

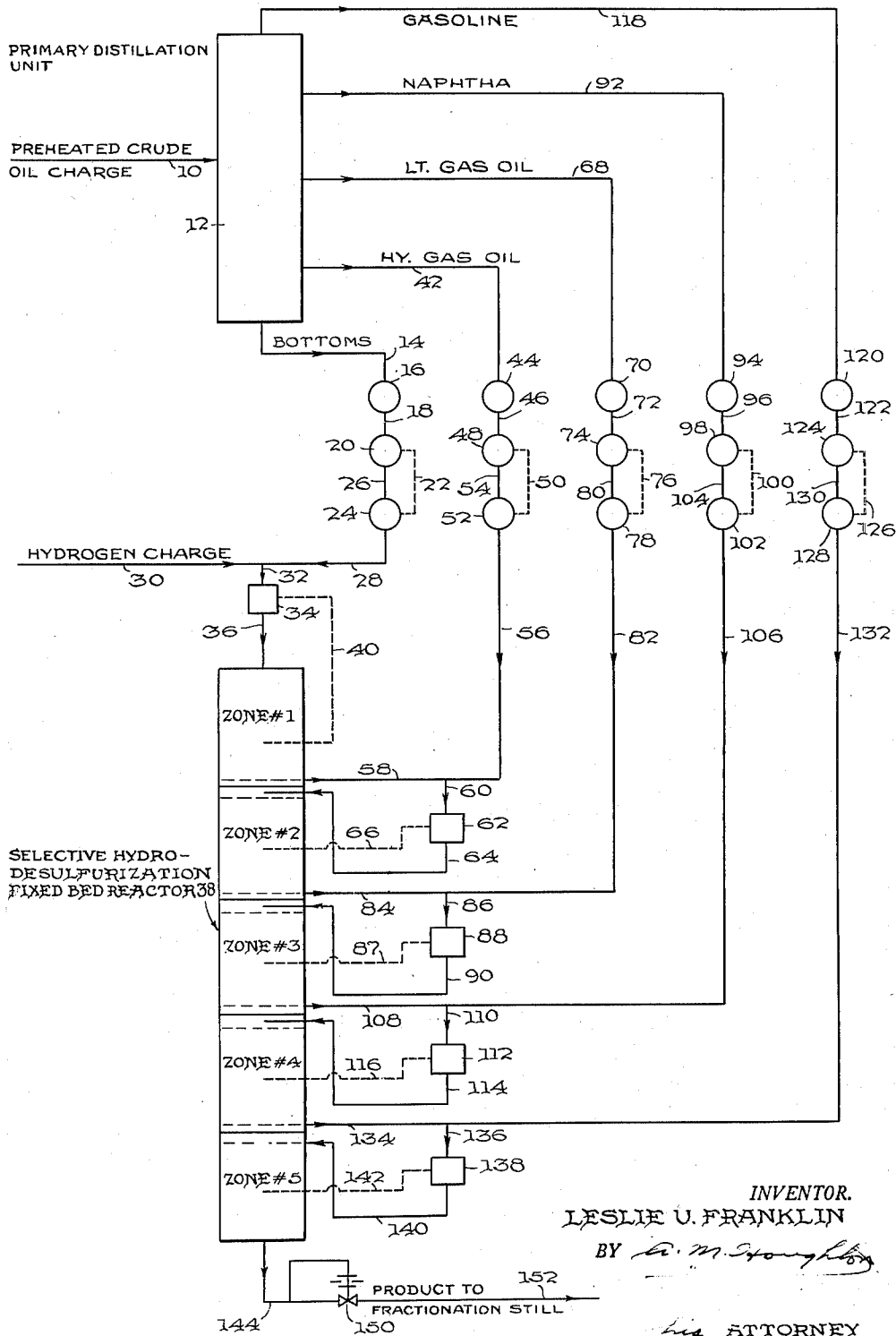
March 4, 1952

L. U. FRANKLIN

2,587,987

SELECTIVE HYDRODESULFURIZATION PROCESS

Filed May 10, 1949



UNITED STATES PATENT OFFICE

2,587,987

SELECTIVE HYDRODESULFURIZATION
PROCESSLeslie U. Franklin, Port Arthur, Tex., assignor to
Gulf Oil Corporation, Pittsburgh, Pa., a cor-
poration of Pennsylvania

Application May 10, 1949, Serial No. 92,385

12 Claims. (Cl. 196—28)

1

This invention relates to a selective hydrodesulfurization process and more particularly to an improved method of conducting hydrodesulfurization reactions.

