July 22, 1958 C. H. O. BERG 2,844,516

COMBINED HYDRODESULFURIZATION PROCESS AND APPARATUS THEREFOR

Filed March 22, 1954

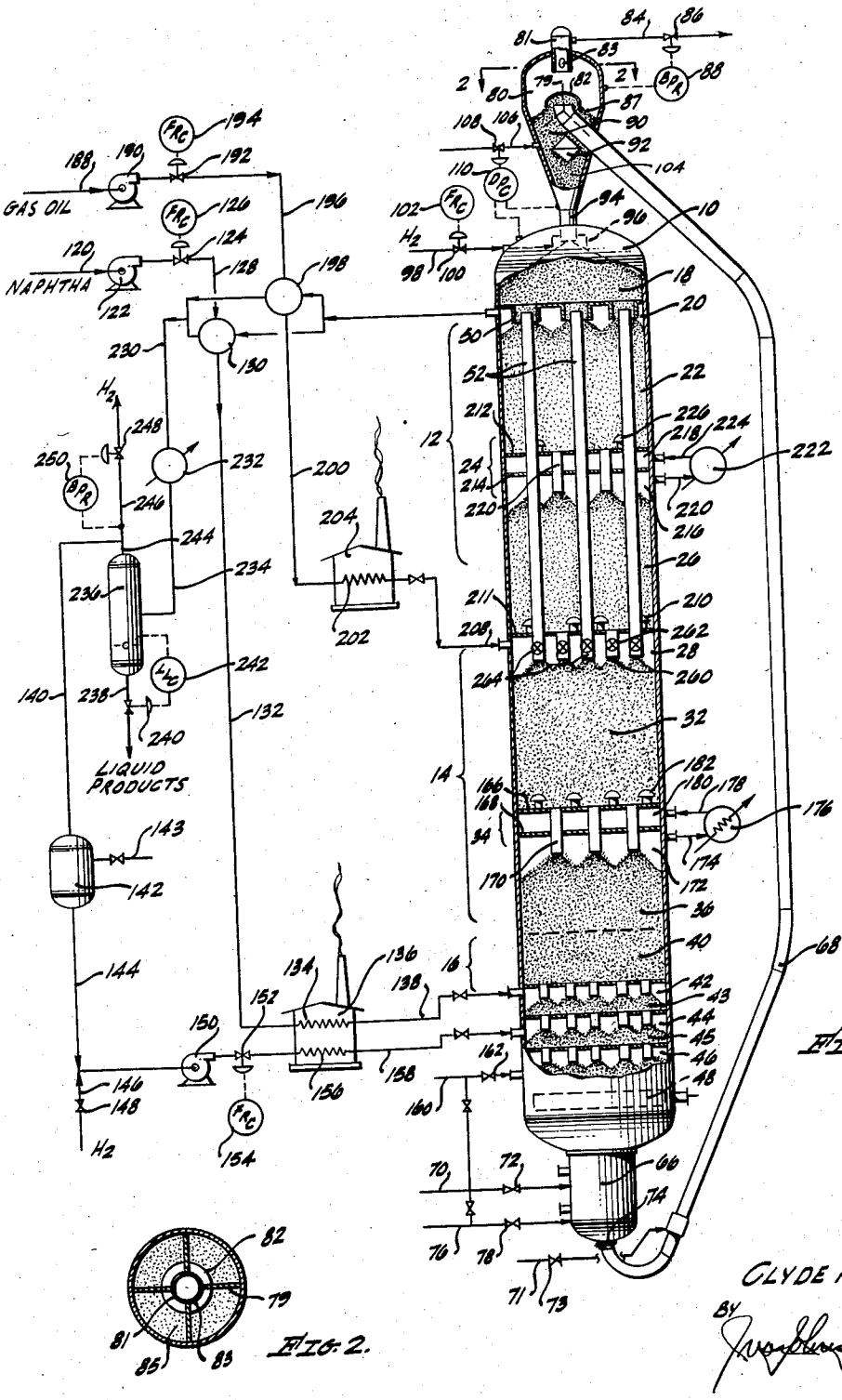


FIG. 1.

FIG. 2.

INVENTOR.
CLYDE H. O. BERG,
BY
AGENT

United States Patent Office 2,844,516 Patented July 22, 1958

2,844,516

COMBINED HYDRODESULFURIZATION AND REFORMING PROCESS AND APPARATUS THEREFOR

Clyde H. O. Berg, Long Beach, Calif., assignor to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application March 22, 1954, Serial No. 417,568

14 Claims. (Cl. 196—28)

This invention relates to an improved process and apparatus for the continuous treating or contacting of fluids with a recirculating stream of solid granular contact material and in particular relates to the conversion of petroleum and other hydrocarbons in the presence of a recirculated stream of granular hydrocarbon conversion catalyst. In its most specific embodiment this invention contemplates an improved combination process and apparatus for the simultaneous treatment of two hydrocarbon fractions of substantially different properties, such as the catalytic reforming of naphtha or gasoline fractions and the catalytic desulfurization, denitrogenation, and deoxygenation of the reformed naphtha and a gas-oil fraction in the presence of a special catalyst which has reforming, desulfurization, denitrogenation and deoxygenation activity and in which the hydrocarbon conversions cooperate with one another in an integrated process of increased efficiency.

The prior practice in hydrocarbon oil refining includes many catalytic operations wherein hydrocarbon fractions are treated and converted in a variety of processes to improve various physical and chemical properties thereof. Many hydrocarbon fractions contain undesirable impurities in the form of hydrocarbon derivatives of sulfur, nitrogen, and oxygen which render them unfit for their intended uses such as cracking stock, internal combustion engine fuels, and the like. In addition, the naphtha or gasoline fraction of these hydrocarbons contain insufficient quantities of hydrocarbon types having high antiknock characteristics and extensive refining operations are effected to increase the quantity of aromatic and branched chain hydrocarbons in these gasoline fractions to make them suitable for use as fuels in high compression engines. Accordingly, modern refining practice tends more and more toward catalytic treatment of such hydrocarbon fractions to remove undesirable fractions and to impart desirable characteristics thereto by such specific processes as catalytic desulfurization, catalytic denitrogenation, and catalytic reforming which involve paraffin hydrocarbon isomerization, dehydrogenation and cyclization, and naphthene hydrocarbon dehydrogenation to produce homologs of benzene which have high antiknock characteristics. The removal of hydrocarbon derivatives of oxygen, nitrogen, and sulfur are required to produce a sweet non-corrosive product having a high lead susceptibility and to avoid problems of corrosion.

The desulfurization and denitrogenation of the naphtha and gas-oil fractions of crude petroleum ordinarily require reaction temperatures ranging from about 575° F. to about 900° F., pressures between about 50 p. s. i. (pounds per square inch) to about 5000 p. s. i. in the presence of a recycled stream of hydrogen. The hydrocarbon compounds of sulfur, nitrogen, and oxygen are decomposed forming a hydrocarbon and either hydrogen sulfide, ammonia or water. In the reforming of low-grade gasoline fractions, the naphtha vapor is contacted with a reforming catalyst at temperatures between about

800° F. and about 1100° F. at pressures in substantially the same range as for desulfurization, and in the presence of a hydrogen gas recycle. Although desulfurization, denitrogenation, and reforming all have desirable beneficial effects upon low-grade gasoline, the difference between the optimum reaction temperatures of these processes and the fact that the hydrogen sulfide, ammonia, and water contaminate the hydrogen recycle stream employed in the first-named operation, have heretofore necessarily required that these operations be effected entirely separately under conditions requiring separate gas plants, and unduly complicated processing steps and apparatus.

It has been found that granular catalyst of the cobalt molybdate type, supported on activated alumina carriers and analyzing between about 2% and 10% by weight of cobalt oxide (CoO) and between about 5% and about 30% by weight of molybdenum trioxide (MoO_3), is highly stable, rugged, and relatively inert to materials which conventionally poison reforming and desulfurization catalysts. It has also been found that catalysts of this type are simultaneously highly active in promoting the rates of reactions involved in hydrocarbon desulfurization, denitrogenation, deoxygenation, and reforming.

