

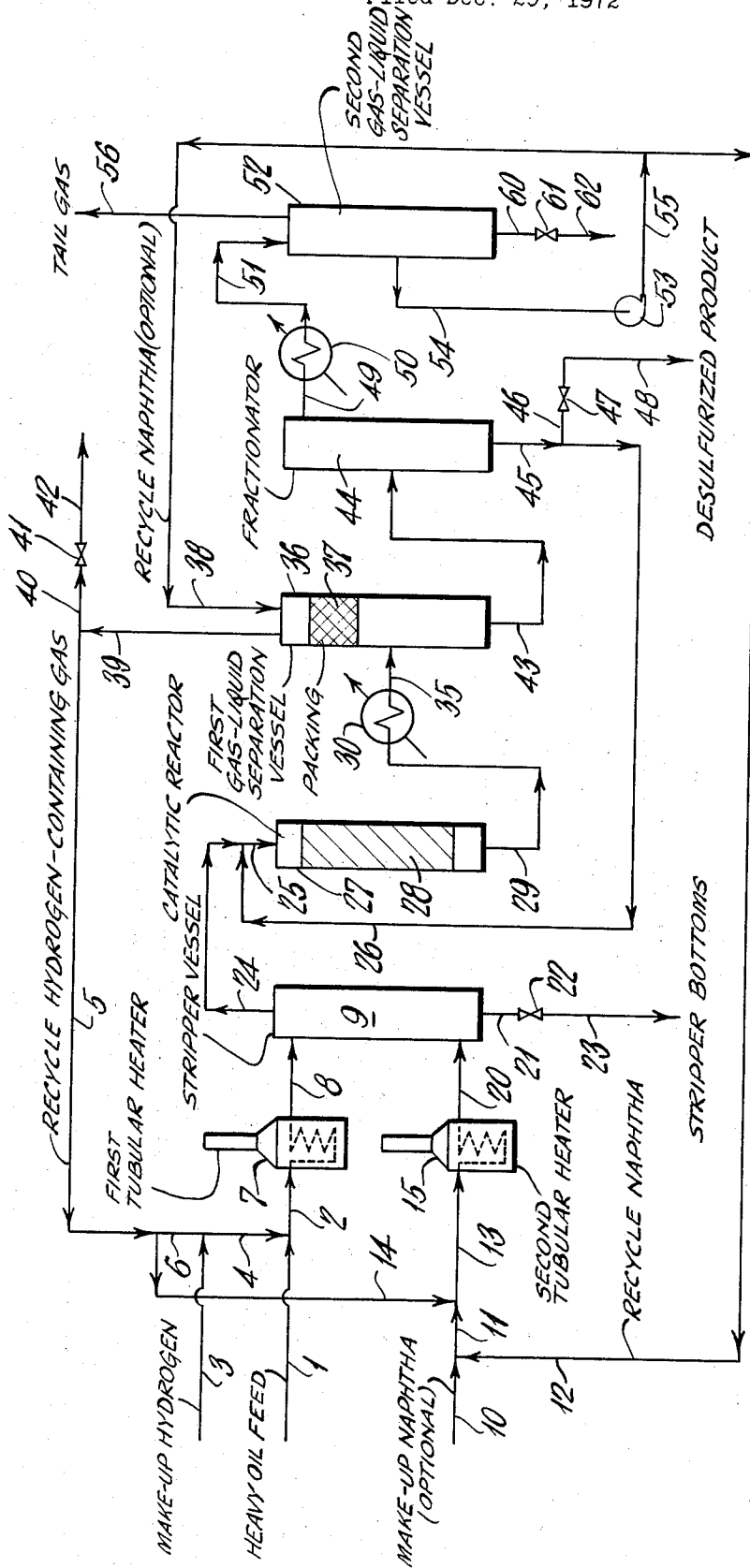
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DESULFURIZATION OF PETROLEUM CRUDE

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DESULFURIZATION OF PETROLEUM CRUDE

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ABSTRACT OF THE DISCLOSURE

Hydrodesulfurization process to convert large volumes of high sulfur oil to liquid industrial fuels with a maximum of 1.0% sulfur by weight, thereby meeting stringent pollution control standards. In the process a low naphtha high sulfur containing petroleum crude or crude fraction is thermally and catalytically hydrocracked and hydro-treated in the presence of a stream of supplemental naphtha from an external source. H₂S, CH₄ and CO₂ produced in the process dissolve in liquid naphtha and are later separated in a fractionator where naphtha is recovered and recycled.