The various hydrodesulfurization processes have proved to be of great importance for the desulfurizing of sulfur-containing petroleum hydrocarbons. The methods of conducting this process are broadly divisible into two basic types, namely the catalytic hydrodesulfurization method and the contact hydrodesulfurization process. The former encompasses those methods in which the sulfur contained in the charge stock is removed therefrom in the form of a gas such as hydrogen sulfide, by the catalytic action of a catalytic material having hydrogenating characteristics such as nickel, nickel oxide, the iron group metal molybdates, sulfides, molybdenum compounds, etc. The contact method on the other hand removes the sulfur by chemically combining it with a contact agent which should be one possessing hydrogenating characteristics such as an iron group metal, metal oxide or combination thereof deposited on a carrier. The sulfur is removed from the charge stock by being absorbed as metallic sulfide on the contact agent and the process is discontinued when the iron group metal content of the contact has been substantially converted into iron group metal sulfide, and the contact is regenerated.

Among the major difficulties encountered with both processes is the undue amount of hydrogen consumption causing concomitant abnormally large facilities for the preparation and storage of hydrogen. An equally great or greater impediment in these processes is the diminution of catalyst activity, and the shortening of catalyst life due to the deposition of coke and carbon upon the catalyst. Not only does this deposition cause the catalytic activity to diminish and consequently decrease the useful on-stream period, but also the coke causes a pulverization and powdering of the contact bed, hence reducing the over-all catalyst life. In turn the adverse effect on the catalyst causes an increased amount of cracking of the charge stock. The problem of hydrogen consumption is also intimately correlated with the coke deposition in that large amounts of hydrogen are wasted by reacting with the coke, or with the cracked charge stock due to the catalytic activity of the coke, to form low boiling gaseous hydrocarbons, such as methane. Furthermore,

2

due to the decrease in catalyst activity, larger reactor sizes must be utilized to achieve commercial practicality.

This invention has as an object the provision of a hydrodesulfurization process in which the hydrogen consumption is materially reduced.

A further object of this invention is to provide a hydrodesulfurization process in which the activity and life of the catalyst is greatly extended.

10 A still further object of this invention is to provide a hydrodesulfurization process in which the coke deposition on the surface of the catalyst is materially reduced.

Another object of the present invention is to 15 provide a hydrodesulfurization process in which the size of the reactor is reduced, without reducing the yield of product. Other objects will appear hereafter.

These and other objects are achieved by the 20 present invention which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a contact material having hydro- 25 genating characteristics in the presence of a hydrogen-containing gas, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas, and contacting the combined mixture with a contact material having hydrogenating characteristics at an incrementally higher temperature.

This invention can be applied with exceptional success to high boiling petroleum hydrocarbon oils, such as total crude containing sulfur. By 35 "total crude" is meant 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. This same principle can be applied with similarly 40 improved results to any fraction or fractions, obtained from a crude oil, by first subdividing such primary fractions into any desired number of subsidiary fractions and hydrodesulfurizing them in the inverses order of their boiling ranges at incrementally higher temperatures, in the manner described herein for the primary fractions.

I have found that the optimum hydrodesulfurization conditions vary with the boiling point range of a petroleum hydrocarbon fraction. 50 Hence by fractionating a crude charge stock prior to hydrodesulfurizing and recombining these fractions as described, definitive optimum conditions

of time, temperature, and hydrogen to oil ratio will be obtained for each fraction. By hydrodesulfurizing crudes in this manner, namely by recombining so as to subject each fraction to its optimum time, temperature and hydrogen to oil ratio conditions, highly superior hydrodesulfurization results may be achieved. Furthermore, I have found that by treating the various charge stock fractions in inverse hydrodesulfurization temperature relationship to the boiling point range of the petroleum fraction the superior results of the present invention may be achieved.