Accordingly, the present invention is directed to a novel and highly efficient integrated process wherein low-grade naphtha or gasoline fractions are catalytically reformed under optimum reforming conditions and gas-oil fractions are desulfurized and denitrogenated also at optimum reaction conditions simultaneously in a single contacting column of unique design and in the presence of one granular catalyst consisting essentially of cobalt molybdate which is recirculated through the column. By means of a particular scheme of simultaneous operation of the desulfurizing and reforming zones in the contacting column, more specifically defined below, it is found that there exists apparently an active cooperation between the two operations whereby novel and unexpected results have been obtained and which are apparently unobtainable when the two operations are conducted separately.

It is therefore a primary broad object of the present invention to provide a new and improved fluid-solids contact process.

It is a more specific object of this invention to provide an improved integrated hydrocarbon conversion process for the simultaneous desulfurization and reforming in a single contacting column.

It is an additional object of this invention to provide in a single contacting zone a downwardly moving bed of granular cobalt molybdate catalyst and in which contacting zone a naphtha fraction is reformed in the lower portion thereof and then the reformed naphtha and a contaminated gas-oil fraction, containing hydrocarbon derivatives of sulfur, nitrogen, and/or oxygen, are simultaneously treated in the upper portion of the contacting zone for the desulfurization, denitrogenation, and deoxygenation thereof.

It is a more specific object of this invention to provide in a hydrocarbon conversion process an improved hydrocarbon-catalyst contact operation wherein the moving bed of conversion catalyst is divided at the upper end of the contacting zone into a first and second stream, the first stream being passed into and directly through a desulfurization zone while the second stream is passed therethrough in indirect heat exchange relation therewith, and is combined with said first stream flowing from said desulfurization zone for passage together through a subjacent reforming zone.

It is an additional object of this invention to provide in a hydrocarbon conversion process employing a recirculated solid catalyst stream a novel and improved catalyst elutriation step for solids fines removal, and a novel

hydrogen pretreatment step which substantially eliminates from the reactor effluent the presence of elemental sulfur and sulfur containing hydrocarbon compounds.

It is also an object of this invention to provide an apparatus for accomplishing the aforementioned objects.

Other objects and advantages of this invention will become apparent to those skilled in the art as the description thereof proceeds.

Briefly the present invention comprises an improved combination process for the simultaneous desulfurization, denitrogenation, and deoxygenation (heretofore and hereinafter referred to collectively as desulfurization) of gas-oil and naphtha hydrocarbon fractions simultaneously with the reforming of the naphtha fraction in a single contacting column or zone which includes isolated and yet communicating desulfurization and reforming zones through which a moving bed of granular catalyst is passed. Preferably the granular catalyst is of the cobalt molybdate type referred to above which has reforming and desulfurization activity. The contacting zone employed in the present invention is provided with a desulfurization zone in the upper portion and a reforming zone in the lower portion and a moving bed of granular cobalt molybdate catalyst passes downwardly by gravity through each zone. The spent catalyst removed from the contacting zone and containing a deactivating hydrocarbonaceous deposit is recirculated to the top of the contacting zone through a regeneration zone in which the hydrocarbonaceous deposit is burned from the catalyst to restore its former activity.

The modification of catalyst distribution within the contacting zone illustrated in the figure involves the division of the entire stream at the upper portion of the zone into the first and second catalyst streams. The first stream passes into and downwardly as a moving bed into and directly through the desulfurization zone and is discharged therefrom at the bottom into the top of the reforming zone. The second stream is passed downwardly through and in indirect heat exchange relationship with the desulfurization zone into the subjacent reforming zone in the lower portion of the contacting column. In this catalyst division, freshly regenerated cobalt molybdate catalyst is supplied to the top of the desulfurization zone and a mixture of fresh catalyst and spent catalyst from the desulfurization zone is introduced into the reforming zone. This operation has several advantages including an extremely thorough naphtha reactant stripping of the spent desulfurization catalyst throughout the entire extent of the reforming zone. Accordingly it is especially well suited to applications of the present invention in which particularly heavy gas-oils are desulfurized in this combination process. Additionally, at particularly high temperatures for reforming such as are employed in benzene production, a tendency toward cracking or hydrocracking of the naphtha feed occurs and it has been found that the presence of spent catalyst eliminates this problem.

In the process of this invention, the endothermic reactions characterizing naphtha reforming and the exothermic reactions occurring during desulfurization, denitrogenation and deoxygenation in the desulfurization zone, normally result in the generation and maintenance of temperature gradients if the reaction zones are permitted to operate adiabatically. Reforming reaction rates decrease significantly with relatively small decreases in temperature and difficultly controllable hydrogenation reactions may occur if the temperature is permitted to increase unduly in the desulfurization zone. Accordingly, in the present invention the reacting mixture of naphtha and hydrogen is preferably heated at one or more points along the length of the reforming zone and the reacting mixture of gas-oil and naphtha vapor and hydrogen is cooled at one or more points along the length of the desulfurization zone to maintain the average reaction temperature in each of said zones substantially uniform at the optimum value.

In the reforming zone of the process of the present invention, naphtha vapor and between about 500 to 10,00 s. c. f. of hydrogen per barrel of naphtha are passe in contact with a cobalt molybdate catalyst at a liqui hourly space velocity (L. H. S. V.) of between about 0. and 2.0, at temperatures between about 800° F. and 100 F., preferably about 900° F., and at a pressure of betwee 50 p. s. i. and 5000 p. s. i., preferably between about 5 and 1000 p. s. i. such as about 400 p. s. i. to dehydrogenat and cyclize paraffin hydrocarbons and to dehydrogenat naphthene hydrocarbons to produce a highly aromati reformed gasoline product containing branched chai hydrocarbons and having a knock rating of above 9 Heat is added along the length of the reforming zone t maintain a uniform temperature profile therein by mear more fully described below. The reformed naphtha an the recycle hydrogen stream, which now contains exce hydrogen produced during the reforming, is mixed wit gas-oil to be treated. The gas-oil may be partly or con pletely vaporized, but in any event is preferably at temperature whereby admixture with the effluent fro the reforming zone will produce a mixture having a tem perature of about 775° F., which is the optimum preferre gas-oil and naphtha desulfurization temperature.

This mixture of gas-oil, naphtha and hydrogen is passe at the reduced temperature of from about 575° F., t 900° F., at an L. H. S. V. between about 0.2 and 15. at substantially the same pressure, and with from 50 t 5000 s. c. f. of hydrogen per barrel of hydrocarbor through the desulfurization zone wherein the naphtha an gas-oil are simultaneously desulfurized, denitrogenatec and deoxygenated to produce respectively, hydrogen sul fide, ammonia, and water vapor. The hydrocarbons re maining are hydrogenated to stable hydrocarbon product maintaining a high liquid product yield. These reaction consume the excess hydrogen which was generated as de scribed during the reforming step. In doing so, con siderable heat is liberated and accordingly the reactan mixture is preferably cooled at one or more points alon the length of the desulfurization zone so as to maintai the optimum desulfurization temperature.

In a preferred modification of the operation of thi process, the naphtha and gas-oil feed rates are balance against one another as a function of the naphthene hydro carbon content of the gasoline and of the sulfur, nitro gen, and oxygen content of the gas-oil so that during th reforming step the naphthene dehydrogenation proceed sufficiently to liberate a quantity of hydrogen which i equal to or greater than that necessary to fully desulfurize denitrogenate, and deoxygenate both the gas-oil and th naphtha. Thus a hydrogen balance is reached and n outside sources of hydrogen are required. This is on of the advantages of the present invention which, togethe with the requirement of only a single catalyst, namel cobalt molybdate, the means for temperature control i the desulfurization and reforming zones, the use of sepa rate cobalt molybdate catalyst streams within a singl contacting zone to treat two hydrocarbon streams, th naphtha stripping of the combined catalyst streams to per mit total recovery of gas-oil thereby eliminating the usua 10% gas-oil loss, and the subsequent steam stripping o the spent catalyst to recover the naphtha therefrom, yield an integrated process of this invention which permit simultaneous treatment of two related hydrocarbon frac tions to produce premium-grade internal combustion en gine fuels. By locating the desulfurization zone above the reforming zone and subsequently passing the spen desulfurization catalyst stream through the reforming zone, either directly or indirectly, the temperature of th spent desulfurization catalyst is raised in the presence o a naphtha and hydrogen flow which has been found t permit the highly efficient gas-oil stripping from the cata lyst with substantially no loss due to catalytic cracking.