BACKGROUND OF THE INVENTION

Field of the invention

This invention pertains to the treatment of low naphtha high sulfur containing hydrocarbonaceous fuels. More particularly, it is concerned with the conversion of sulfur-containing petroleum crude oils into distillate products substantially free from sulfur, nitrogen, metals and ash, and gum-forming constituents.

DESCRIPTION OF THE PRIOR ART

Thermal cracking processes for hydrocarbon oil and purification of crude oil by hydrogen treating with or without catalysts are known in the prior art. For example, reference is made to co-assigned U.S. Pat. 3,089,843, Du Bois Eastman et al.

Treating liquid hydrocarbons with hydrogen by available processes is often uneconomical because of the large quantities of hydrogen that are consumed. Further, such processes require expensive solvents and scrubbing equipment to separate the H₂S, COS, CH₄, and CO₂ produced from the liquid hydrocarbon product.

SUMMARY

This is a process for treating a hydrocarbonaceous feedstock such as a low naphtha comparatively high sulfur containing heavy crude or crude fraction to yield a liquid hydrocarbon product which is substantially free from sulfur, nitrogen and metals. In the process, a hydrocarbonaceous feedstock is mixed with a hydrogen-containing gas and thermally cracked in a thermal cracking zone at a temperature in the range of about 600 to 1,000° F. and at a pressure in the range of about 1,000 to 6,000 p.s.i.g. The thermal cracking zone comprises in sequence an externally fired tubular heater and an adiabatic stripper vessel. The effluent from the tubular heater is introduced directly into said separate free-flow non-catalytic adiabatic stripper vessel. There while in direct contact with a counter-current stream of a hydrogen-containing gas in admixture with vaporized supplemental naphtha, at a temperature in the range of about 600 to 1,000° F., additional thermocracking and hydro-refining take place. By said thermocracking, the petroleum crude is broken into middle distillate materials, heavy distillate materials, and a tar residue. Simultaneously, hydrogen in the stream reacts with sulfur in the feedstock to produce H₂S. Less than 25 weight percent of the petroleum feedstock is removed from the bottom of the stripper vessel as asphaltic material.

The overhead material from the stripper vessel is passed into a conventional catalytic hydrocracker, optionally in admixture with a recycle stream comprising a portion of the fractionator bottoms produced subsequently in the process. In the catalytic reactor at a temperature in the range of about 750 to 850° F. and a pressure in the range of about 800 to 6,000 p.s.i.g., the aforesaid stream is cracked further and treated with hydrogen. Substantially all of the sulfur in the process gas stream is converted by now into H₂S.

The effluent process gas stream leaving the catalytic hydrocracker is cooled to a temperature in the range of about 200 to 400° F. in order to liquefy the naphtha contained therein. The liquid naphtha absorbs substantially all of the H₂S, CH₄ and CO₂ in the process gas stream. The process stream is then passed into a first gas-liquid separation vessel where a hydrogen-containing gas is separated from the liquid portion of the process stream. The hydrogen-containing gas is removed from the top of said first gas-liquid separation vessel and recycled to the front end of the process where it is mixed with the two separate streams of material going into the stripper vessel, as previously described. Preferably, a liquid stream of recycle naphtha recovered subsequently in the process is introduced into the top of said first gas-liquid separation vessel to scrub the recycle hydrogen-containing gas free from H₂S.