Besides increasing the temperature with the addition of each lower boiling fraction, I have found that the higher boiling fractions, such as reduced crude oil, which are more resistant to hydrodesulfurization, tend to thermally crack and deposit coke on the catalyst more readily than do the more thermally stable lower boiling fractions such as gasoline which are less resistant to hydrodesulfurization, and that this deposited coke which stems mainly from the higher boiling fractions decreases the catalyst activity, increases thermal cracking, increases hydrogen consumption, and increases the catalyst regeneration requirements. The coke deposition is accelerated by increasing the temperature and contact time. The rate of this acceleration is much greater with the higher boiling fractions than with the lower boiling fractions. I have found that the rate of coke deposition from the higher boiling fractions is substantially reduced by partially hydrogenating them at lower temperatures, such as between 700° F. and 750° F. at relatively long contact times, and then gradually increasing the temperature while simultaneously decreasing the contact time. By this method of processing, the higher boiling fractions are incrementally fortified with hydrogen to make them more resistant to thermal decomposition at the incrementally higher temperatures which are required for increased degrees of hydrodesulfurization. The lower boiling fractions, which are normally richer in hydrogen when obtained from the crude oil, require less prehydrogenation before being subjected to the higher temperatures for hydrodesulfurization. They also require shorter contact times at these higher temperatures.

While the application of my process to hydrodesulfurization reactions will result in improved process circumstances, my process is affected by such variables as type of catalyst, hydrogen-oil ratio, over-all space velocity, system pressure, etc., in a manner similar to their effects on conventional processes.

For the purposes of illustration I shall indicate the application of the present invention to a contact hydrodesulfurization process. However, as will be indicated hereafter, the invention is equally applicable to catalytic hydrodesulfurization methods. To more fully understand the nature of my invention, reference should be made to the accompanying diagram in which preheated crude oil charge enters primary distillation unit 12 by means of line 10. In primary distillation unit 12 the crude charge is fractionated into a plurality of fractions. In the accompanying figure, I have indicated the fractionation as producing 5 fractions, namely, gasoline, naphtha, light gas oil, heavy gas oil and crude oil bottoms. By gasoline, is meant those hydrocarbons in the crude charge stock boiling in the range of between 100° to 400° F. The naphtha fraction connotes the fraction distilling after the gasoline fraction, namely, the material having a boiling range of about 350° F to

525° F. The light gas oil fraction is that fraction which distills after the naphtha fraction and boils over a range of about 500° to 600° F. The heavy gas oil comprises the fraction boiling between about 600° to 650° F. The bottoms is the material left after the previously mentioned fractions have been distilled from the crude. The crude oil charge may be fractionated into a larger or smaller number of fractions, but I have found that optimum results are obtained when the fractions approximate those given in the accompanying flow diagram.

The bottoms from primary distillation unit 12 are removed by means of line 14 and pass through cooler 16, line 18 into accumulator 20. The amount of bottoms in accumulator 20 is controlled by level controller 22 which is in series with pump 24. From accumulator 20 the crude oil bottoms pass through line 26, pump 24 into line 28. In line 28 the bottoms are joined by hydrogen-containing gases which enter the system by means of line 30. This mixture of hydrogen-containing gases and crude oil bottoms passes through line 32 into heater 34. In heater 34 the crude oil bottoms are heated to the desired reaction temperature for the initial portion of the hydrodesulfurization process, and this mixture is passed by means of line 36 into the uppermost portion of reactor 38 which comprises zone 1. The temperature of the hydrogen-containing gas and crude oil bottoms mixture in zone 1 is regulated by temperature controller 40 attached to heater 34 and zone 1.