The mixture of gas-oil, naphtha, and hydrogen i removed from the reactor effluent at the top of the con tacting zone, cooled, partially condensed, and the vapor

emaining is separated from the liquid. The gas fraction contains recycle hydrogen together with hydrogen sulfide, ammonia, and water vapor which may be separated from the recycle hydrogen by conventional means. It is preferred that the hydrogen recycle contain at least 25% hydrogen by volume and preferably more than 70% hydrogen by volume. The liquid fraction comprises a mixture of naphtha and gas-oil which is substantially free of sulfur, nitrogen, and oxygen and the naphtha fraction of which consists essentially of branched chain paraffin hydrocarbons and aromatic hydrocarbons and is an excellent blending stock for premium and aviation gasolines.

In the process of the present invention, it has been found that the required catalyst recirculation is low and the permissible on-stream time of the catalyst is long and therefore the regeneration of the catalytic material is quite simple. Although the spent catalyst removed from the bottom of the contacting zone may be passed through a separate regeneration zone in which the solids flow downwardly as a moving bed, it is a preferred form of this invention to convey the granular solids from the bottom to the top of the column through an elongated conveyance conduit in which the granular solids are maintained in compact dense packed form, that is, as a mass having a bulk density substantially equal to the static bulk density of the solids when at rest. The conveyance fluid employed is a regeneration gas such as a mixture of flue gas to which air or oxygen has been added to produce a regeneration gas mixture containing between about 1% and about 5% oxygen by volume at the bottom of the lift line. This combination conveyance-regeneration gas is passed through the conveyance zone at a rate sufficient to convey the granular solids upwardly as a compact mass. The fluid and the solids flow concurrently at a relatively low rate and are regenerated during conveyance. The spent regeneration gases are removed at the top of the conveyance conduit, and the regenerated solids are circulated into the top of the contacting zone.

It has been found that in spite of the regeneration of the catalyst, from 20 to 40% of the sulfur present on the spent catalyst remains, possibly in the form of cobalt or molybdenum sulfides or the like, the constitution of which is not known. It has been determined that when such regenerated catalyst is introduced directly into the desulfurization zone and contacts the hydrogen sulfide-containing gas there, the hydrogen sulfide in some way reacts with the sulfided regenerated catalyst to produce elemental sulfur. This sulfur is carried out with the reactor effluent and renders the product sour and corrosive. It has been found that by treating the regenerated catalyst with a countercurrent stream of hydrogen recycle gas substantially free of hydrogen sulfide, the sulfur on the catalyst is liberated as sulfur and sulfur dioxide in a reaction generating considerable heat, and the presence of elemental sulfur in the product is fully eliminated. The character of the reaction is not fully understood, but its effect upon the physical properties of the product is remarkable for the effluent gasoline is sweet.

The conveyance of spent catalyst to a separate regeneration zone and its regeneration therein during downward flow therethrough as a moving bed is conventional and will not be described in further detail. However, the modification wherein the spent catalyst is conducted upwardly as a moving bed through a conveyance-regeneration zone is a novel type of regeneration and the details of its operation will be briefly described below.

The pressure drop characteristic of this type of solids conveyance is of the order of 100 times that characteristic of pneumatic or gas lift (suspended) solids conveyance and the volume of gas required to convey dense packed solids is only a few percent of that required in gas lift. The granular solids to be conveyed are removed from the bottom of the contacting column at substantially the reforming pressure, are passed through a solids pressuring zone to increase the pressure of gases associated with the solids by an amount substantially equal to the characteristic pressure drop of the conveyance conduit, and then the solids are passed into the conveyance element of the apparatus.

The inlet of the conveyance-regenerator conduit is thus maintained at a relatively higher pressure generally than the pressure of the solids before introduction into the conveyance conduit. The granular solids are then transferred through the conveyance conduit in compact dense packed form by means of a concurrently depressuring conveyance-regeneration fluid. The frictional forces generated by the fluid depressuring through the interstices of the compact mass of solids generate a pressure gradient in the conduit sufficient to counteract opposing forces of friction of the sloids sliding against the walls of the conduit as well as the opposing force of gravitation and thereby establish a conveying force permitting movement of the compact porous granular mass in the direction of decreasing conveyance fluid pressure when solids are removed from the outlet and fed into the inlet.

The depressuring conveyance fluid hereby generates a pressure drop per unit length of conduit

$$\frac{dp}{dl}$$

(the pressure gradient) sufficient to overcome the opposing gravitational force ($\rho_s \cos \theta$), wherein ρ_s is the bulk density of the dense packed granular solids and θ is the angular deviation of the conveyance conduit from the vertical. The ratio of the former to the latter is

$$\frac{\frac{dp}{dl}}{\rho_s \cos \theta}$$

This factor is termed the conveyance force ratio and is the ratio of the force tending to move the solids through the conveyance conduit to the opposing forces of gravity tending to restrain such flow. The conveyance fluid must be depressured through the conduit at a rate sufficient to raise the conveyance force ratio to a value greater than 1.0 (factors in consistent units) in order that the conveying force exceed the forces resisting flow. The amount by which the conveyance force ratio must exceed a value of 1.0 is equal to the magnitude of the friction forces also tending to resist solids flow.

The granular solids are maintained during conveyance and regeneration in the compact form by means of the application of a compressive force on the discharge solids issuing from outlet of the conveyance conduit. Various means are available for applying such a force which has the effect of restricting the discharge rate of granular solids from the conveyance conduit but has virtually no effect on the discharge of the conveyance fluid therefrom. A transverse thrust plate or a grid may be spaced opposite and adjacent the outlet opening and against which the mass of solids discharges, or a static bed of solids may be used to submerge this outlet. The rate of solids conveyance is determined by the rate of solids removal from the contacting column which is full of dense packed solids in the form of a moving bed. The solids feeder at the column bottom controls this variable as described below.

The present invention will be more clearly understood by reference to the accompanying drawings in which:

Figure 1 is a schematic flow diagram of the process of this invention including an elevation view in cross section showing the details of the contacting column,

Figure 2 shows a cross-sectional view of the detail of the top part of the structure of Figure 1.

Referring now more particularly to Figure 1, contacting column 10 is divided into three major contacting zones

including first treating or desulfurization zone 12, second treating or reforming zone 14, and combination third treating or reforming and stripping zone 16. Contacting column 10 is provided at successively lower levels with treating gas injection zone 96, hopper and seal zone 18, effluent disengaging zone 20, second desulfurization zone 22, cooling zone 24, first desulfurization zone 26, gas-oil engaging and naphtha mixing zone 28, third reforming zone 32, heating zone 34, second reforming zone 36, first reforming and naphtha stripping zone 40, naphtha engaging zone 42, hydrogen stripping zone 43, hydrogen engaging zone 44, stripping zone 45, stripping gas engaging zone 46, and catalyst feeder zone 48.

The granular catalyst introduced into hopper zone 18 as a single stream is divided into a first and second stream in effluent disengaging zone 20. The first stream passes downwardly through the annular space between downcomers 50 and primary tubes 52 directly into and through desulfurization zone 12 while the second stream passes downwardly indirectly through the desulfurization zone and out of contact with the reactants therein through primary tubes 52. The second stream of catalyst is discharged at gas-oil engaging zone 28 at a rate controlled by valves 264. The first catalyst stream is removed from the bottom of desulfurization zone 12 through tubes 260 at a rate controlled by valves 262. The first and second streams of catalyst are mixed in the top of reforming zone 14 and pass downwardly together therethrough as a moving bed successively through reforming zones 32, 36, and 40. Within zone 40 especially and to some extent entirely throughout reforming zone 14 that portion of the catalyst therein derived from the first catalyst stream which passed through desulfurization zone 12 is thoroughly stripped by the entering stream of fresh naphtha and hydrogen whereby a complete removal of gas-oil from the catalyst is effected. This stripping action is described more fully below.