The process stream from the bottom of the first gas-liquid separation vessel is passed into a conventional fractionator and split into the following streams: a gaseous stream principally comprising vaporized naphtha, H₂S, CO₂ and CH₄ which is removed from the top of the fractionator, cooled to liquefy the naphtha, and introduced into a second gas-liquid separation vessel; and a stream of product which is removed from the bottom and optionally divided into two streams, one stream for recycle to the catalytic hydrocracker as previously described and the other stream for use as fuel oil or to be sent downstream for additional processing. A stream of normally gaseous materials including H₂S, CO₂ and CH₄ is removed from the top of the second gas-liquid separation vessel and sent to conventional downstream processing for sulfur recovery such as a Claus unit. A stream of liquid naphtha is removed from said second gas-liquid separation vessel. A portion of said liquid naphtha is optionally recycled to said first gas-liquid separation vessel as previously described. Another portion of said liquid naphtha, optionally in admixture with make-up naphtha, may be recycled to the front end of the process and mixed with the stripping hydrogen-containing gas as previously described.

DESCRIPTION OF THE INVENTION

According to one aspect of this invention, a hydrocarbonaceous fuel, to be defined later, at a temperature in the range of ambient to about 500° F. is mixed with a stream of hydrogen-rich gas at a temperature in the range of ambient to about 500° F. The ratio of hydrocarbonaceous fuel to hydrogen-containing gas is in the range of about 3,000 to 60,000 standard cubic feet of hydrogen-containing gas per barrel of hydrocarbonaceous fuel (s.c.f./bbl.) and preferably from about 4,000 to about 18,000 s.c.f./bbl. One barrel equals 42 gallons.

By definition, the term "hydrocarbonaceous fuels," which are suitable feedstocks for the subject process, include various liquid hydrocarbon fuels and crudes derived from petroleum containing from about .2 to 10 weight percent of sulfur and less than 10 weight percent of naphtha having an initial atmospheric boiling point in the range of about 200 to 800° F. Typical organic sulfides which may be naturally present in the hydrocarbonaceous fuels include mercaptans and cyclic sulfides such as substituted thiophenes and benzothiophenes.

Typical hydrocarbonaceous fuels included by said definition are petroleum tar and asphalt, petroleum distillates and residua, reduced crude, crude oil or petroleum, heavy fuel oil, topped crude, and mixtures thereof and the like. Other materials which may be advantageously treated are coal tar, coal oil, pitches, crude shale oil, and tar-sand oil.

The term "hydrogen-containing gas" as used herein includes by definition substantially pure hydrogen, e.g. 90-97 volume percent H₂, a recycle hydrogen stream recovered subsequently in the process and containing at least 40 volume percent hydrogen, and hydrogen-rich gas as obtained for example by the partial oxidation of hydrocarbonaceous fuels with or without water-gas shift and with or without CO₂ removal and containing at least 40 volume percent hydrogen.

The mixture of hydrocarbonaceous fuel and hydrogen-rich gas is passed through a first externally fired tubular heater under conditions of violently turbulent flow and at a pressure in the range of about 1,000 to 6,000 p.s.i.g. The turbulence level, as defined by the ratio $\bar{\epsilon}_m/\nu$, where $\bar{\epsilon}_m$ is the average apparent viscosity and ν is the kinematic viscosity, is maintained in the range of about 25 to 100,000, suitably in the range of about 25 to 1,000, and preferably at least 150. The mixture is heated as it passes through the tubular heater to a temperature in the range of about 600 to 1,000° F. The time in the tubular heater is about 1 second to about 10 minutes and preferably about .1 minute to 1 minute.

A finely divided hydrocarbonaceous fuel suspended in hydrogen and vaporized low and intermediate boiling range materials present in the feed is produced in the tubular heater. The higher boiling hydrocarbons are subjected in said tubular heater to viscosity breaking and hydrogenation of the molecular fragments without further breakdown. Production of middle distillates boiling in the 400-700° F. range without substantial increase in lower boiling gasoline range materials and without substantial formation of normally gaseous hydrocarbons and heavy tars and coke is thereby effected. The lower boiling molecular fragments vaporize. The effluent stream from the tubular heater is introduced into the upper portion of a gas-liquid separating tower which is also referred to herein as a stripper vessel.

