. Crude charge enters the system through line 210 and passes, by means of charge pump 212, through line 214, heat exchanger 216, into line 218 where it is joined by fresh hydrogen in line 222.

The mixture of fresh hydrogen and oil feed passes from line 222 and heat exchanger 224 into line 226. From line 226 the hydrogen-oil feed mixture is passed to heater 228 where it is heated to reaction temperature. From heater 228 the mixture is passed by way of line 230 into line 232, valve 234, line 236 into reactor 238. Alternatively, valve 234 may be closed and the oil and hydrogen mixture passed from heater 228 through line 230, into line 240, valve 242, line 244 and thence into reactor 246. By alternating, one reactor may always be kept on-stream while the other is being purged or regenerated. While only two reactors are shown, a greater number may be provided so that one or more may be in the processing stage, while the remaining reactors are at other stages in the reaction cycle. In the reactors the petroleum hydrocarbons are hydrodesulfurized by passing over the hydrodesulfurization catalyst comprising a hydrogenating agent such as a molybdenum compound, or nickel or nickel compound on a carrier, thereby causing sulfur in the feed to be converted into gaseous hydrogen sulfide. Among the compounds which I have found most useful for this purpose are the oxides and sulfides.

The products from the hydrodesulfurization reaction are passed from reactor 238 through line 248, valve 250, line 252, into heat exchanger 224. If reactor 246 is on-stream, the hydrodesulfurization products from reactor 246 are passed by means of line 254, valve 256, line 252 into heat exchanger 224. After passing through heat exchanger 224 these products are conveyed by means of line 258 through reboiler 260, line 262, heat exchanger 264, line 266, cooler 268, line 270, into flash drum 272.

In the flash drum 272 the non-dissolved gases in the hydrodesulfurization products are removed by means of line 274. The liquid hydrodesulfurization products containing dissolved hydrogen and preferentially absorbed hydrocarbon gases, are removed from flash drum 272 by means of line 282, automatic valve 284, line 286, heat exchanger 264, line 288 and passed into fractionator 290. Any water contaminants present in the desulfurized products are removed from flash drum 272 by means of water separator 273, line 275, automatic valve 277 and line 279 from which the water is disposed. In fractionator 290 the liquid hydrodesulfurization products are distilled and the treated oil product bottoms are removed by means of line 292 and heat exchanger 216 from which they are passed out of the system to a suitable storage or utility vessel. The overhead distillate from fractionator 290 containing substantial amounts of absorbed hydrogen and low-boiling hydrocarbons is passed by means of line 294 to condenser 296 where it is partially condensed, and then carried by means of line 298 to reflux drum 300. In reflux drum 300 the liquid condensate is separated from the absorbed gases and returned as reflux by means of line 302, reflux pump 304, line 306 to fractionator 290. The absorbed gases are removed from reflux drum 300 by means of line 308 and valve 310 and are passed to line 278 where they join the gases from flash drum 272.

The gases from flash drum 272 after passing through line 274 enter line 217. From line 217 a portion of these gases may pass through valve 276 and line 278 into hydrogen sulfide scrubber 280. The remainder of these gases are recirculated by means of line 219, recycle gas compressor 221, line 223 and heat exchanger 216 into line 218 where they join the fresh hydrogen in line 222. On occasion, it may be desirable to recirculate all of the gases in line 217, in which case valve 276 is closed.

If desired, a portion of the gases removed from flash drum 272 by means of line 274 may be bled from the system by means of line 281, automatic valve 283 and line 285 to form bleed gas. The percentage of the gases from flash drum 272 which may be utilized for this purpose is controlled by automatic valve 283 and may be regulated to meet any existing conditions. In some cases it may be necessary to add fuel gas through line 211 and valve 213 into line 278 in order to bolster the source materials for the production of hydrogen.