The relative volumetric rates of catalyst flowing in the first and second streams, that is, the control of the portion of the entire catalyst stream which passes through desulfurization zone 12, is effected by adjustment of flow control valves 262. It is not necessary that these control elements be valves, for orifices of fixed or variable area may be substituted at this point in the apparatus so as to control the relative solids flow rate. Orifices are entirely effective since the flow of solids through an orifice is substantially unaffected by the depth of the bed of solids above the orifice provided this depth is greater than two or three orifice diameters. Since the flow of solids through an orifice is effected by simultaneous fluid flow therethrough, vapor risers and caps 210 are provided which effectively bypass the reactant naphtha through tray 211 thus preventing any vapor flow interference with the solids flow rates.

The absolute circulation rate of granular solids through column 10 is fixed by reciprocating tray solids feeder 48 located in the bottom of the column. The details of this apparatus element are not shown because they are well-known in the art. This element also provides for a uniform removal of spent catalyst throughout the entire cross-sectional area of the column and this uniformity of solids flow is reflected entirely throughout the height of the column when primary tubes 52, secondary tubes 54, and the other tubular elements of this apparatus are uniformly distributed throughout the cross-sectional area of the column.

The combined stream of spent granular solids passes downwardly into solids pressuring means 66 in which the spent granular catalyst is pressured from the reaction pressure to a higher pressure exceeding the reaction pressure by an amount substantially equal to the required pressure differential for conveying the spent catalyst as a substantially compact upwardly moving bed through conveyance-regeneration conduit 68. The details of solids pressuring means 66 are not shown for they are described in copending application Serial No. 217,337 filed March 24, 1951, now U. S. Patent No. 2,695,212. The sp catalyst is pressured by means of high pressure gas, pr erably inert such as oxygen-free flue gas, introduc through line 70 controlled by valve 72. The thus pr sured solids then are passed downwardly to subme inlet opening 74 of the conveyance-regeneration zone. conveyance-regeneration gas, containing between ab 1% and about 5% by volume of oxygen, is introduc through line 76 at a rate controlled by valve 78 and pas downwardly concurrently with the pressured spent catal which flows by gravity into inlet opening 74, or oxygen concentration in line 68 may be maintained injection of the oxygen-containing gas directly into line as through line 71 controlled by valve 73. This c veyance-regeneration fluid is depressured concurren through conveyance-regeneration zone 68 as descrit above and the spent catalyst is simultaneously convey and regenerated during transit upwardly through the c veyance regeneration zone. In the present process, catalyst circulation rate is quite low and the heat genera by regeneration may be carried out of the system w the spent regeneration gases as subsequently described, a jacket or vessel may be provided surrounding c veyance zone 68 whereby a coolant may be passed arou zone 68 to remove heat in this way.

The spent regeneration gases discharging from zo 68 with the regenerated solids preferably contain l than 1% oxygen. The regenerated catalyst discharg into solids receiving and elutriation zone 80 direc against baffle 82 whereby the solids thrust or compacti force is applied to the discharging catalyst preventing fluidization and maintaining the granular solids duri conveyance and regeneration at a bulk density substa tially equal to the bulk density of the downwardly movi beds of catalyst in contacting column 10. The spe regeneration gas is disengaged from the solids throu inclined surface 87 of the discharged solids and is moved from the top of solids receiving zone 80 throu outlet 81 and aperture 83 and line 84 at a rate controll by valve 86 which is actuated by back pressure regulat 88. These gases, in being disengaged from the discharg solids, act as an elutriation medium and suspend and car out solids fines. The degree of elutriation is variable, described in connection with Figure 2 by varying the ar open to gas disengagement. The regeneration-elutriati gas is removed at substantially the same pressure as t operating pressure in contacting column 10, and may repressured and recirculated through the regeneration zo with added oxygen.

Referring now to Figure 2, a plan view in cross secti of solids-receiving chamber 80 is shown. Herein a shown the crossed vertical baffles 79 extending downwa into the discharged solids forming 4, 6, 8, or more i dividual circularly disposed elutriation chambers of pi shaped cross section. Only 4 chambers are shown f purposes of illustration. Gas outlet 81 is provided ce trally, between the individual chambers, and is provid with one or more openings 83. Thus, with one such ope ing, only the solids disengaging area in one individu chamber is active and the gas velocity therein is relative high because of the relatively constant conveyance-rege eration gas flow through the lift line and the thus r duced area of solids through which it is disengage By using more such openings, more of the individual el triation chambers actively disengage gas and the dise gagement velocity is lower. With the greater velociti of disengagement larger solids fines are suspended ar carried out, and reductions in velocity as described redu the size of the particles suspended and removed.

The regenerated cobalt molybdate catalyst, freed solids fines, passes downwardly in the form of compa bed 90 downwardly over treating gas disengaging zone 9 and then downwardly through inlet conduit 94 into the tc of column 10. The lower opening of inlet 94 is su rounded by treating gas injection collar 96. Hydroge sulfide-free recycle hydrogen is introduced by means

line 98 at a rate controlled by valve 100 and flow recorder controller 102 into collar 96. This treating gas splits into two streams, the first passing downwardly concurrently with the catalyst through hopper zone 18, and the second passing upwardly through inlet 94 and through treating zone 104 in the lower portion of solids receiving zone 80. This latter hydrogen stream countercurrently contacts the regenerated catalyst, causes the liberation therefrom of the residual quantities of sulfur in the form of sulfur and sulfur dioxide which are removed from treating gas disengaging zone 92 through line 106 at a rate controlled by valve 108 in accordance with differential pressure controller 110 which maintains a positive pressure differential between the extremities of inlet zone 94. This differential pressure is quite small, of the order of a few inches of water and serves to seal the top of the column against hydrogen sulfide contacting the regenerated catalyst. In this manner the reactor effluent is maintained entirely free of elemental sulfur and in this way a long standing problem has been eliminated whereby the conventional post treating operations on the product to render it sweet and non-corrosive are avoided.

The remainder of the description of Figure 1 will be conducted as an illustrative example of the process of the invention in which a straight run naphtha and a straight run gas-oil are simultaneously treated by the process of this invention. Both the naphtha and gas-oil are heavily contaminated with sulfur and nitrogen and their physical properties are as follows:

TABLE 1

Naphtha feed

Gravity, ° API	49.8
Boiling range, ° F	200–400
Sulfur, weight percent	0.10
Nitrogen, weight percent	0.003
Knock rating, F–1 clear	57

TABLE 2

Gas-oil feed

Gravity, ° API	24.5
Boiling range, ° F	500–900
Sulfur, weight percent	3.76
Nitrogen, weight percent	0.24

The naphtha feed rate is 1000 barrels per day and the gas-oil feed rate is 500 barrels per day. The total catalyst circulation rate is 14 tons per day, the rate through the desulfurization zone being 4 tons per day, and the rate through the reforming zone being 10 tons per day. The desulfurization and reforming zones are operated at a pressure of about 400 p. s. i. a. (pounds per square inch absolute), the temperature of the reforming zone is maintained at an average of 900° F. and the temperature of the desulfurization zone is maintained at an average of 750° F.

The naphtha feed passes from storage through line 120 by means of naphtha feed pump 122 at the above-mentioned rate controlled by valve 124 and flow recorder controller 126 through line 128 and interchanger 130. Herein the cold feed is exchanged with part of the reactor effluent described below and is raised to a temperature of 600° F. The preheated naphtha then flows through line 132 through naphtha preheating and vaporizing coil 134 in furnace 136. The naphtha vapor then passes by means of line 138 into naphtha engaging zone 42.