A separate stream comprising another portion of the aforesaid hydrogen-containing gas in admixture with supplemental naphtha is passed through a second externally fired tubular heater where the temperature of the mixture is raised to about 800 to 1,000° F. The outlet pressure of both tubular heaters is substantially the same. About 1,000 to 57,000 standard cubic feet of said mixture of hydrogen-containing gas and supplemental naphtha per barrel of the hydrocarbonaceous fuel fed to said first tubular heater is then introduced into the lower section of said stripper vessel.

All of the supplemental naphtha introduced into the hydrogen-rich gas is preferably recycle naphtha produced subsequently in the process. Optionally, make-up naphtha from an external source may be mixed with the recycle naphtha. The amount of naphtha that might be naturally present in the hydrocarbonaceous fuel is insufficient to accomplish the subject invention. Thus, the term supplemental naphtha refers to additional naphtha that must be added to the fresh hydrocarbonaceous fuel feed over and above any naphtha that may be originally contained therein. The supplemental naphtha is preferably petroleum naphtha. Petroleum naphtha is defined by American Society for Testing and Materials ASTM D288 as a generic term applied to refined, partly refined, or unrefined petroleum products and liquid products of natural gas, not less than 10 percent of which distills below 374° F. (175° C.) and not less than 95 percent of which distills below 464° F. (240° C.), when subjected to distillation in accordance with ASTM Method

D86, Test for Distillation of Petroleum Products. Suitable naphtha include Refined Solvent Naphtha as per ASTM D838-50 (1958), Crude Light Solvent Naphtha as per D839-50 (1958), and Crude Heavy Solvent Naphtha as per D840-50 (1958).

For example, a suitable supplemental naphtha has the following properties: Gravity, API°, 59.7. viscosity: centistokes at 100° F., 0.646; centistokes at 122° F., 0.578.

ASTM DISTILLATION, ° F.

	° F.
Initial boiling point at 1 atm. (IBP) -----	137
10 -----	200
20 -----	222
30 -----	234
40 -----	238
50 -----	258
60 -----	267
70 -----	277
80 -----	288
90 -----	304
95 -----	314
EP -----	357
Recovery -----	(1)

¹ 98.5 percent.

The pressure within the stripper vessel is advantageously maintained within the range of about 1,000 to 6,000 p.s.i.g. and preferably between about 1,200 to 3,200 p.s.i.g.

The liquid hydrocarbonaceous oil which separates from the vaporous hydrocarbons and hydrogen in the upper section of the stripper vessel flows downwardly in direct contact with said separate mixture of hydrogen-rich gas and vaporized naphtha which enters the lower part of the tower and flows upwardly. Cracking and viscosity breaking of the oil take place in the stripper vessel with hydrogenation of the unsaturated fragments. However, the main action of the tower is in stripping of the lighter components from the oil by the hydrogen-naphtha stream. By introducing supplemental naphtha with the hydrogen-containing gas the molecular weight of the stripping medium is increased. By this means, the stripping efficiency is increased and less hydrogen is necessary. The combined effect is to produce additional oil vapors and to reduce the amount of liquid oil that is converted into a heavy residuum. The heavy residuum contains substantially all of the metal and ash-forming constituents of the original charge oil. The weight ratio of supplemental naphtha introduced into the process by way of said second tubular heater to the fresh hydrocarbonaceous fuel feed introduced into the process by way of the first tubular heater is in the range of about 0.2 to 5.

The yield of liquid bottoms leaving the stripper vessel amounts to about 5 to 25 weight percent of the fresh hydrocarbonaceous fuel feed stock charged to the front end of the process. The actual amount of bottoms is a function of the character of the hydrocarbonaceous fuel feed introduced into the first tubular heater; the charge rate; the temperature, pressure, time in the heating coil; the temperature and pressure in the stripping tower; and the quantity of hydrogen and naphtha charged. The severity of treatment should be such as to minimize the yield of residual oil while avoiding carbon deposition within the apparatus or an appreciable quantity of fixed hydrocarbon gases.

