Dec. 18, 1962 W. H. DAVIS 3,069,351

UTILIZATION OF REFORMER MAKE-GAS

Filed July 17, 1959 3 Sheets-Sheet 1

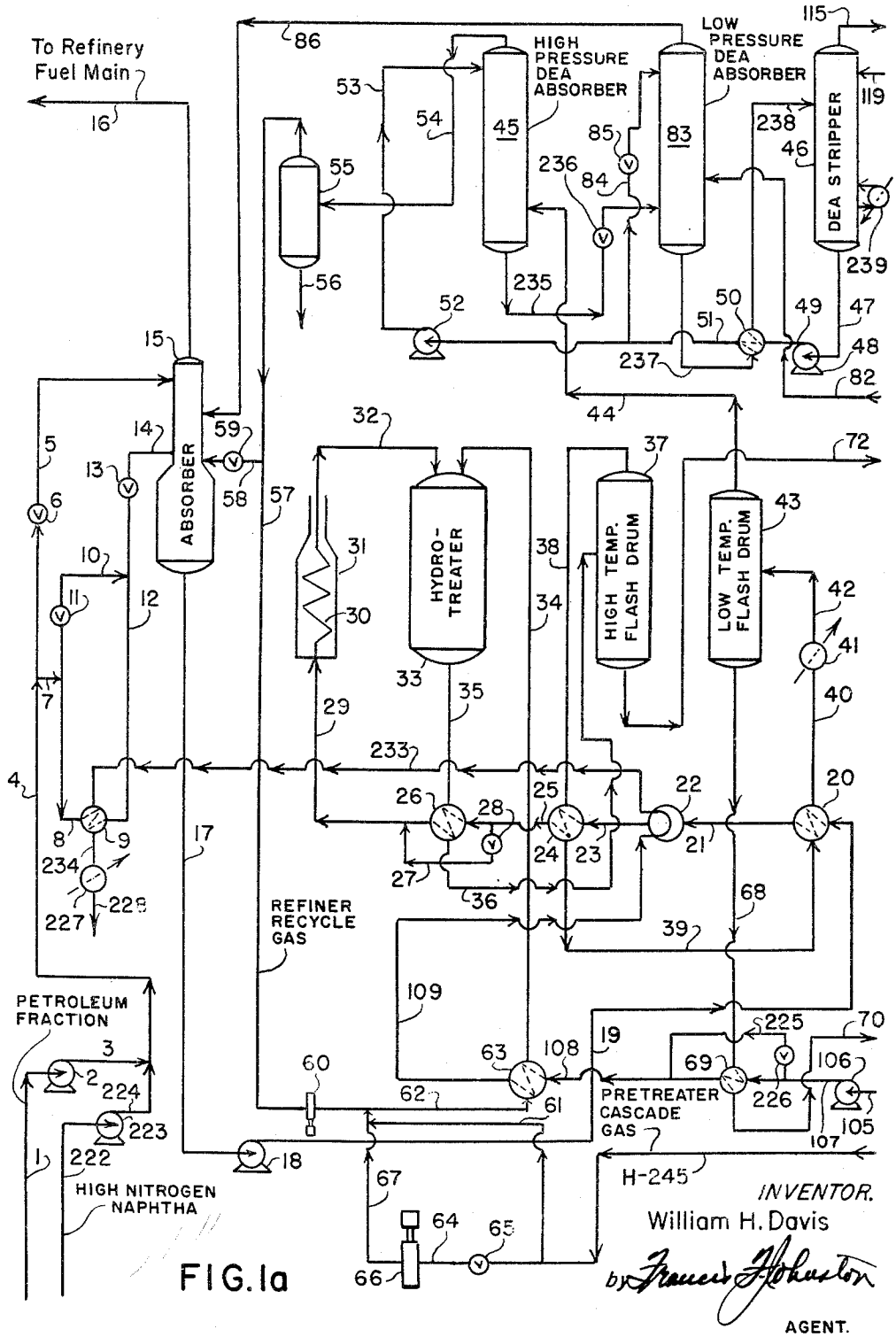


FIG. 1a

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UTILIZATION OF REFORMER MAKE-GAS

Filed July 17, 1959 3 Sheets-Sheet 2

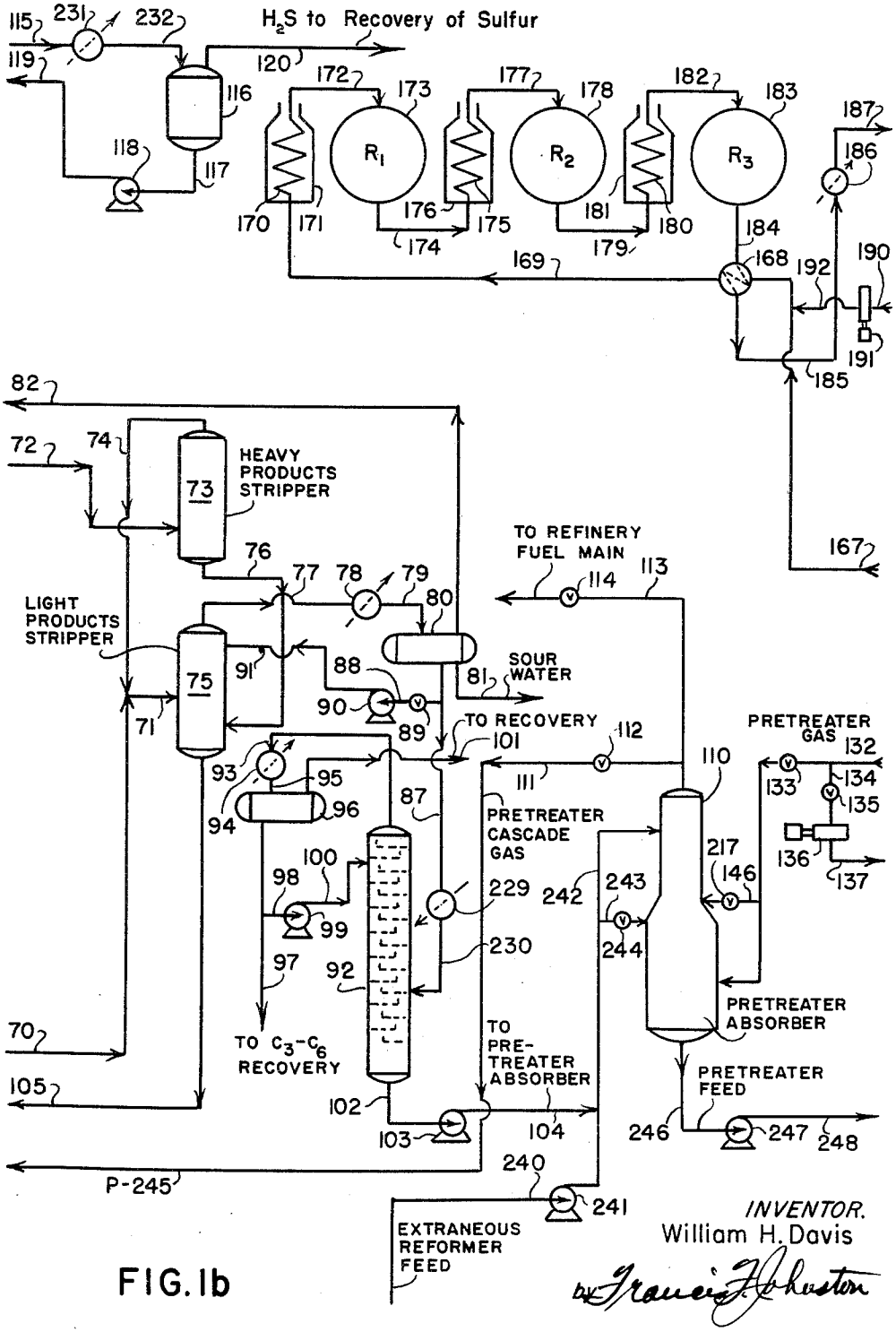


FIG. 1b

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UTILIZATION OF REFORMER MAKE-GAS

Filed July 17, 1959 3 Sheets-Sheet 3

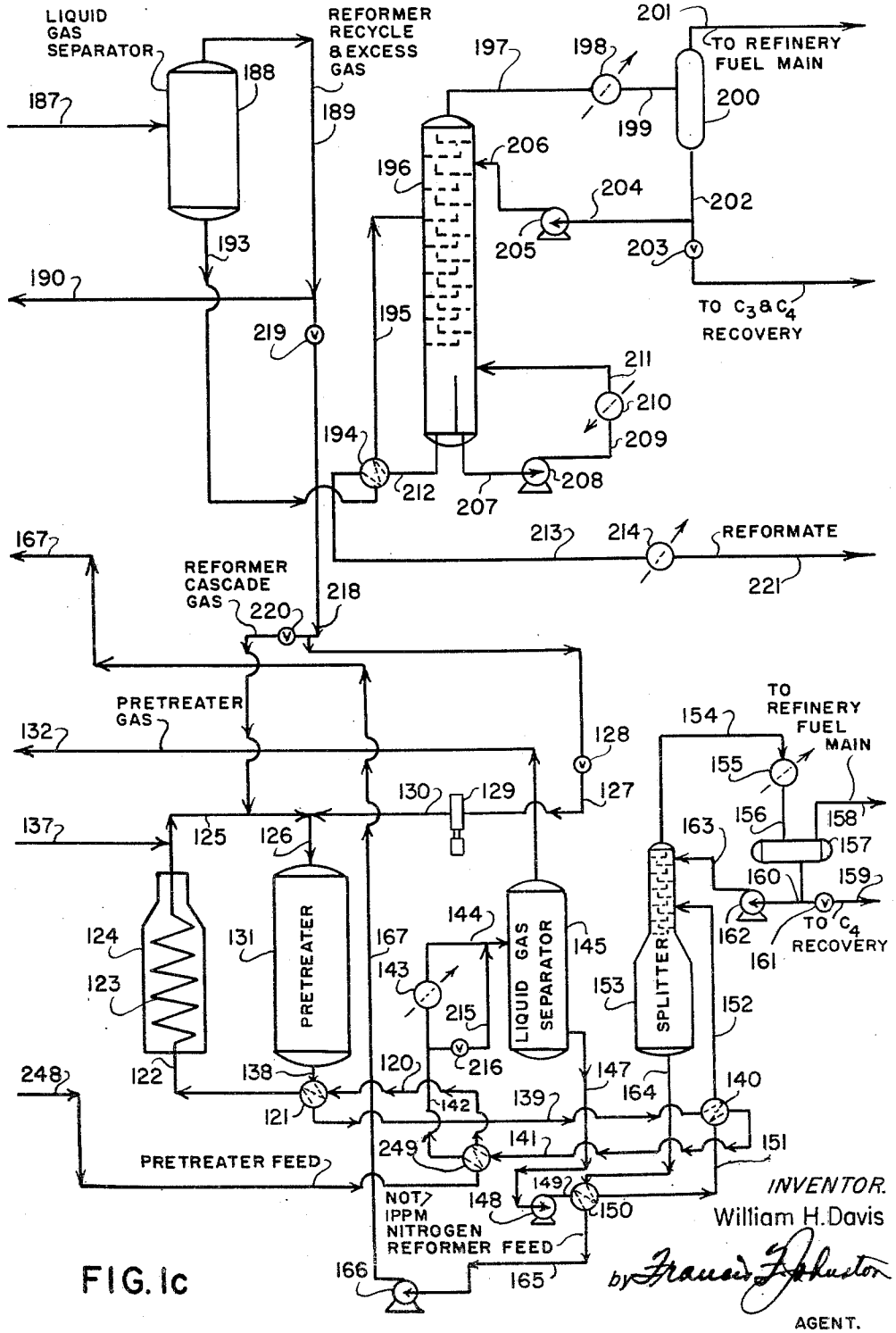


FIG. Ic

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3,069,351

UTILIZATION OF REFORMER MAKE-GAS

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Filed July 17, 1959, Ser. No. 827,957
2 Claims. (Cl. 208—89)

The present invention relates to hydrodecontamination of petroleum fractions boiling above the boiling range of reformer feed, i.e., boiling above about 350° to about 420° F. and the hydrodecontamination of reformer feed employing hydrogen-containing gas produced in a reforming unit and, more particularly, to the hydrodecontamination of high nitrogen content reformer feed stocks in conjunction with the hydrodecontamination of a petroleum fraction boiling above the boiling range of reformer feed, i.e., boiling above about 350° to about 420° F.

Hydrodecontamination as used herein is the treatment of a mixture of hydrocarbons containing compounds of sulfur and/or nitrogen in the presence of hydrogen with a particle-form solid catalytic material having hydrogenating as well as hydrodesulfurizing and/or hydrodenitrogenizing capabilities. In the hydrodecontamination of petroleum fractions boiling above the boiling range of reformer feed, i.e., boiling above about 350° to about 420° F. such as domestic heating oil, the treatment produces a domestic heating oil stable to at least one of color and sediment and containing not more than about 1 to 2 percent of sulfur (total sulfur) and not more than about 1 to 2 percent of mercaptan sulfur [RSH(S)] originally present in the untreated domestic heating oil. In the hydrodecontamination of reformer feed the treatment produces a reformer feed having a sulfur content the corrosive effect of which is within practical limits and a nitrogen content having a deactivating effect upon platinum-group reformer catalyst within practical limits. When the reformer feed is to be reformed over a platinum-group catalyst, e.g., a particle-form platinum-group catalyst comprising about 0.1 to about 2.0, preferably about 0.35 to about 0.6, percent by weight platinum, about 0.35 to about 0.8 percent by weight chlorine on an alumina support, the maximum nitrogen content of the reformer feed is about 1 p.p.m.