In zone 1 the mixture of bottoms and hydrogen-containing gas passes over beds of contact material having hydrogenating characteristics. This contact material is preferably a member of the iron group metals, i. e., nickel, iron or cobalt and may be in the free metallic state or in the form of metal oxide or as a combination of free metal and oxide. In all cases the contact material should be supported on a carrier. I have found that of the iron group metals, those containing nickel comprise the most advantageous contacts, and that contacts having substantial amounts of nickel oxide constitute the preferred contacts for the purposes of my invention. By carrier, I mean any substances widely used in the petroleum industry for this purpose, such as alumina, kieselguhr, silica gel, aluminum silicate, silica-alumina, Alfrax, Magnesol, Porocel, bauxite, diatomaceous earth, etc. The contacts of this invention may be prepared by any of the known methods such as single or multiple impregnation, coprecipitation, adsorption from colloidal solution, etc.

In zone 1 the bottoms are hydrodesulfurized with at least a significant portion of the sulfur content of the bottoms combining with the iron group metal content of the contact to form iron group metal sulfide, thereby removing the sulfur from the charge stock. Simultaneously with the removal of sulfur the contact induces a mild hydrogenation of portions of the petroleum hydrocarbons in the bottoms. I have found that the best temperature for zone 1 is of the order of 700° F., since at this low temperature mild hydrodesulfurization of the bottoms is effectuated with but a minimum amount of cracking and coke deposition.

In primary distillation unit 12 the next lower boiling fraction, namely, the heavy gas oil fraction, is removed by means of line 42 and passes through cooler 44, line 46, into accumulator 48. The level in accumulator 48 is controlled by level controller 50 which is attached to accumulator 48.

5

and to pump 52. From accumulator 48 the heavy gas oil fraction passes through line 54, pump 52 and into line 56. In line 56 the heavy gas oil fraction is joined by the mixture of crude oil bottoms and unreacted hydrogen which leaves zone 1 of reactor 38 by means of line 58. This mixture passes through line 60 and enters heater 62 where it is vaporized and heated to a suitable reaction temperature prior to re-entering reactor 38. From heater 62 the combined mixture passes through line 64 into zone 2 of reactor 38. The temperature of the mixture in zone 2 is regulated by temperature controller 66 which is connected between zone 2 and heater 62. In zone 2 the mixture is hydrodesulfurized by passing over a similar contact to that found in zone 1. I have found that a suitable temperature for zone 2 is of the order of 750° F. and that at this temperature a minimum of cracking and coke deposition is achieved.

The next lower-boiling petroleum fraction, namely, the light gas oil, is removed from primary distillation unit 12 by means of line 68 and passes through cooler 70, line 72 into accumulator 74. The level in accumulator 74 is controlled by level controller 76 attached to pump 78. The light gas oil fraction passes from accumulator 74 through line 80, pump 78 into line 82. In line 82 the light gas oil fraction is joined by the hydrodesulfurized mixture of bottoms and heavy gas oil fractions and unreacted hydrogen-containing gas which leaves zone 2 by means of line 84. This combined mixture then passes through line 86 into heater 88 where the unvaporized constituents are vaporized and the whole mixture is heated to a reaction temperature suitable for zone 3 of reactor 38. From heater 88 the mixture passes by means of line 90 into zone 3. The temperature of the mixture in zone 3 is regulated by temperature controller 87 which is connected between heater 88 and zone 3. In zone 3 this combined mixture is hydrodesulfurized by passing over a contact material similar to that found in zones 1 and 2. I have found a temperature of the order of 800° F. to be suitable for this zone.