The bottoms from the stripper vessel may be used directly as a fuel or it may be used as feed stock for the production of hydrogen-containing gas for use in the process by partial oxidation with a free oxygen-containing gas in the presence of a temperature moderator such as H₂O in the reaction zone of a free-flow noncatalytic synthesis gas generator such as described in co-assigned U.S. Pat. 2,809,104 issued to D. M. Strasser et al., at an autog-

enous temperature in the range of about 1,500 to 2,000° F. and a pressure in the range of about 1 to 250 atmospheres and preferably greater than 1,000 p.s.i.g.

The rate of hydrogen consumption in the first tubular heater and stripper vessel together is in the range of about 1 to 10 volume percent of the total supply.

The overhead from the stripper vessel at a temperature in the range of about 800 to 1,000° F. comprises a mixture of H₂, H₂S and vaporous hydrocarbons, is cooled to a temperature in the range of about 600 to 900° F., and preferably about 700 to 850° F., and then passed through a chamber containing hydrogenation catalyst. Optionally, said cooling may be effected by direct mixing with a recycle stream of liquid product produced subsequently in the process or by indirect heat exchange with recycle hydrogen, or by other conventional means.

Suitable hydrogenation catalysts comprise the oxides and/or sulfides of metals such as cobalt, molybdenum, nickel, tungsten, chromium, iron, manganese, vanadium and mixtures thereof. The catalytic materials may be used alone or may be deposited on or mixed with a support such as alumina, magnesia, silica, zinc oxide or the like. Particularly suitable catalysts are nickel tungsten sulfide, molybdenum oxide on alumina; a mixture of cobalt oxide and molybdenum oxide generally referred to as cobalt molybdate on alumina, molybdenum oxide and nickel oxide on alumina, molybdenum oxide, nickel oxide and cobalt oxide on alumina, nickel sulfide on alumina, molybdenum sulfide, cobalt sulfide and nickel sulfide on alumina. Although these catalysts are generally considered hydrogenation catalysts, a considerable amount of conversion of the heavier hydrocarbons present into lighter boiling materials takes place in the catalyst chamber, probably due at least in part to the treatment to which the feed stock has been subjected prior to its introduction into the catalyst chamber. Preferably, the hydrogenation catalyst is nickel sulfide on alumina.

The catalytic treatment is carried out at a pressure in the range of about 800 to 6,000 p.s.i.g. and preferably in excess of about 1,000 p.s.i.g. The rate of hydrogen consumption in the catalytic treating zone is about 1 to 10 volume percent of the total supply of hydrogen. The space velocity is in the range of about .4 to 10 volumes of feed per volume of catalyst per hour.

The product stream leaving the catalytic hydrogenation zone at a temperature in the range of about 700 to 850° F. is then cooled to liquefy the naphtha and other normally liquid hydrocarbons. H₂S, CO₂ and CH₄ dissolve in the liquid naphtha. The process stream is then introduced into a first gas-liquid separation vessel which may be packed with conventional packing material in the upper section. Hydrogen-containing gas leaves from the top of the tower and is recycled to the front end of the process for reuse. Preferably, a recycle stream of liquid naphtha produced subsequently in the process at a temperature in the range of about 200 to 350° F. is introduced into the top of a first gas-liquid separation vessel to scrub out any H₂S from the hydrogen-containing stream rising to the top of said tower.

The preferred weight ratio of supplemental naphtha to hydrocarbonaceous fuel in the process is in the range of about 0.2 to 3.5. Since the amount of naphtha in the hydrocarbonaceous fuel feedstock is generally less than about 10 weight percent, supplemental naphtha must be added to the stripper vessel and advantageously to said first gas-liquid separator downstream from the catalytic reactor.