Recycle hydrogen, necessary in the operations conducted in this process and separated from the reactor effluent as described below, flows through the line 140 into gas purifier 142. Herein, by conventional means, hydrogen sulfide, ammonia, and water vapor are separated from the recycle gas and if desired any low molecular weight hydrocarbon gas which may be present such as methane, ethane, and the like may also be removed through line 143. The hydrogen thus treated then flows through line 144 together with additional hydrogen, if necessary, injected through line 146 controlled by valve 148 and is pumped by means of recycle blower 150 at a rate controlled by valve 152 and flow recorder controller 154 through hydrogen heating coil 156 in furnace 136. The heated hydrogen, at a temperature of about 900° F. passes through line 158 at a rate of 3000 M s. c. f./d. (thousand standard cubic feet per day) into hydrogen recycle engaging zone 44. Under the influence of a seal or stripping gas such as steam introduced through line 160 controlled by valve 162 into engaging zone 46 at a slightly higher pressure, substantially all of the hydrogen recycle gas passes upwardly from zone 144 and is combined with naphtha vapor in engaging zone 42 to form a reactant naphtha and hydrogen mixture which passes through the reforming zone as described in detail below.

The reactant mixture of naphtha and hydrogen passes upwardly through first reforming and naphtha stripping zone 40 countercurrent to the combined catalyst streams. Herein the initial catalytic reforming of the naphtha takes place simultaneously with exothermic hydrogenation of any olefinic constituents in the naphtha feed. The temperature rises somewhat to values preferably not exceeding about 925° F. This maximum temperature is controlled by reducing the naphtha vapor inlet temperature so that olefin hydrogenation does not raise the temperature above a value of that given. Simultaneously in zone 40, a highly effective naphtha and hydrogen stripping of that part of the catalyst introduced thereinto from desulfurization zone 12 takes place. Substantially all of the residual gas-oil present on the catalyst is removed thereby and vaporized leaving a spent reforming catalyst containing traces of adsorbed naphtha but substantially gas-oil free. As stated above, this spent catalyst is steam stripped in zone 45 immediately above stripping gas engaging zone 46 and the naphtha is returned upwardly into the reactant mixture and passes upwardly therewith. In this manner substantially no gas-oil or naphtha feed is lost by oxidation in the spent catalyst regeneration step and maximum liquid product yields of the order of 95% to 99% are obtained.

The reactant mixture of naphtha and hydrogen, together with minor amounts of gas-oil vapor stripped from the catalyst, passes upwardly into and countercurrently through second reforming zone 36. Herein additional aromatization takes place causing the temperature to drop to a value of preferably not less than 875° F. by the time it reaches heating zone 34.

At this point the naphtha reactants are reheated to a temperature of about 900° F. or slightly higher for subsequent passage through third reforming zone 32. Preferably the disengaging-engaging structure shown in the drawing is employed which consists of upper tray 166, lower tray 168 with a plurality of seal tubes 170 open at both ends and extending from above tray 166 through and to a point below lower tray 168. Seal tubes 170 pass the catalyst downwardly therethrough creating a path having a relatively high resistance to reactant vapor flow. Accordingly only a minor portion of the reactant vapor mixture passes upwardly through tubes 170 generating a pressure differential of about 1.0 p. s. i. which is sufficient to force the major portion of the mixture from lower disengaging zone 172 through line 174, into and through interheater 176 wherein the temperature is increased to compensate for the temperature drop occasioned by endothermic reforming reactions in the reforming zone 36 and the prospective temperature drop in zone 32. The reheated mixture is then passed through line 178 into engaging zone 180 wherefrom it passes upwardly through vapor risers 182 into the bottom of third reforming zone 32.

Herein the reheated vapor mixture contacts fresh reforming catalyst and additional aromatization takes place causing a further temperature decrease. The naphtha re-

forming zone effluent, containing aromatized naphtha vapor together with an excess of hydrogen recycle produced during the reforming, is disengaged from the catalyst in zone **28**. Fresh gas-oil, injected as described below, is mixed herein with the naphtha effluent from third reforming zone **32**, and the naphtha and gas-oil pass upwardly through vapor risers and caps **210** to be treated simultaneously in desulfurization zone **12**.

The gas-oil to be converted is introduced through line **188** and pumped by means of pump **190** at a rate of 500 barrels per day controlled by valve **192** and flow recorder controller **194**. The gas-oil flows through line **196** through preheater **198** in exchange with the remaining part of the reactor effluent. The preheated gas-oil at a temperature of about 650° F. flows through line **200** into and through gas-oil heating and vaporizing coil **202** in furnace **204**. Herein a partial or complete vaporization of gas-oil is effected, depending upon its end point, and the gas-oil is combined in line **206** with the naphtha-hydrogen effluent from reforming zone **14**. The furnace **204** is controlled to have an outlet temperature such that upon admixture of the thus heated gas-oil with the effluent naphtha vapor flowing from third reforming zone **32**, the temperature of the resulting mixture is substantially equal to the preferred desulfurization temperature, that is, about 750° F. In the present example the furnace outlet temperature was about 650° F. and the temperature of the naphtha mixture flowing into line **208** from reforming zone **32** was 900° F.

If it is desired, better mixing of the naphtha and gas-oil vapor to be desulfurized may be obtained by removing the disengaged naphtha and hydrogen from the column, mixing of this stream with the gas-oil at a point outside the column, and returning the mixture to the bottom of the desulfurization zone for passage therethrough.

The reactant mixture of naphtha and gas-oil vapor and recycle hydrogen formed as above described passes upwardly from engaging zone **28** through vapor risers **210** and then through first desulfurization zone **26** countercurrent to the downwardly flowing first stream of cobalt molybdate catalyst. Herein, under the temperature and pressure conditions given, the sulfur, nitrogen, and oxygen compounds are destructively hydrogenated forming the corresponding hydrocarbon derivatives together with hydrogen sulfide, ammonia, and water vapor. Depending upon the extent of gas-oil and naphtha contamination with these compounds, more or less heat is liberated in first desulfurization zone **26** and the temperature of the reactant vapor mixture rises to a value of about 780° F. after passage therethrough. In a manner entirely analogous with the disengaging and engaging of the reactant naphtha vapor described in connection with heating zone **34**, the reactant mixture is disengaged, cooled, and engaged in cooling section **24**. This section is provided with upper tray **212** and lower tray **214** forming disengaging zone **216** and engaging zone **218**. Catalyst seal tubes **220** are equivalent to tubes **170** described above. As before, a minor portion of the reactant vapor passes upwardly through the restricted passageway formed by tubes **220** generating a pressure drop which forces the major portion from disengaging zone **216** through line **220** and intercooler **222** and then back through line **224** into engaging zone **218**. In this example intercooler **222** serves to decrease the temperature of the reactant mixture to about 750° F. at which it enters second desulfurization zone **22** through vapor risers **226**.

Further desulfurization takes place in second desulfurization zone **22** which serves to remove substantially all the residual sulfur, nitrogen and oxygen contaminants therein. The temperature rises somewhat to a value of about 770° F. and accumulates in effluent disengaging zone **20** from which it is removed with a small portion of hydrogen passing downwardly with the catalyst through hopper zone **18**. The reactor effluent includes the naphtha and gas-oil vapors substantially free of the aforementioned contaminants together with moderat amounts of hydrogen sulfide, ammonia, water vapor, hy drogen, and small amounts of low molecular weight hy drocarbon gases.

The reactor effluent passes from disengaging zone 2 through line **228**, and is divided into two streams whic pass through gas-oil preheater **198** and through naphth preheater **130**. Effluent cooling and condensation take place and then the combined streams pass through lin **230** through product effluent cooler **232** and through lin **234** into vapor liquid separator **236**.