The combined mixture of the gases from line 278 is desulfurized in hydrogen sulfide scrubber 280. This may be accomplished by any of the conventional methods. I have found that the commercial ethanolamine solution scrubbing method is suitable for this purpose. In this method the amine solution enters hydrogen sulfide scrubber 280 by means of line 312 where it passes countercurrently to the gases from line 278. The desulfurized gases are removed from hydrogen sulfide scrubber 280 by line 314 and mixed with steam which has entered the system by means of lines 313 and 315. The amine solution containing absorbed hydrogen sulfide is removed from hydrogen sulfide scrubber 280 by line 318.

The mixture of steam and desulfurized gases in line 314 is passed to reformer furnace 316. In reformer furnace 316 the desulfurized gases from H_2S scrubber 280 are converted by the methane reforming reaction into carbon monoxide and hydrogen. These gases are passed from reformer furnace 316 by line 338 to line 340 where they are joined by steam which has entered the system from line 313 and line 342. The mixture of steam, carbon monoxide and hydrogen is passed through cooler 344, line 346 into shift converter 348. In shift converter 348 the carbon monoxide is converted by reaction with the steam to form carbon dioxide and hydrogen. This mixture of carbon dioxide and hydrogen is removed from shift converter 348 by line 350 and passes through raw hydrogen compressor 352 into line 354 and thence into carbon dioxide scrubber 356. In carbon dioxide scrubber 356 the carbon dioxide is separated from the gaseous mixture by being absorbed in ethanolamine solution from line 358.

This amine solution enters carbon dioxide scrubber 356 through line 358 and passes countercurrently to the gases therein. The carbon dioxide component of the gaseous mixture is removed from carbon dioxide scrubber 356 by line 360 where it joins the sulfur containing amine solution in line 318.

The amine solution containing hydrogen sulfide and carbon dioxide passes from line 318

through heat exchanger 320 line 322 into amine solution regenerator 324. Amine solution regenerator 324 is kept under suitable distillation conditions by passing a portion of its contents through line 321, reboiler 323 and line 325. Steam from line 327 is circulated through reboiler 323 and supplies the heat to maintain the regenerator at distillation conditions.

Hydrogen sulfide and carbon dioxide are removed as overhead from amine solution regenerator 324 by line 326. Purified amine solution passes from amine solution regenerator 324 by means of line 328 heat exchanger 320 line 330 cooler 332 line 334 into regenerated solution pump 336. After the solution has passed through regenerator pump 336 a portion of it passes by means of line 312 to hydrogen sulfide scrubber 280. The remainder of the solution is passed by line 358 to carbon dioxide scrubber 356.

Carbon dioxide-free hydrogen is removed from carbon dioxide scrubber 356 by line 362 and fresh hydrogen compressor 364. From fresh hydrogen compressor 364 the purified hydrogen is returned to the hydrodesulfurization system by means of line 222.

During the on-stream period valves 231, 233, 235 and 237 of reaction 238 remain closed. At the completion of this on-stream period when it becomes necessary to regenerate the catalyst due to catalyst deactivation or plugging caused by carbon deposition, valves 234 and 250 are closed and the pressure in reactor 238 is released by opening valves 231 and 235. Reactor 238 may then be vacuum purged in a conventional manner. Alternatively, valves 231 and 235 may be closed and valves 233 and 250 opened and the catalyst purged with an inert gas or steam so as to recover the valuable hydrocarbons in the reactor bed which are passed to line 252. Following the purge valves 233 and 250 are closed and valves 231 and 235 opened and the catalyst bed in reactor 238 is regenerated by the admission of regenerating gas through valves 235 and line 248. The regenerating gas which may comprise oxygen-containing gases such as oxygen or air, regenerates the catalyst and simultaneously forms sulfur-containing gases which are vented from reactor 238 by means of line 236 and valve 231, together with combustion gases from any carbonaceous deposit on the catalyst bed. This regeneration-off gas contains a recoverable quantity of sulfur-containing gases and this sulfur-containing gas may be recovered in any normal manner, such as by solvent absorption and stripping. The sulfur regeneration-off gas may serve to dilute fresh regeneration gases admitted to the reaction chamber. Alternatively, the sulfur-containing regeneration-off gas may serve to dilute fresh regeneration gas.