A liquid stream comprising a mixture of naphtha containing H₂S, CH₄, CO₂ and hydrogen-treated and cracked liquid hydrocarbons, is removed from the bottom of the first gas-liquid separation vessel and introduced into a conventional fractionation tower for separation. The fractionation tower may be operated at a vacuum in the range of about 50 to 760 mm. or at a pressure in the range of about 0 to 6,000 p.s.i.g. Preferably, the pressure in

the fractionator may be dropped to about 75 to 200 p.s.i.g. with respect to the pressure in the first gas-liquid separation vessel so as to flash-off the tail gas from the top of the fractionator. The following streams are removed from the fractionation tower: a gaseous stream comprising principally vaporized naphtha, H₂S, H₂O and CH₄ which is removed from the top of the fractionator; and a normally liquid substantially sulfur-free product stream which is removed from the bottom of the fractionator. The overhead stream is cooled to a temperature of about 200 to 350° F. to liquefy naphtha and introduced into a second gas-liquid separation vessel. The normally gaseous components leave from the top of the second separation vessel and are sent to a conventional downstream system for sulfur recovery, e.g. Claus unit. The naphtha stream is drawn off from the second gas-liquid separation vessel and a portion is recycled to the front end of the process as said supplemental naphtha. Optionally, a second portion of the liquid naphtha is returned to the first gas-liquid separation vessel.

An advantage of the process is that all of the steps and reactions may be conducted at substantially the same pressure, less ordinary line drop. As the process stream passes through the various stages in the process, i.e. tubular heater, stripper vessel, catalytic reactor, etc., the reactants may incur only a slight pressure drop in the range of about 150-250 p.s.i. Thus, the need for intermediate compressors may be eliminated.

By means of the process of the present invention, sulfur-containing heavy oils may be converted into substantially sulfur-free middle distillates boiling in the 400 to 700° F. range without the formation of tars and coke. Yields are much greater than those obtained by conventional atmospheric vacuum distillation methods. Further, the liquid product is valuable as cracking feedstock because of its high hydrogen content and because it is substantially free from sulfur, nitrogen, and metals. In addition, the liquid product is stable, free from gum-forming constituent, and has an excellent temperature-viscosity relationship, i.e. about 100. Industrial fuels may be produced on a volume basis by the subject process having a maximum of 1.0% by weight of sulfur, thereby meeting stringent pollution control standards.

Other advantages of the process include long life of the hydrogenation catalyst, high purity of the recycle hydrogen-containing gas, and reduced hydrogen consumption.

DESCRIPTION OF THE DRAWING AND EXAMPLES

A more complete understanding of the invention may be had by reference to the accompanying schematic drawing which shows a preferred embodiment of the process of this invention. It is not intended to limit the continuous process illustrated to the particular apparatus or materials described. Quantities (on an hourly basis) have been assigned to the various streams so that the description may also serve as Example I.

Example I

10 barrels (bbls.) of heavy oil feedstock at ambient temperature in line 1, having the characteristics shown in Table I below, are mixed in line 2 with a hydrogen-containing gas mixture comprising about 8.8 thousand standard cubic feet (M s.c.f.) of substantially pure make-up hydrogen from line 3-4 and about 101.9 M s.c.f. of recycle hydrogen-containing gas from lines 39, 56 and 4. The resulting hydrogen-containing gas mixture in lines 4 and 2 is described more fully in Table I.

TABLE I.—FEED TO SYSTEM

Heavy oil feedstock (line 1):	
Gravity, ° API	15.3
Viscosity, SSF/122	268
Sulfur, wt. percent	1.86
Nitrogen, wt. percent	.65
Sediment and water	.06
Carbon, wt. percent	85.56
Hydrogen, wt. percent	11.37
Metals, parts per million (p.p.m.):	
Vanadium	125
Nickel	94
Conradson carbon residue, wt. percent	8.9
Distillation range, vol. percent recovered:	
IBP-400° F.	1.3
400-500° F.	7.7
500-700° F.	30.3
700° F.+	60.7
Hydrogen-containing gas (line 4), mole percent:	
H ₂	87.57
CO	.43
CO ₂	0.1
N ₂ +A	2.92
H ₂ S	.23
CH ₄	7.34
C ₂	.77
C ₃	.34
C ₄ +	.39
Naphtha (lines 10 and 12):	
Gravity, ° API	59.7
Viscosity, centistokes:	
At 100° F.	.646
At 122° F.	.578
ASTM distillation, ° F.:	
IBP at 1 atm.	137
10	200
20	222
30	234
40	238
50	258
60	267
70	277
80	288
90	304
95	314
EP	357
Recovery, 98.5%.	