The condensed liquid product accumulates in the lowe portion of separator **236** and is removed therefron through line **238** controlled by valve **240** and liquid leve controller **242**. This liquid product contain some wate and consists essentially of gas-oil and naphtha mixture By means of conventional techniques, the water is sep arated as by settling and decantation and the hydrocarbo product is fractionated into a reformed desulfurizatio gasoline fraction and a desulfurized gas-oil fraction hav ing excellent cracking qualities and containing a larg fraction of hydrocarbons suitable for 50 cetane diesel fue or jet engine fuel. Upon such fractionation 952 barrel per day of C_4-free reformed gasoline having a 400° F end point are obtained, amounting to a liquid naphth yield of 95.2%. The physical properties of this gasolin are as follows:

TABLE 3

Reformed gasoline product

Gravity, ° API	50.4
Boiling range, ° F	100–42(
Sulfur, weight percent	0.00
Nitrogen, weight percent	ni
Knock rating, F–1 clear	85.2
Knock rating, 3 ml. TEL	91.8

The production of desulfurized gas-oil amounts to 55(barrels per day, liquid yield of gas-oil of 101%, and its physical properties are as follows:

TABLE 4

Gas-oil product

Gravity, °API	29.1
Boiling range, °F	400–90(
Sulfur, weight percent	0.53
Nitrogen, weight percent	0.1(
Cetane No	38.(

The uncondensed portion of the reactor effluent is removed from separator **236** through line **244** and is ordinarily divided into two streams. The first stream passes through line **140** to provide the recycle hydrogen employed in the process as described above. Any net production of hydrogen, which may result when highly naphthenic gasolines are reformed and desulfurized in the presence of a gas-oil which either contains relatively small amounts of sulfur or which is fed to the system at relatively low rates, is bled from the system through line **246** at a rate controlled by valve **248** and back pressure regulator **250** which maintains the operating pressure on the system. In the present example, the relative feed rates and compositions were such that no net hydrogen is produced and no net consumption of hydrogen takes place.

In this invention the desulfurization, which term is used to include denitrogenation and deoxygenation, takes place in the upper portion of the contacting column and the naphtha reforming is effected in the lower portion of the column. In the process, one or more interheaters or intercoolers are employed in the reforming or desulfurization zones respectively depending upon the degree of uniformity of the reaction temperature desired. Only one intercooler and interheater has been shown and described for sake of clarity, description and illustration, and it should be understood that as many as 8 or 10 of such heaters can be employed in the present apparatus.

Although other catalysts having desulfurization and reforming activities may be employed or a mixture of known catalysts including a desulfurization catalyst and a reforming catalyst can also be used, the preferred catalytic agent to be used in this process is the cobalt molybdate type containing cobalt and molybdenum oxides in the amounts given above because these have been found to be extremely stable under reforming and desulfurization conditions and in addition have been found to have simultaneously very high activities for reforming, desulfurization, denitrogenation, and deoxygenation properties which are not found in other known catalysts.

Cobalt molybdate catalysts in general comprise mixtures of cobalt and molybdenum oxides wherein the molecular ratio of CoO to MoO_3 is between about 0.4 and 5.0 and are prepared as described below. This catalyst may be employed in unsupported form or alternatively it may be distended on a suitable carrier such as alumina, silica, zirconia, thoria, magnesia, magnesium hydroxide, titania or any combination thereof. Of the foregoing carriers it has been found that the preferred carrier material is alumina and especially alumina containing about 3–8% by weight of silica.

In the preparation of the unsupported cobalt molybdate, the catalyst can be coprecipitated by mixing aqueous solutions of, for example, cobalt nitrate and ammonium molybdate, whereby a precipitate is formed. The precipitate is filtered, washed, dried and finely activated by heating to about 500° C.

Alternatively, the cobalt molybdate may be supported on alumina by coprecipitating a mixture of cobalt, aluminum and molybdenum oxides. A suitable hydrogel of the three components can be prepared by adding an ammoniacal ammonium molybdate solution to an aqueous solution of cobalt and aluminum nitrates. The precipitate which results is washed, dried and activated.

In still another method, a washed aluminum hydrogel is suspended in an aqueous solution of cobalt nitrate and an ammoniacal solution of ammonium molybdate is added thereto. By this means a cobalt molybdate gel is precipitated on the alumina gel carrier.

Catalyst preparations similar in nature to these and which can also be employed in this invention have been described in U. S. Patents 2,369,432 and 2,325,033.

Still other methods of catalyst preparation may be employed such as by impregnating a dried carrier material, e. g. an alumina-silica gel, with an ammoniacal solution of cobalt nitrate and ammonium molybdate. Preparation of this type of cobalt molybdate catalyst are described in U. S. Patent 2,486,361.

In another method for preparing impregnated molybdate catalyst the carrier material may be first impregnated with an aqueous solution of cobalt nitrate and thereafter impregnated with an ammoniacal molybdate. Alternatively, the carrier may also be impregnated with these solutions in reverse order. Following the impregnation of the carrier by either of the foregoing methods the material is drained, dried and finally activated in substantially the same manner as is employed for the other catalysts.

In the preparation of impregnated catalysts where separate solutions of cobalt and molybdenum are employed, it has been found that it is preferable to impregnate the carrier first with molybdenum, e. g., ammoniacal ammonium molybdate, and thereafter to impregnate with cobalt, e. g., aqueous cobalt nitrate, rather than in reverse order.

In another method for the preparation of suitable catalyst, a gel of cobalt molybdate can be prepared as described hereinbefore for the unsupported catalyst, which gel after drying and grinding can be mixed with a ground alumina, alumina-silica or other suitable carrier together with a suitable pilling lubricant or binder which mixture can then be pilled or otherwise formed into pills or larger particles and activated.

In another modification, finely divided or ground molybdic oxide can be mixed with suitably ground carrier such as alumina, alumina-silica and the like in the presence of a suitable lubricant or binder and thereafter pilled or otherwise formed into larger agglomerated particles. These pills or particles are then subjected to a preliminary activation by heating to 600° C. for example, and are thereafter impregnated with an aqueous solution of cobalt nitrate to deposit the cobalt compound thereon. After draining and drying, the particles are heated to about 600° C. to form the catalyst.

It is apparent from the foregoing description of the different types of cobalt molybdate catalyst which may be employed in this invention that we may employ either an unsupported catalyst, in which case the active agents approximate 100% of the composition, or we may employ a supported catalyst wherein the active agents, cobalt and molybdenum oxides, will generally comprise from about 7 to 22% by weight of the catalyst composition. In all of the foregoing catalytic preparations it is desirable to maintain the molecular ratio of cobalt oxide as CoO to molybdic oxide as MoO_3 between about 0.4 and 5.0.

A particular embodiment of the present invention has been described in considerable detail by way of illustration. It should be understood that various other modifications and adaptations thereof may be maintained by those skilled in the particular art without departing from the spirit and scope of this invention as set forth in the appended claims.

I claim:

1. A process for the simultaneous desulfurization and reforming of gas-oil and naphtha hydrocarbon fractions in the presence of a recirculating stream of hydrocarbon conversion catalyst which comprises recirculating said catalyst through a hydrocarbon contacting zone containing a desulfurization zone and a subjacent reforming zone, and through a catalyst regeneration zone, dividing the regenerated catalyst into a first and second catalyst stream prior to passage of said catalyst through said contacting zone, passing said first catalyst stream into and directly through said desulfurization zone as a downwardly moving bed by gravity in direct contact with hydrocarbons passing therethrough and then through a solids flow rate control zone into said reforming zone, passing said second catalyst stream as a downwardly moving bed by gravity indirectly through said desulfurization zone in indirect heat exchange relation thereto and out of direct contact with said hydrocarbons and through said solids flow rate control zone into said reforming zone for combination therein with said first catalyst stream, subsequently passing the combined catalyst stream downwardly by gravity as a moving bed through said reforming zone, maintaining said desulfurization zone at a hydrocarbon desulfurization temperature and at a superatmospheric pressure, maintaining said reforming zone at a substantially higher hydrocarbon reforming temperature and at substantially the same superatmospheric pressure, passing a naphtha hydrocarbon fraction and hydrogen through said reforming zone in direct contact with said combined catalyst stream, combining a gas oil hydrocarbon fraction with the thus treated naphtha fraction flowing from said reforming zone, passing the naphtha, gas oil, and hydrogen mixture thus formed into said contacting zone at a point between said desulfurization and reforming zones and upwardly through said desulfurization zone in contact with said first catalyst stream alone, removing a contacting zone effluent therefrom, cooling and partially condensing said effluent, separating an uncondensed hydrogen-rich gas, recirculating at least part thereof through said contacting zone, passing said combined catalyst stream from said reforming zone downwardly by gravity through a solids feeder zone, controlling therein the absolute circulation rate of said cata-

lyst in said process, removing the combined catalyst stream from said contacting zone, regenerating said catalyst in said regeneration zone by contact with an oxygen-containing gas, elutriating catalyst fines from the regenerated catalyst by disengaging spent regeneration gases therefrom through a variable area of a conveyed dense mass of said catalyst, subsequently treating the regenerated catalyst with a hydrogen-containing gas to remove residual sulfur from said catalyst, and passing the thus treated regenerated catalyst back into said contacting zone for repassage therethrough.