A high nitrogen naphtha, i.e., a naphtha having a high nitrogen content or a high nitrogen content naphtha, is a naphtha containing an amount of nitrogen in excess of that which can be reduced to not more than 1 part per million (p.p.m.) of nitrogen when treating the aforesaid high nitrogen naphtha alone or blended with a low nitrogen naphtha in existing reformer feed preparation facilities.

A low nitrogen naphtha, i.e., a naphtha having a low nitrogen content or a low nitrogen content naphtha, is a naphtha the nitrogen content of which can be reduced to not more than 1 p.p.m. in existing reformer feed preparation facilities.

The stabilization of domestic fuel oil with respect to color and sediment has been a problem of increasing importance as the proportion of cracked stocks in the finished blend increased. One of the most effective means for producing a domestic fuel oil stable at least with respect to color after storage is hydrogenation of the domestic fuel oil in contact with a catalyst having hydrodesulfurizing and hydrogenating capabilities. Among the catalysts having the aforesaid combined capabilities are those comprising a mixture of the oxides of cobalt and molybdenum. The hydrodecontamination of petroleum fractions boiling above the boiling range of reformer feed, i.e., boiling above about 350° to about 420° F. by hydrogenation in the presence of a catalyst comprising a mixture of the oxides of cobalt and molybdenum on alumina is accomplished by contacting the aforesaid petroleum fraction under the following conditions:

Catalyst: About 1.5 to about 3.8 percent by weight of an oxide of cobalt, about 7.0 to about 16.0 percent by weight of an oxide of molybdenum on alumina as a support.

	Broad	Preferred
Reaction Pressure, p.s.i.g.	200–1,000	390–850
Reaction Temperature, ° F	550–850	700–800
Space Velocity, v./hr./v.	2–10	4–6
Hydrogen/Bbl. of Feed, s.c.f.	200–2,000	320–1,000
Hydrogen Partial Pressure, p.s.i.a.	120–900	125–570

With the increased demand for gasolines having octane ratings higher than 90 it has become necessary to reform gasolines, such as thermal gasolines, which until recently met customer demand without reforming. Many of these gasolines have nitrogen contents in excess of that which can be reduced, alone or blended with low nitrogen naphtha, to not more than 1 p.p.m. in existing reformer feed preparation facilities. On the other hand, it has been found that when reforming naphthas over a platinum-type reforming catalyst the nitrogen content of the charge naphtha must not be in excess of 1 p.p.m.

It is also conventional to hydrodesulfurize straight run naphthas and other low nitrogen naphthas prior to reforming in order to reduce corrosion of the heaters, piping and reforming reactors.

All of the foregoing hydrodecontaminating reactions require hydrogen. Yet, generally, the only source of hydrogen in a refinery is that produced in reforming.

Thus, the refiner is confronted with the problem of providing hydrogen (1) for the treatment of petroleum fractions boiling above the boiling range of reformer feed, i.e., above about 350° to about 420° F. for example, of raw domestic heating oil stocks, (2) for the hydrodecontamination of high nitrogen content gasoline stocks to be reformed, and (3) for the hydrodesulfurization of low nitrogen naphtha to be reformed.

It has been found that the hydrogen-containing gas produced in a reforming unit can be used to hydrodecontaminate the reformer feed in a pretreater and the hydrogen-containing gas from the pretreater can be used to hydrodecontaminate a petroleum fraction boiling above the boiling range of reformer feed, i.e., above about 350° to about 420° F. such as domestic heating oil, kerosine, gas oil and the like to provide a more stable domestic heating oil or kerosine and a gas oil having a reduced sediment content and of reduced sulfur and/or nitrogen content in a hydrotreater or refiner. When the pressure in the reforming unit is sufficiently higher than that in the pretreater and the pressure in the hydrotreater treating the petroleum fraction boiling above the boiling range of reformer feed is sufficiently lower than that in the pretreater and the amount of hydrogen circulated in the hydrotreater is not greater than the excess hydrogen produced in the reforming unit the excess hydrogen can flow from the reforming unit through the pretreating unit and through the hydrotreating or refining unit without recompression intermedite to the reformer recycle gas compressor and the pretreating unit and without compression intermediate the pretreating unit and to the hydrotreating or refining unit. Thus, when the pressure drop between the reformer recycle gas compressor and the pretreating reactor or pretreater is of the order of about 30 pounds per square inch or more and the pressure drop between the pretreating unit liquid-gas separator and the hydrotreating or refining unit reactor or hydrotreater is of the order of about 30 pounds per square inch or more the reformer gas in excess of that required in the reformer, i.e.,

the excess reformer gas, can be cascaded from the reformer through the pretreating unit to and through the hydrotreating or refining unit. However, when the pretreater and/or the hydrotreater is or are operated at higher pressures than that of the reformer it is necessary to recompress the excess reformer gas between the reformer and the pretreater and between the pretreater absorber and the hydrotreater.

With certain reformer feeds under various reforming conditions the amount of excess reformer gas produced is less than the quantity of hydrogen required for circulation in the pretreating unit and/or the hydrotreating or refining unit. Under these conditions a portion of the circulating hydrogen-containing gas in the pretreating unit and/or the hydrotreating unit is recycled. The amount of circulating gas recycled in the pretreating unit and/or the hydrotreating unit is the amount of circulating gas required less the amount of available excess reformer gas. Thus, with a reformer producing 1000 s.c.f. of hydrogen and the pretreater requiring 2000 s.c.f. of hydrogen per barrel about 1000 s.c.f. of hydrogen from the liquid gas separator in the pretreating unit is recycled through the pretreating reactor system together with about 1000 s.c.f. of hydrogen as excess reformer gas. Similarly, when the hydrogen circulation rate in the hydrotreater or refiner is 2000 s.c.f./bbl. of refiner feed and the excess reformer hydrogen is 1000 s.c.f./bbl. of refiner feed, 1000 s.c.f. of hydrogen per barrel of refiner feed is recycled together with 1000 s.c.f. of hydrogen per barrel of refiner feed secured from the reformer or the absorber of the pretreater.

Accordingly, it is an object of the present inveniton to provide a means for hydrodecontaminating a petroleum fraction boiling above the boiling range of reformer feed, i.e., boiling above about 350° F. to about 420° F., e.g., kerosine, domestic heating oil, gas oil and the like to produce a treated petroleum fraction boiling above the boiling range of reformer feed, i.e., boiling above about 350° to about 420° F. having a reduced sulfur and/or nitrogen content whilst hydrodecontaminating a reformer feed usually having a maximum boiling point in the range of about 350° to about 420° F. to obtain a treated reformer feed containing not more than about 1 p.p.m. of nitrogen, and to reform the treated reformer feed in the presence of hydrogen and particle-form solid platinum-group reforming catalyst under reforming conditions of temperature and pressure to produce a reformate of improved octane rating and hydrogen-containing gas wherein the aforesaid hydrogen-containing gas, hereinafter designated excess reformer gas, is used in the hydrodecontamination of the aforesaid reformer feed and/or in the hydrodecontamination of the aforesaid petroleum fraction boiling above the boiling range of reformer feed with or without recompression between the reformer and the hydrodecontaminating unit or units. It is another object of the present invention to provide a means for hydrodecontaminating domestic heating oil to produce stabilized domestic heating oil stabilized with respect to at least one of color and sediment, to hydrodecontaminate reformer feed to produce treated reformer feed containing not more than 1 p.p.m. of nitrogen, and not more than 20 p.p.m. of sulfur and to reform the aforesaid treated reformer feed under reforming conditions of temperature and pressure in the presence of particle-form solid platinum-group reforming catalyst and hydrogen-containing gas to produce a reformate of improved octane rating and hydrogen-containing gas wherein the aforesaid hydrogen-containing gas, hereinafter designated excess reformer gas, is used in the hydrodecontamination of the aforesaid reformer feed and/or in the hydrodecontamination of the aforesaid petroleum fraction boiling above the boiling range of reformer feed with or without recompression between the reformer recycle gas compressor and the hydrodecontaminating unit or units.

It is a further object of the present invention to provide a means for hydrodecontaminating a domestic heating oil in conjunction with a high nitrogen naphtha (as defined hereinbefore) to produce a stabilized domestic heating oil (as defined hereinbefore) and an at least partially hydrodecontaminated high nitrogen naphtha which when mixed with a low nitrogen naphtha (as defined hereinbefore) to form a blend, the blend can be hydrodecontaminated in existing reformer feed preparation facilities to provide a reformer feed containing not more than 1 p.p.m. of nitrogen, to blend said at least partially hydrodecontaminated high nitrogen naphtha with low nitrogen naphtha to form a blend, hydrodecontaminating said blend to produce a reformer feed containing not more than 1 p.p.m. of nitrogen, and reforming said blend in the presence of particle-form solid platinum-group reforming catalyst and hydrogen under reforming conditions of temperature and pressure to obtain a reformate having an octane rating higher than that of said blend wherein hydrogen-containing gas produced in said reforming is used in the hydrodecontamination of said blend and in the hydrodecontamination of said domestic heating oil and said high nitrogen naphtha with or without recompression between the reformer recycle gas compressor and the hydrodecontaminating units. Other objects and advantages of the present invention will become apparent to those skilled in this art from the following discussion thereof taken in conjunction with the drawings in which

FIGURE 1*a* is a flowsheet illustrating in a diagrammatic manner the flow of gases and liquids in a unit hydrodecontaminating a petroleum fraction boiling above the boiling range of reformer feed or the aforesaid petroleum fraction and high nitrogen naphtha employing the hydrogen-containing gas from a pretreating unit together with a portion of a hydrogen sulfide recovery unit; and

FIGURE 1*b* is a flowsheet illustrating the separation of the hydrotreater effluent into a gaseous fraction, a reformer feed, and a treated petroleum fraction boiling above the boiling range of reformer feed and reforming of the reformer feed; and

FIGURE 1*c* is a flowsheet illustrating the separation of the pretreater effluent into a gaseous fraction and reformer feed; and fractionation of the final reformer effluent into reformer gas and reformate.

Illustrative of the present invention is the hydrodecontamination of a gas oil to produce an improved gas oil of lower sulfur and/or nitrogen content suitable for catalytic cracking with improved results and an at least partially decontaminated reformer feed. When the quantity of partially decontaminated naphtha produced in the hydrodecontamination of the aforesaid gas oil is insufficient to supply the total throughput capacity of the pretreater and reformer or when the nitrogen content of the reformer feed is higher than that which can be reduced to about 1 p.p.m. in existing pretreating facilities, the reformer feed produced in hydrodecontaminating the gas oil is blended with a naphtha to provide a blend in pretreater-and-reformer capacity volume having a nitrogen content which can be reduced to 1 p.p.m. in existing reformer feed preparation facilities. The reformer feed produced in the hydrodecontamination of the gas oil, i.e., the autogenous refiner reformer feed alone or blend as described hereinbefore is hydrodecontaminated in a pretreater to produce a treater reformer feed containing not more than about 1 p.p.m. of nitrogen. The treated reformer feed is reformed under reforming conditions of temperature and pressure to produce a reformate of higher octane rating than that of the treated reformer feed and hydrogen in excess of that required to maintain a tolerable deposition of coke on the particle-form reforming catalyst.

The following are illustrative for the hydrodecontamination of a petroleum fraction boiling above the boiling range of reformer feed, i.e., boiling above a temperature within the range of about 350° to about 420° F., pretreating the autogenous reformer feed alone or blended

with naphtha to produce a treated reformer feed containing not more than about 1 p.p.m. of nitrogen; and reforming the treated reformer feed to produce a reformate having a higher octane rating than the treated reformer feed and hydrogen in excess of that required to maintain a tolerable deposition of coke on the particle-form reforming catalyst.

Hydrotreater or Refiner

Catalyst: about 1.5 to about 3.8 percent by weight of cobalt oxide; about 7 to about 16 percent by weight of molybdenum oxide
Carrier: alumina
Hydrodecontaminating conditions:

	Broad	Preferred
Reaction pressure, p.s.i.g.	200 to 1,000	390 to 850
Reaction temp., ° F.	550 to 850	700 to 800
Space velocity (LHSV) v./hr./v.	2 to 10	4 to 6
Hydrogen circulated per barrel of refiner feed, s.c.f.	200 to 2,000	320 to 1,000
Mols of hydrogen/mol of hydrocarbon	0.4 to 3.8	0.8 to 2.7

S.c.f.—standard cubic feet.