The naphtha fraction leaves primary distillation unit 12 by means of line 92, and passes through cooler 94, line 96 into accumulator 98. The level in accumulator 98 is controlled by level controller 100 which is attached to pump 102 and accumulator 98. The naphtha fraction leaves accumulator 98 through line 104 and passes through pump 102 into line 106. In line 106 the naphtha fraction is joined by the hydrodesulfurized mixture and unreacted hydrogen-containing gas which has left zone 3 through line 108. This newly combined mixture then passes through line 110 into heater 112. In heater 112 vaporization of the unvaporized portions are effected and the mixtures are heated to a suitable temperature for the hydrodesulfurization conditions maintained within zone 4. The combined mixture is then passed from heater 112 through line 114 and enters zone 4 of reactor 38. In zone 4 the combined mixture is hydrodesulfurized by passing over a similar contact to that found in zones 1, 2 and 3. I have found that a suitable temperature for zone 4 should be of the order of 850° F. The temperature conditions of zone 4 are regulated by means of temperature controller 116 which joins zone 4 to heater 112.

The lowest boiling fraction, i. e., the gasoline, leaves primary distillation unit 12 through line 118 and passes through cooler 120, line 122 into accumulator 124. The level in accumulator 124

6

is controlled by level controller 126 which joins accumulator 124 and pump 128. The gasoline fraction passes from accumulator 124 through line 130, pump 128 into line 132. In line 132 the gasoline fraction is joined by the hydrodesulfurization products and unreacted hydrogen-containing gas mixture from zone 4 which enters line 132 by means of line 134. This final combined mixture passes from line 132 through line 136 into heater 138. In heater 138 this mixture is vaporized and heated to a temperature appropriate for hydrodesulfurization in zone 5 of reactor 38. From heater 138 the mixture passes through line 140 into zone 5 of reactor 38. In zone 5 the mixture is hydrodesulfurized over a similar contact material to that found in zones 1 to 4. I have found that a temperature of about 900° F. is a suitable temperature for this zone. The temperature in zone 5 is controlled by temperature controller 142 which joins zone 5 and heater 138.

From zone 5 the fully hydrodesulfurized crude and the unreacted hydrogen-containing gas is passed by means of line 144 through back pressure controller valve 150. From back pressure controller valve 150 the product is passed to a fractionation still by means of line 152 and thence refined and freed from gaseous contaminants in the customary manner.

The process is continued until regeneration of the contact is required. This is usually commenced when substantial amounts of hydrogen sulfide appear in the effluent. An empirical method for determining when the regeneration is to be commenced is to begin regeneration when the contact contains from 30 to 60% iron group metal sulfide. In some instances when the commercial situation permits the removal of minor amounts of hydrogen sulfide from the product the process may be continued until the entire metal content of the contact has become converted into metallic sulfide. The regeneration of the contact to its original form may be effected by any of the customary prior art methods, such as oxidation etc.

The following example is illustrative of the improvements which can be realized by the process of my invention:

Two hydrodesulfurization runs were made, the first utilizing the conventional hydrodesulfurization process in which the oil is charged to the reaction zone without prior fractionation; and the second utilizing the selective hydrodesulfurization method of the present invention. Identical nickel hydrogenation catalyst was utilized in each run. The results obtained with each hydrodesulfurization process were as follows:

Process.....	Conventional	Selective
Size of Reaction Zone: Bbl.....	100	100
Type of Catalyst.....	(1)	(1)
Sulfur Removal, Percent.....	77	80
Reactor Pressures, p. s. i.:		
Top.....	510	510
Bottom.....	500	500
Hydrogen Charged: Cu. Ft./Bbl.....	4,250	4,250
Hydrogen Consumed: Cu. Ft./Bbl.....	275	225
Oil Charged to Reaction Zone:		
Bbl./Hr.....	100	100
Process Periods before Regeneration:		
Hr.....	4	4
Method of Charging:		
Hydrogen.....	(2)	(2)
Oil.....	(3)	(4)

¹ Hydrogenation.

² At top of reactor.

³ Total crude at top of reactor.

⁴ Five Equal Size Fractions in Five Equal Size Zones Starting with Heaviest Fraction at Top of Reactor.