2. A process according to claim 1 wherein said combined stream of catalyst from said contacting zone is regenerated and returned to said conversion zone by the steps which comprise passing said catalyst from said contacting zone into a solids pressuring zone which communicates at its lower end with an elongated conveyance-regeneration zone, injecting a conveyance fluid thereinto at a pressure substantially above that of said contacting zone whereby the fluid flows therefrom through said conveyance-regeneration zone at a rate sufficient to overcome opposing forces of gravity and friction acting on said catalyst therein and conveys said catalyst upwardly therethrough as a continuous dense packed mass of catalyst solids having substantially the same bulk density of said catalyst when at rest, applying a force against the mass of catalyst emerging from said conveyance-regeneration zone to maintain the dense packed condition of said catalyst therein, and maintaining a concentration of oxygen in the conveyance fluid flowing through said conveyance-regeneration zone whereby the catalyst is regenerated during conveyance.

3. A method according to claim 1 in combination with the steps of maintaining a substantially uniform temperature profile throughout said reforming zone by the steps of separating a part of the reactant mixture of naphtha and hydrogen from said combined stream of catalyst at at least one point along said reforming zone, indirectly heating said mixture, and returning said mixture to contact further quantities of said combined catalyst stream, maintaining a substantially uniform temperature profile throughout said desulfurization zone by the steps of separating the reactant mixture of naphtha, gas oil, and hydrogen from said first stream of catalyst at at least one point along said desulfurization zone, indirectly cooling said mixture, and returning said mixture to contact further quantities of said first catalyst stream.

4. A method according to claim 1 in combination with the step of controlling the relative rates of flow of said first and second catalyst streams in said solids flow rate control zone just prior to the introduction thereof into said reforming zone for combination therein.

5. A process for the simultaneous desulfurization and reforming of gas-oil and naphtha hydrocarbon fractions in the presence of a recirculating stream of cobalt molybdate hydrocarbon conversion catalyst analyzing between about 2% and 10% by weight CoO and between about 5% and 30% by weight of MoO_3 which comprises recirculating said catalyst through a hydrocarbon contacting zone containing a desulfurization and reforming zone and through a catalyst regeneration zone, dividing the regenerated catalyst into a first and a second catalyst stream prior to passage of said catalyst through said contacting zone, passing said first catalyst stream into and directly through said desulfurization zone as a downwardly moving bed by gravity and then in direct contact with hydrocarbons passing therethrough and then through a catalyst flow rate control zone into said reforming zone, passing said second catalyst stream as a downwardly moving bed by gravity through said desulfurization zone in indirect heat exchange relation thereto and out of contact with said hydrocarbons therein and then through said catalyst flow rate control zone into admixture with said first catalyst stream, passing the combined catalyst stream downwardly through said reforming zone in direct contact with hydrocarbons passing therethrough, maintaining said desulfurization zone at a hydrocarbon desulfurization temperature of from about 575° F. to 900° F. and at a superatmospheric pressure of from about 50 p. s. i. to 5000 p. s. i., maintaining said reforming zone at a substantially higher hydrocarbon reforming temperature of from about 800° F. to 1000° F. and at substantially the same superatmospheric pressure, passing a naphtha hydrocarbon fraction and from about 500 to 10,000 s. c. f. of hydrogen per barrel of naphtha through said combined first and second catalyst streams in said reforming zone, introducing into said contacting zone at a point between said desulfurization and reforming zones a gas-oil hydrocarbon fraction, introducing into admixture with said gas-oil fraction the hydrogen and naphtha effluent from said reforming zone, passing the naphtha, gas-oil, and hydrogen mixture thus formed into and upwardly through said desulfurization zone in contact with said first catalyst stream alone, removing an effluent therefrom, cooling and partially condensing said effluent, separating therefrom an uncondensed hydrogen-rich gas, recirculating at least part thereof through said contacting zone, passing said combined catalyst stream from said reforming zone by gravity into and through a solids feeder zone to control the absolute recirculation rate of said catalyst in said process, removing the combined catalyst stream from said contacting zone, regenerating said catalyst in said regeneration zone by contact with an oxygen-containing gas, elutriating catalyst fines from a dense mass of the regenerated catalyst by disengaging spent regeneration gases therefrom through a variable area of said dense nonfluidized mass of catalyst, subsequently treating the regenerated catalyst with a hydrogen-containing gas to remove residual sulfur from said catalyst, and passing the thus treated regenerated catalyst back into said contacting zone for repassage therethrough.

6. A process for the simultaneous desulfurization and reforming of two distinct hydrocarbon fractions of substantially different boiling ranges in a single catalytic hydrocarbon contacting zone which comprises introducing a solid granular reforming and desulfurization catalyst into said contacting zone, dividing said catalyst at the top thereof into a first and second stream, passing said first stream into and downwardly as a moving bed in direct contact with hydrocarbons passing through a first treating zone, maintaining said first treating zone at a relatively low temperature, passing said second stream downwardly through and in direct heat exchange relation with said first treating zone and out of contact with said first catalyst stream, and through a catalyst flow rate control zone into a subjacent second treating zone passing said first stream from said first treating zone through said catalyst flow rate control zone into said second treating zone and into admixture with said second catalyst stream, passing the combined catalyst streams downwardly therethrough as a moving bed by gravity, passing spent catalyst from the bottom of said contacting zone through a regeneration zone to the top of said contacting zone for repassage therethrough, passing the higher boiling hydrocarbon fraction at said relatively low temperature in admixture with hydrogen into said contacting zone between said first and second treating zones and upwardly through said first catalyst stream in said first treating zone to effect exothermic desulfurization therein, passing the lower boiling hydrocarbon fraction at said relatively high temperature in admixture with hydrogen first upwardly through said combined stream of catalyst flowing through said second treating zone to effect endothermic reforming of said lower boiling hydrocarbon and to strip residual quantities of said higher boiling hydrocarbon fraction from the combined catalyst stream, disengaging from said combined catalyst said lower boiling hydrocarbon fraction after passage therethrough, passing said hydrocarbon effluent and hydrogen from said second treating

zone into admixture with said higher boiling hydrocarbon and then upwardly therewith through said first treating zone to effect exothermic desulfurization therein, controlling the absolute recirculation rate of said catalyst through said contacting zone by passing said combined catalyst stream from said second treating zone by gravity through a solids feeder zone, and removing a combined effluent from the top of said contacting zone containing the treated lower and higher boiling hydrocarbon fractions.

7. A process as defined in claim 6 wherein said catalyst comprises a minor proportion of the oxides of cobalt and molybdenum supported on a carrier which is predominantly activated alumina.

8. A process as defined in claim 7 wherein said low-boiling hydrocarbon fraction is naphtha, and said high-boiling hydrocarbon fraction is gas-oil.