Pretreater

Catalyst: about 1.5 to about 3.8 percent by weight of cobalt oxide; about 7 to about 16 percent by weight of molybdenum oxide
Carrier: alumina
Hydrodecontaminating conditions:

	Broad	Preferred
Reaction pressure, p.s.i.g.	100 to 1,000	400 to 500
Reaction temperature, ° F.	600 to 850	675 to 725
Space velocity (LHSV), v./hr./v.	1 to 10	2.5 to 5
Hydrogen circulated per barrel of reformer feed, s.c.f.	350 to 2,500	400 to 800

Reformer

Catalyst: 0.6 percent by weight of platinum; 0.6 percent by weight of chlorine
Carrier: alumina
Reforming conditions:

	Broad
Reaction pressure, p.s.i.g.	100 to 1,000
Reaction temperature, ° F.	800 to 1,000
Space velocity (LHSV), v./hr./v.	0.5 to 10
Mols of hydrogen/mol of reformer feed	4 to 20

Thus, a petroleum fraction boiling above the boiling range of reformer feed, i,e., boiling above a temperature within the range of about 350° to about 420° F., e.g., kerosine, domestic heating oil, diesel fuel, gas oil and the like is drawn from a source not shown through pipe 1 by pump 2. Pump 2 discharges the petroleum fraction into pipe 3 at a pressure in excess of that in absorber 15. The petroleum fraction flows through pipe 3 to pipe 4. A portion of the petroleum fraction flows from pipe 4 to pipe 5 under control of valve 6 to the top of absorber 15. The balance of the petroleum fraction flows from pipe 4 through pipe 7 to pipe 8. In pipe 8 a portion or all of the balance of the petroleum fraction flows through heat exchanger 9 dependent upon the temperature to be maintained in absorber 15. In heat exchanger 9 the portion of the balance of the petroleum fraction flowing through pipe 8 is in indirect heat exchange relation with stabilized petroleum fraction, e.g., gas oil. The heated petroleum fraction boiling above the boiling range of reformer feed, i.e., boiling above a temperature within the range of about 350° to about 420° F., e.g., gas oil and so designated hereinafter, flows from heat exchanger 9 through pipe 12 to pipe 14. The remainder of the balance of the gas oil, if any, flows through pipe 10 under control of valve 11 to pipe 12

where the unheated and heated portions of the balance of the gas oil mix and flow under control of valve 13 through pipe 14 to absorber 15.

The distribution of the gas oil between pipes 5 and 14 is dependent upon the quantity of gas flowing from low pressure diethanolamine absorber 83 when used through conduit 86 and the quantity of gas flowing from knock-out pot 55 through conduit 57. That is to say, the flow of oil through pipes 5 and 14 and the flow of gases through conduits 58 and 86 are balanced to remove substantially all of the C_4 and heavier hydrocarbons from the gases and to remove water and heat exchange deposit precursors from the gas oil. The distribution of the gas oil between pipes 8 and 11 is dependent upon maintaining the maximum temperature in absorber 15 at which substantial absorption of C_4 and heavier hydrocarbons by the oil and stripping of water, oxygen and deposit precursors occurs. Usually, a temperature within the range of about 100° to about 150° F. is satisfactory in absorber 15.

The stripped gases and absorbed water, oxygen, etc. are vented from absorber 15 through conduit 16 to the refinery fuel main. The gas oil flows from absorber 15 through pipe 17 to the suction side of pump 18.

Pump 18 discharges the gas oil into pipe 19 at a pressure greater than the pressure in hydrotreater 33. The gas oil flows through pipe 19 to heat exchanger 20. In heat exchanger 20 the gas oil is in indirect heat exchange relation with the overhead from high temperature flash drum 37 flowing from heat exchanger 24 through conduit 39. From heat exchanger 20 the gas oil flows through pipe 21 to heat exchanger 22 where the gas oil is in indirect heat exchange relation with treated gas oil flowing from heat exchanger 63 through pipe 109. From heat exchanger 22 the gas oil flows through pipe 23 to heat exchanger 24 where the gas oil is in indirect heat exchange relation with the overhead of high temperature flash drum 37 flowing therefrom through conduit 38. From heat exchanger 24 the gas oil flows through pipe 25 to heat exchanger 26 where the gas oil is in indirect heat exchange relation with the total effluent from hydrotreater 33 flowing to heat exchanger 26 through conduit 35. Only that portion of the gas oil flows through heat exchanger 26 which is required to reduce the temperature of the hydrotreater effluent to that at which the separation (described hereinafter) desired in high temperature flash drum 37 occurs. The balance of the gas oil by-passes heat exchanger 26 and flows through pipe 27 under control of valve 28 to pipe 29. From heat exchanger 26 the heat exchanged portion of the gas oil flows through pipe 29 where the heat exchanged portion of the gas oil and the balance, if any, of the gas oil mix and flow to coil 30 in heater 31.

In heater 31 the temperature of the gas oil is raised to a hydrodecontamination temperature within the range of about 550° to about 800° F. as described hereinbefore. From heater 31 the gas oil flows through pipe 32 to hydrotreater 33. Hydrogen-containing gas flowing through conduit 34 from heat exchanger 63 flows into hydrotreater 33 to provide about 200 to about 2000 s.c.f. (standard cubic feet) of hydrogen per barrel of gas oil part or all of which flows from the pretreater absorber 110 through conduits P-245 and H-245 as described hereinafter.

The intimately mixed heated gas oil and the hydrogen-containing gas flow downwardly through hydrotreater 33 in contact with the hydrogenating catalyst having hydrodesulfurizing and/or hydrodenitrogenizing capabilities described hereinbefore. The hydrotreater effluent flows from hydrotreater 33 through conduit 35 to heat exchanger 26 where the hydrotreater effluent is in indirect heat exchange relation with at least a portion of the treated gas oil as described hereinbefore.

From heat exchanger 26 the cooled hydrotreater effluent flows through conduit 36 to high temperature flash drum

37. A temperature is maintained in high temperature flash drum 37 to provide a balanced heat load to reduce the stripping steam requirement in stripper 75 and to volatilize at the existing pressure a major portion of the hydrocarbons boiling within the boiling range of reformer feed. The aforesaid volatile hydrocarbons are taken as overhead, designated hereinafter high temperature overhead. The unvaporized hydrocarbons are designated high temperature bottoms.

The high temperature overhead comprises hydrogen, volatile hydrogen derivatives of contaminants, e.g., hydrogen sulfide, ammonia, etc., and C_{1+} hydrocarbons. The high temperature overhead flows from high temperature flash drum 37 through conduit 38 to heat exchanger 24 where the high temperature overhead is in indirect heat exchange relation with the gas oil as described hereinbefore. From heat exchanger 24 the high temperature overhead flows through conduit 39 to heat exchanger 20 where the high temperature overhead is in indirect heat exchange relation with the gas oil as described hereinbefore. From heat exchanger 20 the high temperature overhead flows through conduit 40 to cooler 41 where the high temperature overhead is cooled to a temperature as low as possible with normal cooling water, so as to produce as high a hydrogen concentration as possible in the overhead from separator 43. From cooler 41 the cooled high temperature overhead flows through conduit 42 to low temperature separator 43.

In separator 43 an equilibrium flash separation is obtained to provide an overhead comprising hydrogen, hydrogen derivatives of contaminants, e.g., hydrogen sulfide and ammonia, and hydrocarbons boiling below the boiling range of reformer feed usually comprising C_1 to C_4 and traces of C_5 and C_6 hydrocarbons which is taken through conduit 44 to high pressure hydrogen sulfide absorber 45.

Presently it is preferred to employ diethanolamine as the absorbent for the hydrogen sulfide. Lean aqueous diethanolamine solution pumped at low pressure from diethanolamine (DEA) stripper 46 by pump 48 through pipe 49 to heat exchanger 50 and a cooler not shown and through pipe 51 to pump 52 as described hereinafter is pumped by pump 52 through pipe 53 to the top of high pressure DEA absorber 45. The pressure in high pressure DEA absorber is substantially that of low temperature separator 43 less pressure drop due to intervening piping.

In high pressure DEA absorber 45 the low temperature overhead flows upwardly countercurrent to the downwardly flowing DEA solution. The low temperature overhead stripped of hydrogen sulfide flows from high pressure DEA absorber 45 through conduit 54 to knock-out pot 55. In knock-out pot 55 any entrained DEA solution falls out of the gas and is drawn-off through pipe 56. The gas comprising hydrogen and C_{1+} hydrocarbons and designated refiner recycle gas flows from knock-out pot 55 through conduit 57.

When the excess reformer gas is sufficient in quantity to supply all of the hydrogen gas required for circulation in the refining unit all of the refiner recycle gas is vented through conduit 58 under control of valve 59 to absorber 15 as described hereinbefore. However, when the excess reformer gas is less than the amount of hydrogen required for circulation in the refiner or hydrotreater section the deficiency of excess reformer recycle gas is made up by recycling a portion of the refiner recycle gas. Under these conditions only that portion of the refiner recycle gas is vented through conduit 58 which is required to keep the pressure at a predetermined level. The balance of the refiner recycle gas flows through conduit 57 to the suction side of refiner recycle gas compressor 60.

At this point the use of pretreater gas containing hydrogen under three conditions of operation will be described. The first condition is that existing when the hydrotreater or refiner is operating at a pressure at least about 30 p.s.i. lower than the pressure at the pretreater absorber 110 and all of the refiner or hydrotreater circulating gas is supplied by the reformer. The second condition is that existing when the hydrotreater or refiner is operating at a pressure higher than the pressure at the pretreater absorber 110 and all of the refiner or hydrotreater circulating gas is supplied by the reformer. The third condition is that existing when the reformer does not produce sufficient excess reformer gas to satisfy the demand for circulating hydrogen in the hydrotreater or refiner and the pressure in the hydrotreater or refiner is at least about 30 p.s.i. lower than the pressure at the pretreater absorber 110 or the pressure in the refiner is higher than that at the pretreater absorber.

For the first condition, i.e., the refiner pressure is at least about 30 p.s.i. less than the pressure at the pretreater absorber 110 and the excess reformer gas is sufficient to supply all of the hydrogen required for circulation in the hydrotreater or refiner circuit or unit (in other words, the hydrogen-containing gas is used in the refiner unit on a once through basis) the hydrogen-containing gas flows from the pretreater absorber 110 through conduits P–245 and H–245 to conduits 61 and 67 and thence to conduit 62. The pretreater cascade gas flows through conduit 62 to heat exchanger 63 where the pretreater cascade gas is in indirect heat exchange relation with the bottoms of light products stripper 75 flowing from heat exchanger 69 through pipe 108. From heat exchanger 63 the pretreater cascade gas flows through conduit 34 to hydrotreater or refiner 33 as described hereinbefore.

For the second condition under which the excess reformer gas is sufficient to meet the demand for the amount of hydrogen required for circulation in the refiner circuit but the refiner circuit is at a higher pressure than the pressure at the pretreater absorber 110 the pretreater cascade gas flows from pretreater absorber 110 through conduits P–245 and H–245 to conduit 64 under control of valve 65 and thence to compressor 66. Compressor 66 discharges the pretreater cascade gas into conduit 67 at a pressure higher than that in hydrotreater or refiner 33. The recompressed preheater cascade gas flows through conduit 67 to conduit 62. The recompressed pretreater cascade gas flows through heat exchanger 63 and conduit 34 to hydrotreater or refiner 33. As under the first condition described hereinbefore, the refiner recycle gas is vented through conduits 57 and 58 to absorber 15 and through conduit 16 to the refinery fuel main.

For the third condition, the supply of excess reformer gas is less than that required for circulation in the refiner unit and (*a*) the hydrotreater pressure is at least about 30 p.s.i. less than the pressure at the pretreater absorber 110 or (*b*) the hydrotreater pressure is higher than the pressure at the pretreater absorber 110.

When the hydrotreater is operated at a pressure at least about 30 p.s.i. less than the pressure at the pretreater absorber 110 the pretreater cascade gas flows from absorber 110 through conduits P–245 and H–245 to conduit 61 and thence through conduit 67 to conduit 62. Sufficient of the refiner recycle gas to provide the total volume of hydrogen required for circulation in the refiner unit flows through conduit 57 to the suction side of compressor 60. Compressor 60 recompresses the refiner recycle gas to a pressure higher than the pressure in hydrotreater 33 but not higher than the pressure of the pretreater cascade gas in conduit 67. The mixture of refiner recycle gas and pretreater cascade gas flows through conduit 62 to heat exchanger 63 and conduit 34 to hydrotreater 33. The overhead from low temperature flash drum 43 after removal of hydrogen sulfide flows through conduit 57. Part of the refiner recycle gas is diverted to the absorber 15 as described hereinbefore to avoid a build-up of pressure in the system and the balance is recycled.

When the hydrotreater is operated at a pressure higher than that at the pretreater absorber 110 and the volume

of excess reformer gas is less than the required volume of refiner circulating hydrogen, the pretreater cascade gas flows from pretreater absorber 110 through conduits P–245 and H–245 to conduit 64 under control of valve 65 and the suction side of compressor 66. Compressor 66 discharges the pretreater cascade gas into conduit 67 at a pressure higher than that in hydrotreater 33. The volume of circulating hydrogen in excess of that supplied in the pretreater cascade gas is supplied by the refiner recycle gas flowing in conduit 57 to the suction side of compressor 60. Compressor 60 discharges the repressured refiner recycle gas into conduit 62 at substantially the pressure of the compressed pretreater cascade gas in conduit 67. The mixture of repressured refiner recycle gas and compressed pretreater cascade gas flows through conduit 62 to heat exchanger 63 and conduit 34 to hydrotreater 33.