Reaction Zone No.-----	1	1	2	3	4	5	Total
Variable Factors Affecting Residence Time of Oil Fractions:							
Oil Feed: Bbl./Hr. (Liq. Basis)-----	100	20	40	60	80	100	-----
Hydrogen Feed: Cu. Ft./Bbl. (approx.) (Measured at 60° F. & Atmos. Press.)-----	4,250	21,250	10,625	7,080	5,130	14,250	-----
Temperature: ° F-----	900	700	750	800	850	900	-----
Residence Time in Seconds (Approx.):							
Gasoline Fraction-----	38.65	0.0	0.0	0.0	0.0	7.18	7.18
Naphtha Fraction-----	38.65	0.0	0.0	0.0	8.36	7.18	15.54
Lt. Gas Oil Fraction-----	38.65	0.0	0.0	8.82	8.36	7.18	24.36
Hy. Gas Oil Fraction-----	38.65	0.0	9.49	8.82	8.36	7.18	33.85
Reduced Crude-----	38.65	10.05	9.49	8.82	8.36	7.18	43.90
Relative Catalyst Regeneration Requirement-----	1.00						0.75

¹ Disregarding amount of H₂ consumed in preceding zones.

In the above example the length of the process periods before regeneration was 4 hours in both hydrodesulfurization processes. It is to be noted that the relative catalyst regeneration requirement for my process was but 0.75 of that required for the conventional hydrodesulfurization process, due to the fact that there was much less coke to be burned off the catalyst. Alternatively, I could have increased the process period length of my process to a degree, so as to result in the same regeneration requirement as that shown for the conventional method, and thereby have achieved a longer effective on-stream cycle for a given amount of catalyst. In addition, this would have effected a further decrease in the amount of hydrogen consumed per barrel of oil by my process. This is due to the fact that some hydrogen is consumed by reduction of the catalyst after each oxidative regeneration cycle.

When the catalytic hydrodesulfurization process is utilized, the conditions will be relatively analogous to those utilized in the contact hydrodesulfurization method. However, since the catalyst may be varied over a much wider range of substances, the specific operational requirements for this type of process may differ somewhat from those given above. As indicative of the wide range of catalysts that may be employed in the catalytic hydrodesulfurization method, I have found that any of the iron group metals, metal oxides, mixtures of metal and metal oxide, or the iron group metal molybdates, may be utilized as can molybdenum sulfide, the iron group metal sulfides, etc. In all cases, for optimum results the catalyst should be impregnated on a carrier.

The aforementioned description should be taken as merely illustrative of the type process that is contemplated by the present invention. In place of the foregoing five fractions a larger or smaller number of fractions may be utilized. Furthermore, additional hydrogen-containing gas may be injected at each stage concurrently with each lower boiling fraction. In addition, in place of the fixed bed catalyst system herein described, a downward moving bed of catalyst in which the regeneration steps are conducted outside of the reactor may be utilized, and the process variables would remain similar to those described herein for the stationary bed. The mechanics of moving the catalyst from one zone to the next may be accomplished by any of the suitable methods which are conventionally employed at the present time. For example, catalyst vapor disengaging tubes could be placed at the plates separating each reaction zone and a purge gas could be introduced at low differential pressure into these tubes to permit the downward flow of catalyst and to force the oil-hydrogen vapor through the

heaters. Alternatively, a free-flowing type of catalyst could be utilized and with a suitably designed heater the catalyst could be allowed to flow through the heater with the hydrogen-oil vapors.

This invention permits smaller amounts of hydrogen to be utilized in the course of a hydrodesulfurization process since there is a significant decrease in the large amounts of hydrogen normally consumed by the formation of low boiling gaseous hydrocarbon contaminants. This is due to the fact that cracking of the crude charge stock to low boiling fractions is materially reduced. Furthermore, the on-stream period of the hydrodesulfurization cycle will be lengthened, since, by the use of this invention, smaller amounts of coke and carbon will be deposited on the catalyst and hence it will not be necessary to regenerate the catalyst as frequently as in the prior methods. There will be a concomitant saving of hydrogen since the hydrogen consumption normally attendant with the reduction of the catalyst which accompanies the regeneration is lessened. Also the invention enables the use of the highest hydrogen to oil ratios when the heaviest portions are most susceptible to carbon deposition thus further reducing the formation of carbon and gases.