9. A process for the simultaneous desulfurization and reforming of gas-oil and naphtha hydrocarbon fractions in the presence of a recirculating stream of catalyst having desulfurization and reforming activity, which comprises recirculating said catalyst through a hydrocarbon contacting zone containing an upper desulfurization zone and a lower reforming zone, and through a catalyst regeneration zone, dividing the regenerated catalyst into a first and second catalyst stream prior to passage of said catalyst through said contacting zone, passing said first catalyst stream into and directly through said desulfurization zone as a downwardly moving bed by gravity in direct contact with hydrocarbons passing therethrough, passing said first catalyst stream therefrom through a catalyst flow rate control zone into said reforming zone, passing said second catalyst stream as a downwardly moving bed by gravity indirectly through said desulfurization zone in indirect heat exchange relation thereto and out of contact with said hydrocarbons therein, passing said second catalyst stream therefrom through said catalyst flow rate control zone into said reforming zone for admixture therein with said first catalyst stream, subsequently passing the combined catalyst stream downwardly by gravity as a moving bed through said reforming zone in direct contact with hydrocarbons passing therethrough, maintaining said desulfurization zone at a hydrocarbon desulfurization temperature and at a superatmospheric pressure, maintaining said reforming zone at a subtsantially higher hydrocarbon reforming temperature and at substantially the same superatmospheric pressure, passing a naphtha hydrocarbon fraction and hydrogen upwardly through said reforming zone in direct contact with said combined catalyst stream, introducing a gas-oil hydrocarbon fraction into said contacting zone at a point between said desulfurization and reforming zones and into admixture with the thus treated naphtha fraction flowing into said desulfurization zone from said reforming zone, passing the naphtha, gas-oil, and hydrogen mixture thus formed into and upwardly through said desulfurization zone in contact with said first catalyst stream alone, removing a contacting zone effluent therefrom controlling the absolute recirculation rate of said catalyst through said contacting zone by passing said combined catalyst stream from said reforming zone by gravity into and through a solids feeder zone, then removing spent catalyst at the thus controlled rate from said contacting zone, and returning it through a catalyst regeneration zone to the contacting zone for repassage therethrough.

10. An apparatus for the contacting of two fluid streams with a recirculating stream of granular solid contact material which comprises an elongated vertical contact column adapted to the downward passage by gravity of a moving bed of solid granular contact material and provided at successively lower levels therein with a solids hopper and seal section, a first treating section, a solids flow rate control section, a second treating section, a contact material stripping section, and a reciprocating solids feeder section, a solids inlet conduit at the top of said column, an inlet conduit for a first solids stream from said hopper into the top of said first treating section, at least one elongated conduit for a second solids stream opening from said hopper and extending entirely through said first treating section through said solids flow rate control section into the top of said second treating section, a solids outlet conduit for said first solids stream opening from the bottom of said first treating section through said solids flow rate control section into the top of said second treating section, means below said first treating section in said solids flow rate control section for controlling the relative flow rates of said first and second solids streams, at least one heat exchange means disposed along each of said first and second treating sections, means for passing fluid from said sections respectively into and through said heat exchange means and back into said treating sections, a solids outlet at the bottom of said column communicating with a solids regenerator, a solids-receiving vessel communicating with said regenerator and with the solids inlet to said column, means for passing a treating fluid upwardly through said solids inlet and into said solids-receiving vessel, controllable outlet means for disengaging a fluid from a dense mass of solids in said solids-receiving vessel to elutriate solids fines, means for introducing one fluid stream at the bottom of said first treating section, means for introducing another fluid stream into the bottom of said first treating section, means for conducting fluid flow opening from the top of said second treating section and into the bottom of said first treating section, effluent outlet means for removing a fluid effluent at the top of said first treating section, cooling and condensing means communicating with said effluent outlet means and communicating with vapor-liquid separator means, and a vapor recycle conduit and pump means communicating from said separator means and opening into the bottom of said column through a vapor heating means.

11. An apparatus according to claim 10 wherein said solids outlet from said column comprises a mechanically sealable solids pressuring means in solids-receiving relation to said column and adapted to increase the fluid pressure in interstices of said solids, said solids regenerator comprises an elongated conveyance-regenerator conduit opening from said pressuring means, means for depressing a fluid from said pressuring means through said conveyance-regenerator conduit at a rate sufficient to overcome forces of gravity and friction acting on said solids, means for introducing an oxygen-containing gas into said fluid, and means within said solids-receiving vessel to apply a force against solids emerging from said conveyance-regenerator conduit to maintain solids therein during conveyance and regeneration substantially at their static bulk density.

12. An apparatus according to claim 11 wherein said solids-receiving vessel is provided in its upper end above the conveyance-regenerator conduit outlet with a plurality of angularly disposed baffles intersecting along the vertical axis of said vessel and sealed at their outer and upper edges against the inner walls of said vessels and having their lower edges submerged in the dense mass of solids emerging from the outlet of said conveyance-regenerator conduit to provide a plurality of sealed individual elutriation chambers of pi-shaped cross section therein and controllable fluid outlet means therefrom to remove said conveyance fluid from at least one of said elutriation chambers whereby said fluid is disengaged from said dense mass of emerging solids through the upper exposed surface area of the solids mass in each of said individual chambers from which fluid is removed to elutriate solids fines from said dense mass of solids.

13. An apparatus for the contacting of two fluid streams with a recirculating stream of granular solid contact material which comprises an elongated vertical contact column adapted to the downward passage by

gravity of a moving bed of solid granular contact material and provided at successively lower levels therein with a solids hopper and seal section, a first treating section, a solids flow rate control section, a second treating section, and a reciprocating solids feeder section, a solids inlet conduit at the top of said column, an inlet conduit for a first solids stream opening from said hopper into the top of said first treating section, at least one elongated conduit for a second solids stream opening from said hopper and extending entirely through said first treating section into the top of said second treating section, a solids outlet conduit for said first solids stream opening from the bottom of said first treating section into the top of said second treating section, a solids flow rate control means disposed at the outlet of each of said elongated and outlet conduits below said first treating section for controlling the relative flow rates of said first and second solids streams in said solids flow rate control section, said solids feeder being adapted to control the absolute circulation rate of said solid contact material through said contacting column, at least one heat exchange means disposed along each of said first and second treating sections, means for passing fluid from said sections respectively into and through said heat exchange means and back into said sections, a solids outlet conduit at the bottom of said column communicating with a solids regenerator, a solids-receiving vessel communicating with said regenerator and with said solids inlet conduit to said column, means for passing a treating fluid upwardly through said solids inlet conduit and into said solids-receiving vessel, controllable outlet means for disengaging a fluid from the variable surface area of a dense mass of solids in said solids-receiving vessel to elutriate solids fines therefrom, inlet means for introducing one fluid stream at the bottom of and for passage upwardly through said second treating section, inlet means for introducing another fluid stream at the bottom of and for upward passage through said first treating section, conduit means opening from the top of said second treating section into the bottom of said first treating section, and effluent outlet means for removing a fluid effluent at the top of first treating section.

14. An apparatus according to claim 13 wherein said means for passing fluid through said heat exchange means comprises a pair of parallel horizontal trays disposed adjacent one another and filling the entire cross section of said treating section and spaced adjacent one another therein, at least one solids downcomer conduit opening from a point above the upper tray and extending downwardly through said lower tray and terminating at a point substantially therebelow and adapted to the downward passage of said solids therethrough, a connecting conduit communicating said heat exchange means with the space below the lower tray, a connecting conduit communicating said heat exchange means with the space between said trays, and means for passing fluid from the space between said trays into the space above the upper tray whereby a minor portion of the fluid passing through said treating section passes through said downcomer conduit generating therein a pressure differential which forces the remaining major portion of said fluid from the contacting column successively through said connecting conduits and said heat exchange means and back into said contacting column to contact further quantities of said further contact material.

References Cited in the file of this patent

UNITED STATES PATENTS

2,293,759	Penisten	Aug. 25, 1942
2,393,288	Byrns	Jan. 22, 1946
2,439,372	Simpson	Apr. 6, 1948
2,459,824	Leffer	Jan. 25, 1949
2,489,863	Collins et al.	Nov. 29, 1949
2,494,794	Bonnell	Jan. 17, 1950
2,558,769	McKinney	July 3, 1951
2,647,587	Berg	Aug. 4, 1953
2,689,821	Imhoff et al.	Sept. 21, 1954
2,724,683	Nadro	Nov. 22, 1955

OTHER REFERENCES

"New Lift Technique," Weber, Oil and Gas Journal, Aug. 11, 1952, page 75.