Illustrative of the foregoing conditions are the following:

Reformer cascade gas pressure, p.s.i.g.	Pretreater cascade gas pressure, p.s.i.g.	Refiner reactor pressure, p.s.i.g.	Required circulating gas in pretreater, s.c.f./bbl. of pretreater feed	Reformer cascade gas, s.c.f./bbl. of pretreater feed	Pretreater gas recycled to pretreater, s.c.f./bbl. of pretreater feed	Required circulating gas in refiner, s.c.f./bbl. of refiner feed	Pretreater cascade gas, s.c.f./bbl. of refiner feed	Refiner gas recycled, s.c.f./bbl. of refiner feed
500	420	390	202	202	0	319	319	0
500	420	390	533	533	0	1,025	340	685
500	420	390	2,430	200	2,230			
500	420	550	500	150	350	1,000	97	953
500	420	850	505	505	0	1,000	386	614
500	420	850	333	333	0	1,000	255	745
500	420	850	534	534	0	1,000	225	775
500	420	750	592	592	0	1,000	622	378

Having described the flow of the high temperature overhead and the flow of the low temperature overhead, the flow of the low temperature bottoms and the flow of the high temperature bottoms will now be described. As stated hereinbefore a temperature as low as normally obtained by water cooling is maintained in low temperature flash drum 43. The separation is not sharp and consequently the low temperature flash drum bottoms is fractionated a second time. Accordingly, the low temperature flash drum bottoms flows through pipe 68 to heat exchanger 69 where the low temperature flash drum bottoms is in indirect heat exchange relation with hot light products stripper bottoms flowing from pump 106 through pipe 107. From heat exchanger 69 the low temperature flash drum bottoms flows through pipe 70 to pipe 71. The high temperature flash drum bottoms is hydrocarbons boiling above the reformer feed range. The high temperature flash drum bottoms flows through pipe 72 to heavy products stripper 73 where the bottoms is stripped by steam fed to the top plate. In heavy products stripper 73 a temperature is maintained at which hydrocarbons boiling in a range which gives too low a flash point to the stripper bottoms, are taken overhead through pipe 74 to pipe 71 where the heavy products stripper overhead is mixed with the low temperature flash drum bottoms. The mixture of heavy products stripper overhead and low temperature flash drum botoms flows through pipe 71 to light products stripper 75. The bottoms from heavy products stripper 73 flows through pipe 76 to the bottom of light products stripper 75.

In light products stripper 75 a temperature is maintained at which hydrocarbons boiling at a temperature which gives too low a flash point to the bottoms of stripper 75 are volatile and taken overhead through pipe 77. The light products stripper overhead flows through pipe 77 to cooler 78 where the light products stripper overhead is cooled to a temperature at which C_4 and heavy hydrocarbons are condensed with small amounts of lighter hydrocarbons. The cooled light products stripper overhead flows from cooler 78 through conduit 79 to accumulator 80. In accumulator 80 water is drawn off through pipe 81. Hydrogen, hydrogen sulfide and light hydrocarbons flow from accumulator 80 through conduit 82 to low pressure DEA absorber 83. Alternatively, the hydrogen, hydrogen sulfide and light hydrocarbons flow directly to the refinery fuel gas main.

In low pressure DEA absorber 83 the hydrogen, hydrogen sulfide and light hydrocarbons flow upwardly countercurrent to downwardly flowing lean aqueous diethanolamine solution flowing from pipe 51 through pipe 84 under control of valve 85. The gas stripped of hydrogen sulfide flows from low pressure DEA absorber 83 through conduit 86 to absorber 15.

The hydrocarbons boiling in the boiling range of reformer feed and having a maximum boiling point of about 350° to about 420° F. flow from accumulator 80 through pipe 87. A portion sufficient for use as reflux flows through pipe 88 under control of valve 89 to pump 90. Pump 90 discharges the reflux portion of the condensed portion of the light products stripper overhead into pipe 91 through which the reflux portion flows to light products stripper 75 for use as reflux. The balance of the condensed portion of the light products stripper overhead flows through pipe 87 to fractionator 92. Alternatively, the condensed hydrocarbons in accumulator 80 flow directly to pretreater absorber 110.

In fractionator 92 a temperature is maintained at which C_4 and lighter hydrocarbons are volatile. The C_4 and lighter hydrocarbons are taken overhead through pipe 93. The C_4 overhead flows through pipe 93 to cooler 94 where the C_4 overhead is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed. The condensed and uncondensed C_4 overhead flows through conduit 95 to accumulator 96. Uncondensed hydrocarbons, C_1 to C_3, flow from accumulator 96 through pipe 101 to the refinery gas plant for the recovery of light hydrocarbons or to the refinery fuel gas main.

Condensed C_4 overhead flows from accumulator 96 through pipe 97 under control of a valve not shown to facilities for separating isobutane from normal butane. A portion of the condensed C_4 overhead is diverted through pipe 98 to the suction side of pump 99. Pump 99 discharges the diverted portion of the condensed C_4 overhead into pipe 100 through which the diverted overhead flows to fractionator 92 for use as reflux. The bottoms in fractionator 92, i.e., hydrocarbons boiling in the boiling range of reformer feed and having a maximum boiling point of about 350° to about 420° F. and preferably comprising C_5 and heavier hydrocarbons flows through pipe 102 to the suction side of pump 103. Pump 103 discharges the bottoms into pipe 104 through which the bottoms flow to pipe 104 and the pretreater absorber.

Returning now to the light products stripper 75; the hydrocarbons boiling above the minimum temperature needed to give the desired flash point to the bottoms are the bottoms in light products stripper 75. The bottoms is the treated gas oil. The bottoms flows from light products stripper 75 through pipe 105 to the suction side of pump 106. Pump 106 discharges the hot treated gas oil into pipe 107. The treated gas oil flows through pipe 107 to heat exchanger 69 where the treated gas oil is

in indirect heat exchange relation with the bottoms of the low temperature flash drum flowing therefrom through pipe 68. From heat exchanger 69 the treated gas oil flows through pipe 108 to heat exchanger 63 where the treated gas oil is in indirect heat exchange relation with hydrogen-containnig gas flowing to hydrotreater or refiner 33. From heat exchanger 63 the treated gas oil flows through pipe 109 to heat exchanger 22 where the treated gas oil is in indirect heat exchange relation with the gas oil feed. From heat exchanger 22 the treated gas oil flows through pipe 233 to heat exchanger 9 where the treated gas oil is in indirect heat exchange relation with a portion of the gas oil feed whereby the temperature in absorber 15 is maintained as described hereinbefore. From heat exchanger 9 the treated gas oil flows through pipe 234 to cooler 227. In cooler 227 the temperature of the treated gas oil is lowered to that at which the most volatile constituent is condensed. From cooler 227 the cooled treated gas oil flows through pipe 228 to storage, further treatment, addition of additives and the like dependent upon its use.

Those skilled in the art will recognize that the fractionations achieved in the high temperature flash drum 37, the low temperature flash drum 43, the heavy products stripper 73, the light products stripper 75 and fractionator 92 are those of separating the hydrotreater or refiner effluent into a gaseous fraction comprising the major portion of the hydrogen of the hydrotreater or refiner effluent with as small a pressure drop as practical, a hydrocarbon fraction boiling in the range of reformer feed and having a maximum boiling point within the range of about 350° to about 420° F., a light hydrocarbon fraction boiling below the range or reformer feed, and a heavy hydrocarbon fraction boiling above the boiling range of reformer feed. Those skilled in the art will recognize that any method other than that shown to accomplish the aforesaid separation can be substituted for that shown.

Before tracing the path of the C_{5+} hydrocarbons separated as bottoms in fractionator 92 through the pretreating and reforming units the hydrogen sulfide absorption unit will be described. While diethanolamine solution has been used to illustrate the removal of hydrogen sulfide from the gaseous fraction of the hydrotreater or refiner effluent those skilled in this art will recognize that other absorbents for hydrogen sulfide can be used. Furthermore, when necessary or desirable, other components of the gaseous fraction can be removed from the gaseous fraction of the hydrotreater effluent.

As has been described hereinbefore, hydrogen- and hydrogen sulfide-containing gases flowing from accumulator 80 at relatively low pressure and hydrogen- and hydrogen sulfide-containing gases flowing from low temperature flash drum 43 at relatively high pressure are treated for the removal of hydrogen sulfide.

Lean absorbent, in the illustration diethanolamine (DEA), flows from stripper 46 through pipe 47 to the suction side of pump 48. Pump 48 discharges the lean DEA into pipe 49 at a pressure about that of the gas flowing from accumulator 80 through conduit 82. The low pressure lean DEA flows through pipe 49 to heat exchanger 50 where the low pressure lean DEA is in indirect heat exchange relation with the relatively cold fat DEA solution flowing from absorber 83 through pipe 237. From heat exchanger 50 the low pressure lean DEA solution flows to a cooler (not shown) where it is cooled by indirect heat exchange with water and then flows through pipe 51 to the suction side of pump 52. A portion of the low pressure lean DEA solution is diverted through pipe 84 under control of valve 85 to the top of absorber 83. In absorber 83 the low pressure lean DEA solution flows downwardly countercurrent to the upwardly flowing low pressure gas from accumulator 80. The balance of the low pressure lean DEA solution is discharged into pipe 53 by pump 52 at a pressure at least equal to that of the gas in conduit 44. The high pressure lean DEA flows through pipe 53 to the top of absorber 45. The lean DEA solution flows downwardly through absorber 45 countercurrent to the upwardly flowing high pressure gas from conduit 44. The fat high pressure DEA solution flows through pipe 235 and pressure reducing valve 236 to the lower part of absorber 83. The fat DEA solution from absorber 45 and the fat DEA solution in absorber 83 mix and flow from absorber 83 through pipe 237 to heat exchanger 50. In heat exchanger 50 the fat DEA solution is in indirect heat exchange relation with the hot lean low pressure DEA solution as described hereinbefore. From heat exchanger 50 the fat DEA solution flows through pipe 238 to DEA stripper 46. In any suitable manner as by steam coil 239 a temperature is maintained in stripper 46 at which hydrogen sulfide is volatilized. The hydrogen sulfide and water vapor flows from stripper 46 through conduit 115 to cooler 231 where the vapors are cooled to a temperature at which water is condensed. The cooled vapors flow through conduit 232 to accumulator 116. In accumulator 116 the condensed water drops out. The water is drawn from accumulator 116 through pipe 117 by pump 118. Pump 118 discharges the water into pipe 119 through which the water flows to stripper 46 for use as reflux. The hydrogen sulfide gas flows from accumulator 116 through conduit 120 to means for the recovery of sulfur.

Returning now to fractinator 92 the course of the bottoms thereof, i.e., the reformer feed produced in hydrodecontaminating the petroleum fraction boiling above the boiling range or reformer feed, i.e., boiling above a temperature within the range of about 350° F. to about 420° F., will be traced. The reformed feed produced in the hydrodecontamination of the gas oil for example and hereinafter designated autogenous reformer feed flows through pipe 102 to the suction side of pump 103. Pump 103 discharges the autogenous reformer feed into pipe 104 through which the autogenous reformer feed flows to pipe 242 (see FIGURE 1*b*).

Usually the quantity of autogenous reformer feed is not sufficient to make it practical to operate a pretreating and reforming unit using the autogenous reformer feed as the sole feed thereto. Consequently, the autogenous reformer feed is mixed with extraneous naphtha. Furthermore, existing reformer feed preparation facilities usually are not capable of hydrodecontaminating reformer feed containing more than 10 p.p.m. of nitrogen to produce a reformer feed containing not more than 1 p.p.m. of nitrogen. Therefore the autogenous reformer feed when containing more than 10 p.p.m. of nitrogen is blended with a low nitrogen naphtha to produce a pretreater blend containing nitrogen not in excess of that which can be reduced to 1 p.p.m. in existing reformer feed preparation facilities. In other words, depending upon the nitrogen content and the volume of autogenous reformer feed, the autogenous reformer feed is blended with an extraneous reformer feed in quantity to produce the volume of blend for economical operation of the pretreater and reformer; the extraneous reformer feed having a nitrogen content such that when blended with the autogenous reformer feed in the aforesaid proportions the blend has a nitrogen content which can be reduced to not more than 1 p.p.m. in existing reformer feed preparation facilities.

Thus, for example, a reformer and the feed preparation facilities therefore are designed to treat an economic minimum of 10,000 barrels per day. The autogenous reformer feed produced is 1,000 barrels per day and has a nitrogen content of 15 p.p.m. The reformer feed preparation facilities are designed to reduce the nitrogen content of a reformer feed from 10 p.p.m. to 1 p.p.m. In this instance the 1,000 barrels per day of autogenous reformer feed is mixed with 9,000 barrels of extraneous reformer feed containing not more than about 9 p.p.m.

of nitrogen. On the other hand, with the same reformer feed preparation facilities and 1,000 barrels per day of autogenous reformer feed having a nitrogen content of 90 p.p.m. the autogenous reformer feed is mixed with 9,000 barrels per day of extraneous reformer feed having a nitrogen content of not more than about 1 p.p.m. Those skilled in the art understand that reformer feed preparation facilities can be designed to treat a reformer feed having a nitrogen content greater than 10 p.p.m. to reduce the nitrogen content thereof to 1 p.p.m.

To provide the required reformer feed blend, extraneous reformer feed meeting the requirements set forth hereinbefore, for example, straight-run naphtha is drawn from a source not shown through pipe 240 by pump 241. The extraneous reformer feed, e.g., straight-run naphtha and so designated hereinafter is discharged by pump 241 into pipe 242 at a pressure greater than that in pretreater absorber 110. The autogenous reformer feed flowing through pipe 104 at substantially the same pressure as that under which the straight-run naphtha is in pipe 242 mixes in pipe 242 to form the pretreater blend having a nitrogen content not in excess of that which can be reduced to 1 p.p.m. in pretreater 131. The pretreater blend flows in part through pipe 243 under control of valve 244 and in part through pipe 242 to pretreater absorber 110. In pretreater absorber 110 the blend is in contact with gas flowing from pretreater liquid-gas separator 145 through conduit 132 and branch 146 under control of valve 217.

The distribution of pretreater blend between pipes 242 and 243 and the distribution of gas between conduit 132 and branch 146 is balanced to remove substantially all of the C_4 and heavier hydrocarbons from the gas while removing substantially all the water, oxygen and heat exchanger deposit precursors from the pretreater blend.