Depending upon the nature of the catalyst it may be treated with various gases following regeneration treatment. In the case of oxide catalysts this step is usually omitted. However, in the case of free metal catalysts such as nickel, or mixtures of free metal-metal oxide catalysts such as nickel-nickel oxide catalysts it is desirable to reduce or partially reduce the contact agent with a reducing gas such as a hydrogen-containing gas. In the case of sulfide catalysts such as molybdenum sulfide it is desirable to sulfurize the catalyst prior to the commencement of the on-stream period by the use of a sulfur-containing gas such as hydrogen sulfide.

In any event, if additional treatment with one or more of these gases is desirable after the oxidation step, a suitable gas may be introduced into reactor 238 by first closing the valves 235 and 231 and then opening valves 237 and 233 and introducing the gas through valve 237 and line 248 into reactor 238. The gas is then vented through line 236 and valve 233.

In those cases in which treatment with an additional gas is omitted it is usually desirable to flush the system after the oxidation has been concluded with an inert gas and/or purge. This may be accomplished by passing the inert gas or steam through valve 237 and line 248 into the reactor bed and then out of the reactor by passage through line 236 and valve 233. When the regeneration treatment is concluded the reactor is put on-steam by closing off valves 231, 233, 235, and 237 and opening valves 234 and 250.

As has been heretofore described one reactor may be on-steam while the other may be in the regeneration portion of the cycle. Thus, for example, reactor 238 may be on-steam while reactor 246 is being regenerated. In this case reactor 246 will be treated in an exactly analogous manner to that described for reactor 238 by the utilization of valves 241, 243, 245 and 247.

The description of the apparatus described in Figures 1 and 2 is to be considered merely illustrative of the methods which may be utilized. Thus, for example, multiple or single beds of catalyst may be used, as well as systems in which the catalyst is continuously charged and removed from the reaction zone and followed by external regeneration. In addition this invention is applicable to methods in which the catalyst is finely divided and employed in the fluidized state.

As has been shown the utilization of this hydrodesulfurization process permits the mellifluous production of hydrogen from the hydrocarbon gases formed in the process, due to the fact that these gases are preferentially absorbed in the hydrodesulfurized liquid hydrocarbon products. This permits maximum possible efficiency in the hydrocarbon conversion into hydrogen inasmuch as the recycle gases from the high pressure separator, e. g., the first gas portion, have a much lower hydrocarbon content than the gases recovered from the desulfurized product and therefore the recovered gases are capable of producing a higher yield of hydrogen. Furthermore, the utilization of this invention permits substantial savings in the cost of equipment and apparatus in that the customary absorption system normally used to remove the gaseous hydrocarbons such as methane is completely dispensed with.

What I claim is:

1. In the process for hydrodesulfurizing a petroleum hydrocarbon by contacting the petroleum hydrocarbon containing sulfurous material at an elevated temperature and pressure with a hydrogen-containing gas in the presence of a contact material having hydrogenating characteristics, cooling the effluent from the aforesaid hydrodesulfurizing treatment to obtain a first gas portion and a hydrocarbon liquid portion which liquid portion contains dissolved gases, separating said hydrocarbon liquid portion and removing the dissolved gases from said hydrocarbon liquid portion to obtain a second gas portion, the improvement in the above which comprises subjecting this second gas portion, without previous separation of the hydrogen and hydrocarbon components thereof, to a reforming and shift reaction whereby the hydrocarbon gas components of the second gas portion are converted into hydrogen without requiring physical separation of the hydrogen gas

from the hydrocarbon gases and whereby the hydrogen contained in the second gas portion is caused to improve the operation of the reforming reaction, adding the gas stream from the reforming and shift reaction to the first gas portion and recycling said combined gas mixture into contact with the petroleum hydrocarbon to be desulfurized.