In addition to the foregoing, the contact life will be increased since the lessening of the carbon deposition reduces the amount of contact decrepitation and pulverization normally encountered in this process. Furthermore, due to the lengthening of the period of catalyst activity and hence of the on-stream cycle, the size of the reactor may be decreased, which permits a substantial saving in the cost of commercial installation.

What I claim is:

1. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a hydrogenation catalyst in the presence of a hydrogen-containing gas, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas, heating this mixture to an incrementally higher temperature and contacting this heated mixture with a hydrogenation catalyst.

2. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting the highest boiling fraction with a hydrogenation catalyst in the presence of a hydrogen-containing gas, combining the next lower boiling fraction with the mixture of

said highest boiling fraction and hydrogen-containing gas, heating this mixture to an incrementally higher temperature and contacting this heated mixture with a hydrogenation catalyst at an incrementally higher temperature, and combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions, heating said successive combined mixtures to incrementally higher temperatures and contacting said successive combined and heated mixtures with a hydrogenation catalyst.

3. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a hydrogenation catalyst, in the presence of a hydrogen-containing gas containing sufficient hydrogen to enable the entire charge stock to be hydrodesulfurized, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas, heating this mixture to an incrementally higher temperature and contacting this heated mixture with a hydrogenation catalyst.

4. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting the highest boiling fraction with a hydrogenation catalyst, in the presence of a hydrogen-containing gas containing sufficient hydrogen to enable the entire charge stock to be hydrodesulfurized, combining the next lower boiling fraction with the mixture of said highest boiling fraction and hydrogen-containing gas, heating this mixture to an incrementally higher temperature and contacting this heated mixture with a hydrogenation catalyst, combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions heating said successive combined mixtures to incrementally higher temperatures and contacting said successive combined and heated mixtures with a hydrogenation catalyst.

5. A selective hydrodesulfurization process which comprises absorbing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur from the petroleum hydrocarbons to form an iron group metal sulfide on the contact, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas and contacting the combined mixture at an incrementally higher temperature, with a contact agent selected from the group consisting of an iron group metal, metal oxides and combinations thereof on a carrier, and absorbing sulfur from the petroleum hydrocarbons to form iron group metal sulfide on the contact.

6. A selective hydrodesulfurization process which comprises absorbing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting the highest boiling fraction with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur

from the petroleum hydrocarbons to form an iron group metal sulfide on the contact, combining the next lower boiling fraction with the mixture of said highest boiling fraction and hydrogen-containing gas and contacting the combined mixture at an incrementally higher temperature, with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier, absorbing sulfur from the petroleum hydrocarbons to form iron group metal sulfide on the contact, combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions, and contacting said successive combined mixtures with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier.

7. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfides on the contact, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas and contacting the combined mixture at an incrementally higher temperature with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof on a carrier, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact.

8. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting the highest boiling fraction with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact, combining the next lower boiling fraction with the mixture of said highest boiling fraction and hydrogen-containing gas and contacting the combined mixture at an incrementally higher temperature with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof on a carrier, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact, and combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions, and contacting said successive combined mixtures with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof on a carrier.

9. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting a high boiling fraction with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur from the petroleum hydrocarbons to form iron group sulfide on the contact, combining a lower boiling fraction with the mixture of said high boiling fraction and hydrogen-containing gas,

and contacting the combined mixture at an incrementally higher temperature with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier, absorbing sulfur from the petroleum hydrocarbons to form iron group metal sulfide on the contact, and continuing said process until regeneration of the contact is required, then regenerating said contact material to substantially its original form.

10. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a petroleum hydrocarbon charge stock into a plurality of fractions, contacting the highest boiling fraction with a contact agent selected from the group consisting of nickel, nickel oxide, and combinations thereof on a carrier, in the presence of a hydrogen-containing gas, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact, combining the next lower boiling fraction with the mixture of said highest boiling fraction and hydrogen-containing gas, and contacting the combined mixture at an incrementally higher temperature with a contact agent selected from the group consisting of nickel, nickel oxide, and combinations thereof on a carrier, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact, combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions and contacting said successive combined mixtures with a contact agent selected from the group consisting of nickel, nickel oxide, and combinations thereof on a carrier, at incrementally higher temperatures, absorbing sulfur from the petroleum hydrocarbons to form nickel sulfide on the contact, and continuing said process until substantial amounts of hydrogen sulfide appear in the effluent, and the nickel content of the contact has been substantially converted into nickel sulfide, then regenerating said contact material to substantially its original form.

11. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a high boiling petroleum hydrocarbon charge stock into a plurality of fractions, said fractions being substantially in the vapor state, contacting the highest boiling fraction with a contact agent selected from the group consisting of iron group metals, metal oxides, and combinations thereof on a carrier, in the presence of a hydrogen-containing gas at a temperature of between 650° and 750° F., absorbing sulfur from the hydrocarbon vapors to form iron group metal sulfide on the contact, combining the next lower boiling fraction with a mixture of said highest boiling fraction and hydrogen-containing gas, and contacting the combined mixture at an incrementally higher temperature with a contact agent selected from the group consisting of iron group metals, metal oxides, and combinations thereof on a carrier, absorbing sulfur from the hydrocarbon vapors to form iron group metal sulfides on the contact, and combining each remaining lower boiling fraction with the mixture of the previously combined higher boiling fractions and contacting

said successive combined mixtures with a contact agent selected from the group consisting of iron group metals, metal oxides and combinations thereof on a carrier at incrementally higher temperatures, absorbing sulfur from the hydrocarbon vapors to form iron group metal sulfide on the contact, so that the lowest boiling fraction is introduced at a temperature of between 850° and 950° F.

12. A selective hydrodesulfurization process which comprises removing sulfur from petroleum hydrocarbons by fractionating a crude petroleum hydrocarbon charge stock into a plurality of fractions, said fractions being substantially in the vapor phase and consisting of gasoline, naphtha, light gas oil, heavy gas oil, and bottoms, contacting the bottoms with a contact agent selected from the group consisting of nickel, nickel oxide and combinations thereof supported on a carrier at a temperature of about 700° F., in the presence of a hydrogen-containing gas containing sufficient hydrogen to hydrodesulfurize the original petroleum hydrocarbon charge stock, absorbing sulfur from the hydrocarbon vapors to form nickel sulfide on the contact, then combining with this fraction the heavy gas oil and contacting with a similar contact agent at a temperature of about 750° F., absorbing sulfur from the hydrocarbon vapors to form nickel sulfide on the contact, then combining the light gas oil with the mixture of heavy gas oil, bottoms and hydrogen-containing gas and contacting said mixture with a similar contact agent at a temperature of about 800° F., absorbing sulfur from the hydrocarbon vapors to form nickel sulfide on the contact, then combining the naphtha with the mixture of light gas oil, heavy gas oil, bottoms and hydrogen-containing gas, and contacting the combined mixture with a similar contact agent at a temperature of about 850° F., absorbing sulfur from the hydrocarbon vapors to form nickel sulfide on the contact, then combining the gasoline with the combined mixture of naphtha, light gas oil, heavy gas oil, bottoms and hydrogen-containing gas and contacting the combined mixture with a similar contact agent at a temperature of about 900° F., absorbing sulfur from the hydrocarbon vapors to form nickel sulfide on the contact, and continuing said process until substantial amounts of hydrogen sulfide appear in the effluent, and before the available nickel content of the contact has been entirely converted into nickel sulfide.

LESLIE U. FRANKLIN.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,073,578	Gwynn	Mar. 9, 1937
2,174,510	Gwynn	Oct. 3, 1939
2,371,298	Hudson	Mar. 13, 1945

FOREIGN PATENTS

Number	Country	Date
489,544	Great Britain	July 25, 1938