The gas, containing hydrogen, hydrogen sulfide and other components of the liquid-gas separator off-gas or pretreater cascade gas not absorbed by the pretreater blend flows from pretreater absorber 110 through conduit 111 under control of valve 112 to conduits P–245 and H–245 and thence to conduit 61 or conduit 64 as described hereinbefore. The balance of the gas not flowing to the hydrotreating or refining unit, if any, flows through conduit 113 under control of valve 114 to sulfur recovery or to the refinery fuel main.

The pretreater blend including hydrocarbons absorbed from the pretreater cascade gas but substantially devoid of water, oxygen and heat exchanger deposit precursors flows from pretreater absorber 110 through pipe 246 to the suction side of pump 247. Pump 247 discharges the pretreater blend into pipe 248 through which the pretreater blend and absorbed hydrocarbons (hereinafter designated pretreater blend) flow to heat exchanger 249.

In heat exchanger 249 the pretreater blend is in indirect heat exchange relation with the pretreater effluent flowing through conduit 141. From heat exchanger 249 the pretreater blend flows through pipe 120 to heat exchanger 121 where the pretreater blend is in indirect heat exchange relation with the pretreater effluent flowing from the pretreater 131 through conduit 133. From heat exchanger 121 the pretreater blend flows through pipe 122 to coil 123 in heater 124.

In heater 124 the pretreater blend is heated to a temperature such that when mixed with hydrogen-containing gas to form a pretreater charge mixture, the charge mixture will be at a hydrodecontaminating temperature within the range set forth hereinbetfore for pretreating. From heater 124 the heated pretreater blend flows through conduit 125 to conduit 126. In conduit 126 the heated pretreater blend is mixed with hydrogen in the proportions set forth hereinbefore for pretreating.

The hydrogen is supplied wholly or in part as excess reformer gas flowing from reforming liquid-gas separator 188 through conduit 218 under control of valve 219. When none of the pretreater cascade gas is recycled through the pretreating unit as described hereinafter and the pretreater 131 is operating at a pressure at least 25 p.s.i. lower than the pressure in reformer liquid-gas separator 188 excess reformer gas, i.e., reformer cascade gas, flows from reformer liquid-gas separator 188 through conduit 218 under control of valve 220 to conduit 125 where the excess reformer gas is mixed with the pretreater blend. When the pretreater is operating at a pressure higher than the pressure in reformer liquid-gas separator 188 the excess reformer gas, i.e., reformer cascade gas flows through conduit 218 (valve 220 closed) and conduit 127 under control of valve 128 to the suction side of pretreater compressor 129. Pretreater compressor 129 discharges the excess reformer recycle gas into conduit 130 at a pressure higher than the pressure in pretreater 131. The compressed excess reformer recycle gas flows through conduit 130 to conduit 126 where it is mixed with the heated pretreater blend in the proportions set forth hereinbefore under pretreating.

When the volume of the excess reformer recycle gas is less than the volume of hydrogen to be circulated in the pretreating unit a portion of the pretreater gas is recycled. Thus, when the excess reformer hydrogen is about 500 s.c.f. per barrel of pretreater blend and about 1,000 s.c.f. of hydrogen are circulated in the pretreater unit about 500 s.c.f of pretreater hydrogen is recycled. Thus, with the pretreater operating at a pressure at least 25 p.s.i. less than the pressure in the reformer liquid-gas separator 188 about 500 s.c.f. of hydrogen per barrel of pretreater blend as reformer cascade gas flows through conduit 218 under control of valve 220 to conduit 125 where the excess reformer gas is mixed with the pretreater blend. About 500 s.c.f. of hydrogen as pretreater cascade gas per barrel of pretreater blend is diverted from conduit 132 through conduit 134 under control of valve 135 to the suction side of compressor 136. Compressor 136 discharges the diverted portion of the pretreater cascade gas into conduit 137 at a pressure higher than the pressure in pretreater 131. The compressed portion of the pretreater cascade gas flows through conduit 137 to conduit 125 where the compressed portion of the pretreater cascade gas is mixed with the heated pretreater blend. Similarly, when the pretreater pressure is greater than the pressure at reformer liquid-gas separator 188 and the volume of excess reformer hydrogen as reformer cascade gas is less than the volume of hydrogen being circulated in the pretreating unit the excess reformer hydrogen as reformer cascade gas flows through conduit 218 (valve 220 closed) to conduit 127 under control of valve 128 and thence to the suction side of compressor 129. Compressor 129 discharges the compressed reformer cascade gas into conduit 130 at a pressure higher than the pressure in pretreater 131. The compressed reformer cascade gas flows through conduit 130 to conduit 126 where the compressed reformer cascade gas is mixed with the heated pretreater blend and recycled pretreater gas. The recycled pretreater gas flows from conduit 132 through conduit 134 under control of valve 135 to the suction side of compressor 136. Compressor 136 discharges the recycled pretreater gas into conduit 137 at a pressure higher than that in pretreater 131 and about equal to the pressure in conduits 125 and 130. The sum of the volume of hydrogen as pretreater gas and the volume of hydrogen as reformer cascade gas is about equal to the volume of hydrogen circulated in the pretreating unit as set forth hereinbefore.

The heated pretreater blend together with the hydrogen wholly as reformer cascade gas or partly as reformer cascade gas and recycled pretreater gas flows downwardly through pretreater under hydrodecontaminating conditions as set forth hereinbefore in contact with a particle-form hydrogenating catalyst having hydrodesulfurizing and/or hydrodenitrogenizing capabilities. The pretreater effluent flows through conduit 133 to heat exchanger 121 where the pretreater effluent is in in-

direct heat exchange relation with the pretreater blend flowing through pipe 120 as described hereinbefore. From heat exchanger 121 the pretreater effluent flows through conduit 139 to heat exchanger 140. In heat exchanger 140 the pretreater effluent is in indirect heat exchange relation with the condensed portion of the pretreater effluent flowing from heat exchanger 150 through pipe 151. From heat exchanger 140 the pretreater effluent flows through conduit 141 to heat exchanger 249 where the pretreater effluent is in indirect heat exchange relation with the pretreater blend as described hereinbefore. From heat exchanger 249 the pretreater effluent flows through conduit 142 to cooler 143.

In cooler 143 the pretreater effluent is cooled to a temperature at which hydrocarbons boiling in the boiling range of reformer feed are condensed. Depending upon the temperature of the pretreater effluent and the temperature to be maintained in liquid-gas separator 145 a part of the pretreater effluent flows through conduit 215 under control of valve 216 to conduit 144 to separator 145 by-passing cooler 143. The pretreater effluent flows from cooler 143 through conduit 144 to liquid-gas separator 145.

In liquid-gas separator 145 the hydrocarbons boiling below the boiling range of reformer feed together with hydrogen and some hydrogen sulfide separate from hydrocarbons boiling in the boiling range of reformer feed and that amount of hydrogen sulfide soluble in the condensed hydrocarbons at the existing temperature and pressure. The hydrocarbons boiling below the boiling range of reformer feed, i.e., light hydrocarbons together with the hydrogen and hydrogen sulfide flow as pretreater gas from separator 145 through conduit 132 and thence in part or wholly as described hereinbefore under control of valve 133 through branch 146 under control of valve 217 and conduit 132 to pretreater absorber 110 as described hereinbefore.

The condensed hydrocarbons boiling in the boiling range of reformer feed and usually having a maximum boiling point at a temperature within the range of about 350° to about 420° F. flow from liquid-gas separator 145 through pipe 147 to the suction side of pump 148.

Pump 148 discharges the condensed pretreater effluent, i.e., hydrocarbons having a maximum boiling point at a tempetrature within the range of about 350° to about 420° F. into pipe 149 through which the condensed pretreater effluent flows to heat exchanger 150. In heat exchanger 150 the condensed pretreater effluent is in indirect heat exchange relation with the bottoms of splitter 153 flowing from splitter 153 through pipe 164. From heat exchanger 150 the condensed pretreater effluent flows through pipe 151 to heat exchanger 140 where the condensed preheater effluent is in indirect heat exchange relation with pretreater effluent as described hereinbefore. In heat exchanger 140 the condensed pretreater effluent is heated to a temperature at which hydrogen, hydrogen sulfide, and hydrocarbons boiling below reformer feed range are volatile. From heat exchanger 140 the partially condensed pretreater effluent flows through pipe 152 to splitter 153.

In splitter 153 hydrocarbons boiling below the boiling point at 180° to 250° F. end point naphtha or any other desired cut and lighter hydrocarbon together with hydrogen and hydrogen sulfide dissolved in the condensed pretreater effluent at the temperature and pressure existing in separator 145 are taken overhead through conduit 154 to cooler 155. In cooler 155 C_4 and heavier hydrocarbons are condensed. The condensed and uncondensed splitter overhead flows from cooler 155 through conduit 156 to accumulator 157. (In place of the splitter type of separation a stripper type of separation employing stripping gas can be used).

In accumulator 157 the uncondensed splitter overhead is vented through conduit 158 to the refinery fuel main. The condensed splitter overhead flows from accumulator 157 to the debutanizer or light straight-run naphtha stabilizer through pipe 159 under control of valve 161. A portion of the condensed splitter overhead is diverted through pipe 160 to the suction side of pump 162. Pump 162 discharges the diverted portion of the condensed splitter overhead into pipe 163 along which the condensed splitter overhead flows to splitter 153 for use as reflux.

The bottoms of splitter 153, i.e., hydrocarbons boiling in the boiling range of reformer feed and usually having a maximum boiling point within the range of about 350° and 420° F. flows from splitter 153 through pipe 164 to heat exchanger 150 where the bottoms is in indirect heat exchange relation with the condensed pretreater effluent as described hereinbefore. The splitter bottoms, i.e., reformer feed having a maximum boiling point within the range of about 350° and about 420° F. and containing not more than 1 p.p.m. of nitrogen flows from heat exchanger 150 through pipe 165 to the suction side of pump 166.

Pump 166 discharges the reformer feed into conduit 167 at a pressure greater than that in reformer 173. The reformer feed containing not more than 1 p.p.m. of nitrogen flows through conduit 167 to heat exchanger 168 where the reformer feed is in indirect heat exchange relation with the final reformer effluent flowing from reformer 183 through conduit 184. At some point in conduit 167 up-stream of heat exchanger 168 hydrogen-containing reformer recycle gas in the proportion set forth hereinbefore flowing from compressor 191 through conduit 192 at a pressure at least equal to that in conduit 167 is mixed with the reformer feed to provide a reformer charge mixture.

From heat exchanger 168 the reformer charge mixture flows through conduit 169 to coil 170 in heater 171. In heater 171 the reformer charge mixture is heated to a reforming temperature dependent upon the activity of the platinum-group reforming catalyst, the required octane rating of the reformate and other factors known to those skilled in the art and being no part of the present invention.

From heater 171 the charge mixture flows through conduit 172 to reformer 173. In reformer 173 the charge mixture contacts platinum-group particle-form reforming catalyst. The effluent from reformer 173 designated first effluent flows from reformer 173 through conduit 174 to coil 175 in heater 176. In heater 176 the first effluent is heated to a reforming temperature the same as, higher or lower than that to which the charge mixture is heated.

From heater 176 the re-heated first effluent flows through conduit 177 to reformer 178. In reformer 178 the re-heated first effluent contacts platinum-group particle-form reforming catalyst. The effluent from reformer 178 designated second effluent flows from reformer 178 through conduit 179 to coil 180 in heater 181.

In heater 181 the second effluent is re-heated to a reforming temperature the same as, higher or lower than the temperatures to which the reformer charge mixture and the first effluent are heated. From heater 181 the re-heated second effluent flows through conduit 182 to reformer 183.

In reformer 183 the re-heated second effluent contacts platinum-group particle-form reforming catalyst. The effluent from reformer 183, designated final effluent, flows from reformer 183 through conduit 184 to heat exchanger 168. In heat exchanger 168 the final effluent is in indirect heat exchange relation with the reformer charge mixture as described hereinbefore.

From heat exchanger 168 the final effluent flows through conduit 185 to cooler 186. In cooler 186 the final effluent is cooled to a temperature at which C_4 and heavier hydrocarbons are condensed. The condensed and uncondensed final effluent flows from cooler 186 through conduit 187 to reformer liquid-gas separator 188.

In separator 188 the uncondensed final effluent separates from the condensed final effluent. The uncondensed final

effluent, designated reformer recycle and excess gas, flows from separator **188** through conduit **189**. Excess reformer gas, designated reformer cascade gas, flows through conduit **218** under control of valve **219** to the pretreating unit as described hereinbefore. Reformer recycle gas in an amount to provide the hydrogen to reformer feed mol ratio set forth hereinbefore flows from conduit **189** through conduit **190** to the suction side of compressor **191**. Compressor **191** recompresses the reformer recycle gas to a pressure higher than that in reformer **173**. The recompressed reformer recycle gas flows through conduit **192** to conduit **167** as described hereinbefore.

The condensed final effluent flows from separator **188** through pipe **193** to heat exchanger **194**. The condensed final effluent, designated final condensate, is in indirect heat exchange relation with the bottoms of fractionator **196** flowing thereto through pipe **212**. In heat exchanger **194** the final condensate is heated to a temperature at which C_4 and lighter hydrocarbons are volatile. From heat exchanger **194** the heated final condensate flows through pipe **195** to fractionator **196**.

In fractionator **196** C_4 and lighter hydrocarbons are taken as overhead through pipe **197** to cooler **198**. In cooler **198** the overhead is cooled to a temperature at which C_3 and heavier hydrocarbons are partially condensed. From cooler **198** the uncondensed and condensed overhead flows through pipe **199** to accumulator **200**.