2. In the process of hydrodesulfurizing a high boiling petroleum hydrocarbon by contacting the petroleum hydrocarbon containing sulfurous material at a temperature between about 750° and 950° F., at a pressure between about 100 and 1000 p. s. i. with a hydrogen-containing gas in the presence of a contact material selected from the group consisting of iron group metals, iron group metal oxides and combinations thereof on a carrier, absorbing sulfur from the high boiling hydrocarbon to form iron group metal sulfide, cooling the effluent from the aforesaid hydrodesulfurizing treatment to obtain a first gas portion and a hydrocarbon liquid portion which liquid portion contains dissolved gases, separating said hydrocarbon liquid portion and removing the dissolved gases from said hydrocarbon liquid portion to obtain a second gas portion, the improvement in the above which comprises subjecting this second gas portion, without previous separation of the hydrogen and hydrocarbon components thereof, to a reforming and shift reaction whereby the hydrocarbon gas components of the second gas portion are converted into hydrogen without requiring physical separation of the hydrogen gas from the hydrocarbon gases and whereby the hydrogen contained in the second gas portion is caused to improve the operation of the reforming reaction, adding the gas stream from the reforming and shift reaction to the first gas portion and recycling said combined gas mixture into contact with the high boiling petroleum hydrocarbon to be desulfurized.

3. In the process for hydrodesulfurizing a petroleum hydrocarbon by contacting the petroleum hydrocarbon containing sulfurous material at a temperature between about 700° and 900° F. at a pressure between about 100 and 1000 p. s. i., with a hydrogen-containing gas in the presence of a contact material having hydrogenating characteristics, cooling the effluent from the aforesaid hydrodesulfurizing treatment to obtain a first gas portion and a hydrocarbon liquid portion which liquid portion contains dissolved gases, separating said hydrocarbon liquid portion and removing the dissolved gases from said hydrocarbon liquid portion to obtain a second gas portion, the improvement in the above which comprises removing hydrogen sulfide from the second gas portion, subjecting this second gas portion, without previous separation of the hydrogen and hydrocarbon components thereof, to a reforming and shift reaction whereby the hydrocarbon gas components of the second gas portion are converted into hydrogen without requiring physical separation of the hydrogen gas from the hydrocarbon gases and whereby the hydrogen contained in the second gas portion is caused to improve the operation of the reforming reaction, adding the gas stream from the reforming and shift reaction to the first gas portion and recycling said combined gas mixture into contact with the petroleum hydrocarbon to be desulfurized.

4. In the process for hydrodesulfurizing a petroleum hydrocarbon by contacting the petroleum hydrocarbon containing sulfurous material at a temperature between about 700° and 900° F. at a pressure between about 100 and 1000 p. s. i., with a hydrogen-containing gas in the presence of a contact material having hydrogenating characteristics, cooling the effluent from the aforesaid hydrodesulfurizing treatment to obtain a first gas portion and a hydrocarbon liquid portion which liquid portion contains dissolved gases, separating said hydrocarbon liquid portion and removing the dissolved gases from said hydrocarbon liquid portion to obtain a second gas portion, the improvement in the above which comprises combining part of the first gas portion with the second gas portion, removing hydrogen sulfide from the combined mixture, subjecting the combined mixture, without previous separation of the hydrogen and hydrocarbon components thereof, to a reforming and shift reaction whereby the hydrocarbon gas components of the combined mixture are converted into hydrogen without requiring physical separation of the hydrogen gas from the hydrocarbon gases and whereby the hydrogen contained in the combined mixture is caused to improve the operation of the reforming reaction, adding the gas stream from the reforming and shift reaction to an additional part of the first gas portion and recycling the resultant mixture into contact with the petroleum hydrocarbon to be desulfurized.

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