In accumulator **200** uncondensed hydrocarbons lighter than C_3 are separated from condensed C_3 and heavier hycarbons. The uncondensed overhead flows from accumulator **200** through pipe **201** to the refinery fuel main. The condensed overhead flows from accumulator **200** through pipe **202** under control of valve **203** to means for recovering C_3 and C_4 hydrocarbons. A portion of the condensed overhead is diverted through pipe **204** to the suction side of pump **205**. Pump **205** discharges the diverted portion of condensed overhead into pipe **206** through which the condensed overhead flows to fractionator **196** for use as reflux.

A portion of the bottoms of fractionator **196** flows from fractionator **196** through pipe **207** to the suction side of pump **208**. Pump **208** discharges that portion of the fractionator bottoms into pipe **209** through which the fractionator bottoms flow to heat exchanger **210**.

In heat exchanger **210** the fractionator bottoms is heated to a temperature at which the lighter hydrocarbons are volatile. From heat exchanger **210** the heated fractionator bottoms flows through pipe **211** to fractionator **196**. Any other means for maintaining the required temperature in fractionator **196** can replace the reboiler described.

The bottoms of fractionator **196**, designated reformate and usually comprising C_5 and heavier hydrocarbons usually having a maximum boiling point within the range of about 350° to about 420° F. flows from fractionator **196** through pipe **212** to heat exchanger **194**. In heat exchanger **194** the reformate is in indirect heat exchange relation with final condensate as described hereinbefore. From heat exchanger **194** the reformate flows through pipe **213** to cooler **214**. In cooler **214** the reformate is cooled to a temperature at which the lowest boiling component of the reformate is liquid. The cooled reformate flows from cooler **214** through pipe **221** to means (not shown) for removing residual hydrogen sulfide, such as a caustic wash employing an aqueous sodium hydroxide solution having a density of 5° to 35°, preferably 20° Baumé and thence to means for adding additives, e.g., tetraethyl lead, etc., to storage and/or distribution.

The following are illustrative reaction conditions for hydrogenation and hydrodesulfurization of a petroleum fraction boiling above the boiling range of reformer feed and usually having an initial boiling point above a temperature within the range of about 350° to about 420° F., e.g., domestic heating oil in conjunction with at least partial hydrodecontamination of high nitrogen content naphtha as defined hereinbefore:

Hydrotreater

Catalyst: about 1.5–3.8 wt. percent cobalt oxide; about 7–16 wt. percent molybdenum oxide
Carrier: alumina

	Broad	Preferred
Reaction pressure, p.s.i.g.	200 to 1,000	390 to 850
Reaction temperature, ° F.	550 to 850	700 to 800
Space velocity, v./v./hr.	2 to 10	4 to 6
Hydrogen/barrel of mixed feed, scf.	200 to 2,000	320 to 1,000
Mols hydrogen/mol hydrocarbon	.4 to 3.8	.8 to 2.7
Hydrogen Partial Pressure, p.s.i.a.	120 to 900	125 to 570

Illustrative of the hydrodecontamination of a blend of autobenous naphtha, i.e., naphtha boiling within the range 100° F. to 420° F. obtained from the first unit with low nitrogen content naphtha as defined hereinbefore, such as straight-run naphtha are the following:

Pretreater

Catalyst: about 1.5 to 3.8 wt. percent cobalt oxide; about 7 to 16 wt. percent molybdenum oxide
Carrier: alumina

	Broad	Preferred
Reaction pressure, p.s.i.g.	100 to 1,000	400 to 500
Reaction temperature, ° F.	600 to 850	675 to 725
Space velocity, v./v./hr.	1 to 10	2.5 to 5
Hydrogen/bbl. of charge, s.c.f.	350 to 2,500	400 to 800

Illustrative of the conditions under which the hydrodecontaminated blend of high nitrogen naphtha and straight-run naphtha is reformed are the following:

Reformer

Catalyst: 0.6 wt. percent platinum; 0.6 wt. percent chlorine
Carrier: alumina

	Broad
Reaction pressure, p.s.i.g.	100 to 1,000
Reaction temperature, ° F.	800 to 1,000
Mols hydrogen/mol naphtha	4 to 20
Space velocity, v./v./hr.	0.5 to 10

As an example of the conjunct treatment of a high nitrogen naphtha and an unstable domestic fuel oil to produce an at least partially desulfurized and denitrogenized naphtha suitable for blending with a straight-run naphtha to be desulfurized and denitrogenized to provide a reformer feed containing not more than about 1 p.p.m. of nitrogen and a domestic fuel oil stable with respect to color and sediment after storage at 100° F. for twelve weeks, and reforming the naphtha blend over a platinum catalyst are the flows of liquids and gases illustrated in FIGURES 1*a* and *b*.

An unstable domestic fuel oil, i.e., a petroleum fraction boiling above the boiling range of reformer feed, having a 10 percent point of 454° F., a 90 percent point of 589° F. and an end point of 641° F. is drawn from a source not shown through pipe **1** by pump **2**. Pump **2** discharges the unstable domestic heating oil into pipe **3** at a pressure greater than the pressure in refining reactor **33**. The unstable domestic heating oil flows through pipe **3** to pipe **4**. A high nitrogen content naphtha, as defined hereinbefore, such as a coker naphtha is drawn from a source not shown through pipe **222** by pump **223**. Pump **223** discharges the coker naphtha into pipe **224** (at a pressure in excess of the pressure in refining reactor **33**) through which the coker naphtha flows to pipe **4**. In pipe **4** the unstable domestic heating oil and coker naphtha are mixed in the proportions of about 1 to about 100 volumes of coker naphtha to 100 volumes of unstable domestic heating oil, e.g., about 17 volumes of unstable

heating oil to about 5 volumes of coker naphtha. The mixture of unstable domestic heating oil and coker naphtha flows in part through pipe 5 to the top of absorber 15 and the balance through pipe 7 wholly or in part to heat exchanger 9 and thence through pipe 12 to absorber 15 or wholly or in part through pipe 10 under control of valve 11 to pipe 12. The distribution of the mixture of unstable domestic heating oil and coker naphtha between pipes 5 and 7 is dependent upon the temperature required in the upper and lower portions of the absorber. That is to say, the flow of hydrocarbon oil, i.e., unstable domestic heating oil and coker naphtha and the flow of gases through conduits 86 and 58 to absorber 15 are balanced to remove substantially all of the C_4 and heavier hydrocarbons from the gases and to remove water and heat exchanger deposit precursors from the hydrocarbon oil. The distribution of the mixture of unstable domestic heating oil and coker naphtha between pipes 8 and 10 is dependent upon maintaining the maximum temperature in absorber 15 at which substantial absorption of C_4 and heavier hydrocarbons by the oil and stripping of water, oxygen and deposit precursors by the gases occurs. Usually a temperature of about 100° to about 150° F. is satisfactory in absorber 15.

The stripped gases and absorbed water, oxygen, etc. are vented from absorber 15 through conduit 16 to the refinery fuel main. The hydrocarbon oil containing absorbed C_4 and heavier hydrocarbons flows from absorber 15 through pipe 17 to the suction side of pump 18.

Pump 18 discharges the mixture of unstable domestic heating oil and coker naphtha into pipe 19. The mixture flows through pipe 19 to heat exchanger 20 where the mixture of unstable domestic heating oil and coker gasoline is in indirect heat exchange relation with the uncondensed vapors flowing from the high temperature flash drum 37 through conduit 39. From heat exchanger 20 the mixture of unstable domestic heating oil and coker naphtha flows through pipe 21 to heat exchanger 22 where the mixture is in indirect heat exchange relation with the bottoms of the light product stripper flowing through pipe 109. The mixture of unstable domestic heating oil and coker naphtha flows through pipe 23 to heat exchanger 24 where the unstable mixture is in indirect heat exchange relation with the uncondensed vapors flowing from high temperature flash drum 37 through conduit 38. From heat exchanger 24 the unstable mixture of domestic heating oil and coker naphtha, i.e., refiner feed mixture, flows through pipe 25 to heat exchanger 26. In heat exchanger 26 the refiner feed mixture is in indirect heat exchange relation with the effluent of hydrotreater or refiner 33 flowing through conduit 35. A portion or all of the refiner feed mixture can flow around heat exchanger 26 through pipe 27 under control of valve 28 to maintain a temperature in high temperature flash drum 37 required to maintain the specified flash point for the bottoms. From heat exchanger 26 the refiner feed mixture flows through pipe 29 to coil 30 in heater 31.

In heater 31 the refiner feed mixture is heated to a temperature such that when mixed with hydrogen-containing gas to form a refiner charge mixture, the refiner charge mixture is at a reaction temperature within the limits set forth hereinbefore for the treatment of a petroleum fraction boiling above the boiling range of reformer feed, say about 650° to about 725° F. The heated mixture flows from heater 31 through pipe 32 to hydrotreater 33.

Hydrogen-containing gas flowing at about 850 p.s.i.g. from heat exchanger 63 through conduit 34 is introduced into the hydrotreater or refiner 33 at the rate of about 1000 to about 1500 standard cubic feet (s.c.f.) of hydrogen per barrel of the refiner feed mixture.

In hydrotreater or refiner 33 the refiner feed mixture is contacted with a catalyst having the capabilities of hydrodesulfurization, broadly hydrodecontaminating, and hydrogenating hydrocarbon fractions at the temperatures and pressures employed. Presently preferred is the aforedescribed mixture of oxides of cobalt and molybdenum supported on alumina.

The effluent from hydrotreater or refiner 33 comprising hydrogen sulfide, ammonia, hydrogen, and C_1 and heavier hydrocarbons flows through conduit 35 to heat exchanger 26 where the hydrotreater effluent is in indirect heat exchange relation with the relatively cold refiner feed mixture as described hereinbefore. From heat exchanger 26 the hydrotreater effluent flows through conduit 36 to high temperature flash drum 37.

In high temperature flash drum 37 a temperature is maintained at which under the existing pressure the bottoms thereof have the specified end point. Usually the temperature in high temperature flash drum 37 is about 560° to about 580° F. for pressures of about 790 p.s.i.g.

The uncondensed portion of the hydrotreater effluent flows from high temperature flash drum 37 through conduit 38 to heat exchanger 24 where the uncondensed refining reactor effluent is in indirect heat exchange relation with the refiner feed mixture flowing to the hydrotreater as described hereinbefore. From heat exchanger 24 the uncondensed refining reactor effluent flows through conduit 39 to heat exchanger 20 where the uncondensed refining reactor effluent is in indirect heat exchange relation with the refiner feed mixture as described hereinbefore. From heat exchanger 20 the uncondensed hydrotreater effluent flows through conduit 40 to cooler or condenser 41 where the temperature of the uncondensed refining reactor effluent is lowered to a practical limit. Usually the pressure is about 740 p.s.i.g. and a temperature of about 70° to about 90° F. is maintained. From condenser 41 the cooled uncondensed hydrotreater effluent flows through conduit 42 to low temperature flash drum 43.

In low temperature flash drum 43 the hydrocarbons of the condensed portion of the refining reactor effluent are separated from the hydrogen, C_1 to C_3 hydrocarbons, hydrogen sulfide and ammonia. The low temperature flash drum overhead comprising principally hydrogen, C_1 to C_3 hydrocarbons, hydrogen sulfide, and ammonia flows from flash drum 43 through conduit 44 to high pressure means for absorbing hydrogen sulfide 45. Presently it is preferred to use diethanolamine as the absorbent for hydrogen sulfide. The low temperature flash drum overhead flows upwardly through absorber 45 countercurrent to the downwardly flowing diethanolamine (DEA). The low temperature flash drum overhead stripped of hydrogen sulfide flows from scrubber 45 through conduit 54 to knock-out pot 55 where entrained DEA (if any) is dropped-out and thence through conduit 57 to compressor 60. A portion of the overhead from the low temperature flash drum flowing through conduit 57 and in excess of the amount of hydrogen to be recycled to hydrotreater 33 is diverted through conduit 58 under control of valve 59 to absorber 15 where any C_4 and heavier hydrocarbons are stripped from the low temperature flash drum overhead. Any entrained DEA is removed from knock-out pot 55 through conduit 56.

Returning to low temperature flash drum 43 and following the flow of the liquid phase separated therein, it will be manifest that the bottoms of the low temperature flash drum 43 comprising the aforesaid hydrocarbons flow therefrom through pipe 68 to heat exchanger 69 where the low temperature flash drum bottoms is in indirect heat exchange relation with at least a portion of the bottoms of the light products stripper 75 flowing through pipe 107. From heat exchanger 69 the low temperature flash drum bottoms flows through pipe 70 to pipe 71 where the low temperature flash drum bottoms is mixed with the overhead from the heavy products stripper flowing through pipe 74.

Returning to high temperature flash drum 37 the flow

of the condensed hydrotreater effluent will be followed. The condensed hydrotreater effluent comprising treated domestic heating oil flows from high temperature flash drum 37 through pipe 72 to heavy products stripper 73. In heavy products stripper 73 the treated domestic heating oil is steam stripped of hydrocarbons boiling in the boiling range of reformer feed, designated naphtha, and the naphtha taken as an overhead through pipe 74. The overhead from the heavy products stripper flows through pipe 74 to pipe 71 where the overhead from the heavy products stripper is mixed with the bottoms of the low temperature flash drum 43. The bottoms from the heavy products stripper 73 flows through pipe 76 to the bottom of light products stripper 75.

In light products stripper 75 the mixture of heavy products stripper overhead and low temperature flash drum bottoms is fractionated or stripped with steam to provide an overhead comprising components boiling in the boiling range of reformer feed and a bottoms comprising hydrocarbons having a 10 percent point not lower than about 370° F. and preferably not lower than about 420° F., i.e., treated domestic heating oil and meeting the desired flash point. The light products stripper bottoms flows therefrom through pipe 105 to the suction side of pump 106. Pump 106 discharges the light products stripper bottoms into pipe 107 through which the bottoms flow to heat exchanger 69. Dependent upon the temperature of the low temperature flash drum condensate leaving heat exchanger 69 all or a portion of the light products stripper bottoms is diverted to pipe 225 under control of valve 226 to by-pass heat exchanger 69. The light products stripper bottoms then flows through pipe 108 to heat exchange 63 where the bottoms is in indirect heat exchange relation with hydrogen-containing gas flowing at a pressure in excess of that in hydrotreater 33 from compressor 60 through conduit 62. From heat exchanger 63 the bottoms flows through pipe 109 to heat exchanger 22 where the bottoms is in indirect heat exchange relation with the refiner feed mixture flowing to the hydrotreater through pipe 21. From heat exchanger 22 the light products stripper bottoms flows through pipe 233 to heat exchanger 9 where the bottoms is in indirect heat exchange relation with the refiner feed mixture flowing to the hydrotreater as described hereinbefore. From heat exchanger 9 the light products stripper bottoms flows through pipe 234 to cooler 227 where the temperature of the bottoms is reduced to about 140° F. or lower. From cooler 227 the bottoms flows through pipe 228 alternatively to a caustic wash (not shown) to remove residual sulfur compounds soluble in aqueous caustic, if any, and/or means to remove water and then to storage, etc., or to storage, admixing of additives, distribution, etc., to provide domestic heating oil stable to color and sediment.

Returning to light products stripper 75, the flow of the components of the feed to light products stripper 75 which boil in the boiling range of reformer feed or lower will be traced. The overhead from the light products stripper comprises residual amounts of hydrogen, hydrogen sulfide, and C_1 and heavier hydrocarbons boiling in the boiling range of reformer feed and usually having a maximum boiling point within the range of about 350° to about 420° F. The overhead flows from light products stripper 75 through conduit 77 to cooler 78 where the C_4 and heavier hydrocarbons are condensed. From the cooler 78 the condensed and uncondensed overhead flows through conduit 79 to accumulator 80. In accumulator 80 the uncondensed overhead comprising hydrogen, hydrogen sulfide, and C_1 to C_3 hydrocarbons is separated from the condensed overhead and flows through pipe 82 to low pressure means for removing hydrogen sulfide 83. Presently, it is preferred to use diethanolamine as the absorbent for hydrogen sulfide. In absorber 83 the uncondensed overhead flows upwardly counter-current to the downwardly flowing diethanolamine. The stripped uncondensed overhead flows from absorber 83 through conduit 86 to absorber 15 where the stripped uncondensed overhead is contacted with the feed to the hydrotreater 33 as described hereinbefore.

The condensed overhead from light products stripper 75 flows from accumulator 80 through pipe 87 to heat exchanger 229. A portion, to serve as reflux in light products stripper 75, is drawn by pump 90 through conduit 88 under control of valve 89 and discharged into pipe 91. The discharge from pump 90 flows through pipe 91 to light products stripper 75 for use as reflux. The condensed overhead flowing through pipe 87 is heated in heat exchanger 229 to a temperature at which C_4 and lighter hydrocarbons are volatile. From heater 229 the heated condensed stripper overhead flows through pipe 230 to reformer feed fractionator 92. Alternatively, the condensed overhead flows directly from accumulator 80 to pump 103.

Fractionator 92 can be operated to provide a pretreater naphtha blend component as a bottoms comprising a substantially dehexanized, or a substantially depentanized, or a substantially debutanized or a substantially depropanized pretreater naphtha blend component boiling in the boiling range of reformer feed and usually having a maximum boiling point within the range of about 350° to about 420° F.

In fractionator 92 the C_6, or C_5, or C_4, or C_3, and lighter hydrocarbons are taken as overhead through pipe 93. The overhead is cooled in cooler 94 to a temperature at which hydrocarbons heavier than C_6 or heavier than C_5 or heavier than C_4 or heavier than C_3 are condensed dependent upon whether a dehexanized or a depentanized or a debutanized or a depropanized pretreater naphtha blend component is required or, in other words, hydrocarbons boiling in the range of the required reformer feed are condensed. The condensed and uncondensed fractionator overhead flow from cooler 94 through conduit 95 to accumulator 96. The uncondensed overhead flows from accumulator 96 through conduit 101 to means for recovering the valuable hydrocarbons.

The condensed fractionator overhead boiling predominantly below the boiling range of the pretreater naphtha blend component flows from accumulator 96 through pipe 97 to recovery of the C_3 to C_6 hydrocarbons the presence of which is dependent upon the split made in fractionator 92. A portion sufficient for use as reflux in fractionator 92 is diverted by means of conduit 98 under control of a valve not shown to the suction side of pump 99. Pump 99 discharges the reflux portion of the condensed overhead into pipe 100. The reflux portion of the condensed overhead flows through pipe 100 to fractionator 92.

The bottoms of fractionator 92 is the pretreater naphtha blend component and comprises the autogenous reformer feed produced in the hydrotreater or refiner 33 and the partially treated high nitrogen content naphtha which formed a portion of the refiner feed mixture. The bottoms boil in the boiling range of reformer feed and usually have a maximum boiling point within the range of about 350° to about 420° F. The bottoms flows from fractionator 92 through pipe 102 to the suction side of pump 103. Pump 103 discharges the bottoms, i.e., pretreater naphtha blend component into pipe 104 through which the pretreater naphtha blend component flows to pipe 242 (FIG. 1*b*) where the pretreater naphtha blend component is mixed with a low nitrogen naphtha (as defined hereinbefore) to provide the pretreater feed mixture.

A low nitrogen content naphtha (as defined hereinbefore) capable of being reformed, such as straight-run naphtha, is drawn from a source not shown through pipe 240 by pump 241 and discharged into pipe 242. The low nitrogen content naphtha, hereinafter designated straight-run gasoline, is mixed in pipe 242 with the aforesaid pretreater naphtha blend component flowing from the refining section through pipe 104 and P–104 to form a pretreater blend the nitrogen content of which can be reduced in existing reformer feed preparation facilities to not more than 1 p.p.m. of nitrogen. The blend flows

through pipe 242 and branch 243 under control of valve 244 to absorber 110. Hydrogen-containing gas flowing from pretreater liquid-gas separator 145 through conduit 132 under control of valve 133 and through branch conduit 146 under control of valve 217 to absorber 110 contacts the pretreater blend therein. The flow of pretreater blend through pipes 242 and 243 and the flow of gas through conduit 132 and branch conduit 146 are proportioned so that the C_4 and heavier hydrocarbons in the hydrogen-containing gases are substantially completely removed by the naphtha blend without substantial absorption of hydrogen sulfide while water, oxygen and exchange deposit precursors are stripped from the pretreater blend with the hydrogen-containing gases.

The hydrogen-containing gases stripped of C_4 and heavier hydrocarbons flow from absorber 110 through conduit 113. Gas in excess of that required in hydrotreater or refiner 33 (FIG. 1*a*) is diverted through conduit 113 under control of valve 114 to the refinery fuel main. The balance and usually major portion, i.e., the pretreater cascade gas flows through conduit P–245 (FIG. 1*b*) to conduit H–245 (FIG. 1*a*) and thence either to conduit 62 (hydrotreater pressure less than pretreater pressure) through conduits 61 and 71 or to the suction side of compressor 66 (hydrotreater pressure greater than pretreater pressure). The pretreater blend flows from absorber 110 through pipe 246 to the suction side of pump 247. The pretreater blend the nitrogen content of which can be reduced in existing reformer feed preparation facilities to not more than 1 p.p.m of nitrogen is discharged by pump 247 at a pressure greater than that in pretreater 131 into pipe 248. The pretreater blend flows through pipe 248 to heat exchanger 249 where the pretreater blend is in indirect heat exchange relation with the effluent from pretreater 131 flowing through conduit 141. From heat exchanger 249 the pretreater blend flows through pipe 120 to heat exchanger 121 where the pretreater blend is in indirect heat exchange relation with the effluent of pretreater 131 flowing through conduit 138. From heat exchanger 121 the pretreater blend flows through pipe 122 to coil 123 in heater 124.

In heater 124 the pretreater blend is heated to a temperature at which, when mixed with hydrogen-containing gas under the pressure existing and in the presence of hydrogen and a desulfurizing, denitrogenizing and hydrogenating catalyst, the naphtha blend is hydrodecontaminated to provide a reformer feed containing not more than about 1 p.p.m. of nitrogen. Temperatures within the limits set forth hereinbefore for hydrodecontamination with a mixture of oxides of cobalt and molybdenum are illustrative. The heated pretreater blend flows from heater 124 through pipe 125 to pretreater 131. Hydrogen-containing gas, i.e., reformer cascade gas, flowing from the reforming unit through conduits 189 and 218 under control of valve 220 or from compressor 129 through conduit 130 is mixed with the heated pretreater blend within the range of proportions set forth hereinbefore for hydrodecontamination of the pretreater blend. The mixture of pretreater blend and hydrogen-containing gases flows downwardly through pretreater 131.

The effluent of pretreater 131 flows therefrom through conduit 138 to heat exchanger 121 where the pretreater effluent is in indirect heat exchange relation with the pretreater blend as described hereinbefore. The pretreater effluent flows from heat exchanger 121 through conduit 139 to heat exchanger 140 where the pretreater effluent is in indirect heat exchange relation with the condensate from liquid-gas separator 145 flowing from pump 148 and exchanger 150 through pipe 151. From heat exchanger 140 the pretreater effluent flows through conduit 141 to heat exchanger 249 where the pretreater effluent is in indirect heat exchange relation with the pretreater blend as described hereinbefore. From heat exchanger 249 the pretreater effluent flows through conduit 142 to cooler or condenser 143 where the temperature of the pretreater effluent is lowered to that at which under the existing pressure a major portion of the C_4 and substantially all of the heavier hydrocarbons are condensed. From condenser 143 the cooled pretreater effluent flows through conduit 144 to liquid-gas separator 145. A portion or all of the pretreater effluent can by-pass condenser 143 to avoid over-cooling the pretreater effluent. Thus, a portion of the pretreater effluent can flow from conduit 142 through conduit 215 under control of valve 216 to conduit 144.

In liquid-gas separator 145 a minor portion of the C_4 and substantially all of the lighter hydrocarbons together with hydrogen, hydrogen sulfide and ammonia are separated from the condensed C_4 and heavier hydrocarbons. The overhead gas flows from separator 145 through conduit 132 under control of valve 133 to absorber 110 as described hereinbefore. When the amount of reformer cascade gas is insufficient to meet the needs of pretreater 131 a portion of the pretreater gas is diverted through conduit 134 under control of valve 135 to the suction side of compressor 136. The repressured pretreater gas is discharged through conduit 137 into conduit 125 and mixed therein with the heated pretreater blend.

The condensed C_4 and heavier hydrocarbons together with small amounts of hydrogen derivatives of contaminants, hereinafter designated pretreater condensate, flows from separator 145 through pipe 147 to the suction side of pump 148. Pump 148 discharges into pipe 149 through which the pretreater condensate flows to heat exchanger 150. In heat exchanger 150 the pretreater condensate is in indirect heat exchange relation with the bottoms of splitter 153 flowing through pipe 164. From heat exchanger 150 the pretreater condensate flows through pipe 151 to heat exchanger 140 where the pretreater condensate is in indirect heat exchange relation with the pretreater effluent flowing from pretreater 131 and heat exchanger 121 through conduit 139 as described hereinbefore. From heat exchanger 140 the pretreater condensate flows through pipe 152 to splitter 153.

In splitter 153, which is provided with a reboiler or other means for maintaining a temperature at which a substantially dehexanized or a substantially depentanized, or a substantially debutanized, or a substantially depropanized reformer feed is prepared, the overhead comprising respectively C_6, or C_5, or C_4, or C_3 and lighter hydrocarbons, hydrogen, and hydrogen derivatives of contaminants is taken through conduit 154.

The overhead flows through conduit 154 to cooler 155 where C_6, or C_5, or C_4, or C_3 and heavier hydrocarbons are condensed. The condensed and uncondensed overhead flows from cooler 155 through conduit 156 to accumulator 157.

The uncondensed hydrocarbons, hydrogen, and hydrogen derivatives of contaminants flow from accumulator 157 through conduit 158 to the refinery fuel main. The condensed hydrocarbons flow from accumulator 157 through pipe 159 under control of valve 161 to recovery of condensed hydrocarbons. A portion of the condensed hydrocarbons is diverted through pipe 160 to the suction side of pump 162. Pump 162 discharges the diverted condensed overhead into pipe 163 through which the condensed hydrocarbons flow to fractionator 153 for use as reflux.

The splitter bottoms flows through pipe 164 to heat exchanger 150 and thence through pipe 165 to the suction side of pump 166. Pump 166 discharges the splitter bottoms, now designated reformer feed containing not more than 1 p.p.m. of nitrogen into pipe 167. The reformer feed flows through pipe 167 to heat exchanger 168 where the bottoms is in indirect heat exchange relation with the final effluent of the reforming section. The bottoms contains not more than 1 p.p.m. of nitrogen. The bottoms is the hydrocarbon feed to the reforming unit.

Before describing the flow of liquids and gases through

the reforming unit the flow of gases through the pretreating unit and the refining unit will be summarized. Hydrogen-containing gas produced in the reformer unit in excess of that required for reforming, designated reformer cascade gas, flows from liquid-gas separator **188** through conduit **189** to conduit **218** in the reforming unit under control of valve **219** at substantially the pressure in reforming reactor **183** less line pressure drop to conduit **218** and from conduit **218** to conduit **125** and pretreater **131** under control of valve **220** when pretreater pressure is less than reformer pressure. The reformer cascade gas flows through conduit **127** (valve **220** closed; valve **128** open) to the suction side of compressor **129** when pretreater pressure is greater than reformer pressure. Compressor **129** discharges the recompressed reformer cascade gas at a pressure greater than pretreater pressure into conduit **130**. Hydrogen-containing gas, pretreater gas from separator **145** flows to absorber **110**. From absorber **110** a portion of the pretreater gas, designated pretreater cascade gas, flows through conduits P–245 and H–245 and **61** to conduit **67** (pretreater pressure greater than refiner pressure) or through conduits P–245, H–245 and **64** to the suction side of compressor **66**. Compressor **66** discharges the pretreater cascade gas into conduit **67** at a pressure higher than that of the hydrotreater **33**. The hydrogen-containing gas from low temperature flash drum **43** (FIGURE 1*a*) flows through high pressure DEA absorber **45** to knockout pot **55** and thence through conduit **57** to compressor **60**. Thus, the hydrogen-containing gas in excess of that required for reforming is used to pretreat a naphtha blend and then is used to refine a mixture of the petroleum fraction boiling above the boiling range of reformer feed and high nitrogen content naphtha.

The flow of liquids and gases in the removal of hydrogen sulfide in the high pressure and low pressure diethanolamine scrubbers is substantially as described hereinbefore.

The reformer feed containing not more than 1 p.p.m. of nitrogen flows through pipe **165** (FIGURE 1*c*) to the suction side of pump **166**. Pump **166** discharges the reformer feed into conduit **167** at a pressure greater than the pressure in reformer **173** (FIGURE 1*b*). At some point in conduit **167** intermediate to pump **166** and to heat exchanger **168** hydrogen-containing gas discharged at a pressure at least equal to that in reformer **173** by compressor **191** flows through conduit **192** into conduit **167**. The hydrogen-containing gas is mixed with the naphtha blend in conduit **167** in the proportions set forth hereinbefore. The mixture of hydrogen-containing gas and reformer feed, hereinafter designated reformer charge mixture, flows through conduit **167** to heat exchanger **168**. In heat exchanger **168** the reformer charge mixture is in indirect heat exchange relation with the effluent from reformer **183** (final effluent) flowing thereto through conduit **184**. From heat exchanger **168** the reformer charge mixture flows conduit **169** to coil **170** in furnace **171**. In coil **170** the reformer charge mixture is heated to a reforming reaction temperature within the limits set forth hereinbefore. The heated reformer charge mixture flows from coil **170** through conduit **172** to reformer **173**. The effluent of reformer **173**, hereinafter designated first reformer effluent, flows through conduit **174** to coil **175** in furnace **176**. In coil **175** the first reformer effluent is reheated to a reforming temperature equal to, lower than, or higher than the inlet temperature of reformer R_1. From coil **175** the reheated first reformer effluent flows through conduit **177** to the second reformer **178**. From the second reformer **178** the second reformer effluent flows through conduit **179** to coil **180** in furnace **181**. In coil **180** the second reformer effluent is reheated to reforming temperature within the range set forth hereinbefore and equal to, higher than or lower than the vapor inlet temperatures of reactors R_1 and R_2. From coil **180** the reheated second reformer effluent flows through conduit **182** to third reformer **183**. The effluent of third reformer **183**, i.e., final effluent, flows therefrom through conduit **184** to heat exchanger **168** where the final effluent is in indirect heat exchange relation with the reformer feed as described hereinbefore. From heat exchanger **168** the final effluent flows through conduit **185** to cooler **186**. In cooler **186** the final effluent is cooled to a temperature at which under the existing pressure C_4 and heavier hydrocarbons are condensed. The uncondensed portion and the condensed portion of the final effluent flow from cooler **186** through conduit **187** to liquid-gas separator **188**.

In liquid-gas separator **188** the uncondensed portion of the final effluent separates from the condensed portion of the final effluent. The uncondensed portion of the final effluent comprising hydrogen and C_1 to C_4 hydrocarbons and designated reformer recycle gas hereinafter flows from separator **188** through conduit **189**. At some point in conduit **189** a portion of the reformer recycle gas about equal to the gas made in the reformers is diverted through conduit **218** under control of valve **219** to the pretreating unit. The diverted portion of the reformer gas, designated reformer cascade gas, flows through conduit **218** to pretreater **131** as described hereinbefore. The balance is reformer recycle gas which flows through conduit **190** to the suction side of compressor **191**. Compressor **191** discharges the recycle gas into conduit **192** through which the recycle gas flows to conduit **167** to mix with the reformer feed to form the reformer charge mixture as previously described.

The condensed portion of the final effluent, hereinafter designated condensate, is separated from the recycle gas in separator **188** and flows therefrom through pipe **193** to heat exchanger **194** where the condensate is in indirect heat exchange relation with the bottoms of fractionator **196** flowing therefrom through pipe **212**. From heat exchanger **194** the condensate flows through pipe **195** to fractionator **196**.

In fractionator **196** a temperature is maintained at which C_4 and lighter hydrocarbons are volatile. The C_4 and lighter hydrocarbons are taken overhead from fractionator **196** through pipe **197**. The overhead from fractionator **196** flows through pipe **197** to cooler **198** where the overhead is cooled to a temperature at which C_3 and C_4 hydrocarbons are condensed. The cooled overhead flows through pipe **199** to separator **200**. In separator **200** the uncondensed overhead is separated from the condensed overhead and is vented to the refinery fuel main through pipe **201**. The condensed overhead flows from accumulator **200** through pipe **202** under control of valve **203** to C_3 and C_4 recovery. A portion of the condensed overhead sufficient to serve as reflux in fractionator **196** is diverted from pipe **202** through pipe **204** to the suction side of pump **205**. Pump **205** discharges the reflux into pipe **206** through which the reflux flows to fractionator **196**.

Bottoms from fractionator **196**, i.e., C_5 and heavier hydrocarbons flow through a reboiler comprising pipe **207**, pump **208**, pipe **209**, heat exchanger **210**, and pipe **211** or any other suitable means for maintaining a temperature in fractionator **196** at which C_4 and lighter hydrocarbons are volatile. The net bottoms product from fractionator **196**, i.e., the raw reformate yield, flows from fractionator **196** through pipe **212** to heat exchanger **194** where the bottoms is in indirect heat exchange relation with the condensate from separator **188** as described hereinbefore. From heat exchanger **194**, the bottoms flows through pipe **213** to cooler **214** where the bottoms is cooled to a temperature at which the lowest boiling hydrocarbon is a liquid. From cooler **214** the reformate, C_5 and heavier hydrocarbons, flows through pipe **221** to means (not shown) for removing residual hydrogen sulfide, such as a caustic wash employing an aqueous sodium hydroxide solution having a density of 5° to 35°, preferably 20° to

25° Baumé and thence to means for the addition of additives, blending, storage and distribution.

I claim:

1. In the method of upgrading a hydrocarbon mixture boiling above the boiling range of reformer feed and below the boiling range of lubricating oil, designated hydrotreater feed, and obtaining a hydrocarbon mixture boiling above the boiling range or reformer feed and below the boiling range of lubricating oil and having substantially lower concentrations of sulfur and nitrogen than said hydrotreater feed, designated hydrotreater product, and upgrading reformer feed containing more than 1 p.p.m. of nitrogen and obtaining reformer feed containing not more than 1 p.p.m. of nitrogen wherein the aforesaid hydrotreater feed is contacted with a static bed of sulfur— and nitrogen—insensitive particle-form solid hydrogenating catalyst having hydrodesulfurizing and hydrodenitrogenizing capabilities in a hydrotreater at hydrotreater hydrodecontaminating conditions of pressure in the range of 200 to 1000 p.s.i.g., temperature in the range of 550° to 850° F., liquid hourly space velocity in the range of 2 to 10, and hydrogen-to-hydrotreater feed mol ratio in the range of 0.4 to 3.8; wherein a hydrotreater effluent comprising hydrogen, hydrogen sulfide, ammonia, and C_1 and heavier hydrocarbons is obtained; wherein said hydrotreater effluent is separated into hydrotreater gas comprising hydrogen, hydrogen sulfide, ammonia, and C_1 to C_3 hydrocarbons, autogenous reformer feed having a nitrogen concentration greater than 1 p.p.m., and comprising C_4 and heavier hydrocarbons having an end boiling point in the range of about 350° to about 420° F., designated pretreater blend stock, and upgraded hydrocarbon mixture being the aforesaid hydrotreater product having concentrations of sulfur and nitrogen substantially lower than those of said hydrotreater feed; wherein said hydrotreater gas is vented; wherein said pretreater blend stock is admixed with extraneous reformer feed having a lower concentration of nitrogen in proportion to form a blended pretreater feed having a nitrogen content reducible to not more than 1 p.p.m. in the aforesaid pretreater at pretreater hydrodecontaminating conditions set forth hereinafter to provide blended pretreater feed; wherein said blended pretreater feed is contacted with a static bed of particle-form solid sulfur- and nitrogen-insensitive hydrogenating catalyst having hydrodesulfurizing and hydrodenitrogenizing capabilities under pretreater hydrodecontaminating conditions of pressure in the range of 100 to 1000 p.s.i.g., temperature in the range of 600° to 850° F., liquid hourly space velocity in the range of 1 to 10, and hydrogen circulation in the range of 350 to 2500 s.c.f. of hydrogen per barrel of said blended pretreater feed; wherein pretreater effluent comprising hydrogen sulfide, ammonia, hydrogen, and C_1 and heavier hydrocarbons is obtained; wherein said pretreater effluent is separated into pretreater gas comprising hydrogen sulfide, ammonia, hydrogen, and C_1 to C_3 hydrocarbons, an intermediate fraction comprising C_4 hydrocarbons, and reformer feed comprising C_5 and heavier hydrocarbons containing not more than 1 p.p.m. of nitrogen; wherein sufficient of said pretreater gas flows to said hydrotreater to supply the aforesaid 0.4 to 3.8 mols of hydrogen per mol of hydrotreater feed; wherein said reformer feed is contacted in a reformer with a static bed of nitrogen-sensitive particle-form solid platinum-group metal reforming catalyst at reforming conditions of pressure in the range of 100 to 1000 p.s.i.g., temperature in the range of 800° to 1000° F., liquid hourly space velocity in the range of 0.5 to 10, and hydrogen-to-reformer feed mol ratio in the range of 4 to 20; wherein a reformer effluent comprising hydrogen and C_1 and heavier hydrocarbons is obtained; wherein said reformer effluent is separated into reformer gas comprising hydrogen and C_1 to C_3 hydrocarbons, and raw reformate comprising C_4 and heavier hydrocarbons; wherein said reformer gas is separated into reformer recycle gas and reformer make-gas; wherein said reformer recycle gas flows to said reformer to maintain the aforesaid hydrogen-to-reformer feed mol ratio; and wherein said reformer make-gas flows to said pretreater to maintain the aforesaid hydrogen circulation in the range of 350 to 2500 s.c.f. of hydrogen per barrel of blended pretreater feed; the improvement which comprises mixing the aforesaid hydrotreater feed with high nitrogen content hydrocarbon mixture in the proportion of about 100 volumes of hydrotreater feed per 1 to 100 volumes of high nitrogen content hydrocarbon mixture to form novel hydrotreater feed, said high nitrogen content hydrocarbon mixture boiling in the boiling range of reformer feed and having a higher concentration of nitrogen than can be reduced to not more than 1 p.p.m. in the aforesaid pretreater at the aforedescribed pretreater hydrodecontaminating conditions, even when mixed with the aforesaid extraneous reformer feed; contacting the aforesaid novel hydrotreater feed in the aforesaid hydrotreater with the aforesaid particle-form solid sulfur- and nitrogen-insensitive hydrogenating catalyst at the aforesaid hydrotreater hydrodecontaminating conditions; obtaining hydrotreater effluent comprising hydrogen sulfide, ammonia, hydrogen, and C_1 and heavier hydrocarbons; separating said hydrotreater effluent into hydrotreater gas comprising hydrogen sulfide, ammonia, hydrogen, and C_1 to C_3 hydrocarbons, pretreater blend stock consisting of autogenous reformer feed and partially hydrodenitrogenized high nitrogen content hydrocarbon mixture, said pretreater blend stock comprising C_4 and heavier hydrocarbons having an end boiling point in the range of about 350° to about 420° F., and having a higher concentration of nitrogen than can be reduced to more than 1 p.p.m. in the aforesaid pretreater at the aforesaid pretreater hydrodecontaminating conditions, and the aforesaid upgraded hydrotreater product; treating a major portion of said hydrotreater gas to remove hydrogen sulfide; and recycling at least a portion of the so-treated hydrotreater gas to the aforesaid hydrotreater.

2. The method set forth in claim 1 wherein the aforesaid hydrocarbons fraction boiling above the boiling range of reformer feed and below the boiling range of lubricating oil is raw domestic fuel oil, wherein the hydrotreater product has a ten percent point in the range of 370° to 420° F., and wherein the hydrotreater product is washed with aqueous caustic, the caustic-washed hydrotreater product is water-washed, and stabilized domestic fuel oil is obtained, said domestic fuel oil being stable to at least one of color and sediment, containing not more than 1 to 2 percent total sulfur, and not more than 1 to 2 percent of the mercaptan-sulfur originally present in the aforesaid raw domestic fuel oil.

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