The mixture of oil and hydrogen-containing gas in line 2 is passed through externally fired tubular heater 7 at a sufficient velocity to produce a turbulence level of about 180. The dwell time of the oil in the heater is about 30 seconds. Some thermocracking takes place in the tubular heater along with vaporization and atomization of the hydrocarbon oil and entrainment of the atomized liquid particles in the hydrogen and other gaseous materials present. The effluent stream leaves heater 7 by way of line 8 at a temperature of about 880° F. and a pressure of about 1,635 p.s.i.g., and enters at the top of stripper vessel 9.

About 30 pounds (lbs.) of supplemental make-up naphtha from an external source as described in Table I are passed through line 10 and are mixed in line 11 with about 930 lbs. of a recycle stream of supplemental naphtha from line 12. About 165.5M s.c.f. of hydrogen-containing gas from line 14 are mixed with said naphtha mixture in line 13. The resulting mixture is then passed through externally fired tubular heater 15 at a sufficient velocity to produce a turbulence level of about 180. The dwell time in heater 15 is about 30 seconds, and the pressure is about 1,700 p.s.i.g. The effluent stream leaves tubular heater 15 at a temperature of about 875° F. by way of line 20 and enters at the bottom of stripper vessel 9.

In stripper vessel 9, the stream of finely divided hydrocarbonaceous fuel suspended in hydrogen and vaporized low and intermediate boiling range materials from line 8 come in direct contact with the upflowing stream of naphtha vapor and hydrogen-containing gas. At a temperature of about 880° F. and a pressure of about 1630 p.s.i.g., cracking and viscosity breaking of the oil take place in the stripper vessel 9 along with hydrogenation of the unsaturated fragments, reaction of hydrogen with sulfur in the fuel to produce H₂S, and stripping of the lighter components from the oil.

The liquid bottoms leaving the stripper vessel 9 by way of line 21, valve 22 and line 23 amounts to about 17.2 weight percent of the oil feed stock in line 1. It has a ° API gravity of -4.8; Conradson carbon residue of 41.6 wt. percent; vanadium, 237 p.p.m.; nickel, 500 p.p.m.; and sulfur, 1.41 wt. percent. The apparent hydrogen consumption in tubular heater 7 and stripper vessel 9 is about 466 standard cubic feet per barrel (s.c.f./bbl.).

The remainder of the process stream is removed from the top of stripper vessel 9 by way of line 24 at a temperature of 865° F. This stream is then mixed in line 25 with desulfurized product oil from line 26 at a temperature of 530° F. to produce a mixed stream having a temperature of 720° F. The mixed stream is then passed through catalytic reactor 27 containing hydrogenation catalyst 28 at a space velocity of 1.68 volumes of oil per volume of catalyst per hour. Catalyst 28 comprises nickel sulfide on alumina.

Catalytic hydrogenation takes place in reactor 27 at a pressure of about 1,600 p.s.i.g. The apparent hydrogen consumption in reactor 27 is 391 s.c.f./bbl. of liquid hydrocarbon charge to line 1. The effluent stream leaves from line 29 at the bottom of reactor 27 at a temperature of 750° F. and is cooled to a temperature of 150° F. in heat exchanger 30. By this means, naphtha in the process stream is liquefied containing dissolved H₂S, CO₂, and CH₄. The process stream is then passed through line 35 into a gas-liquid separator 36 which contains conventional packing 37 in the upper section.

Optionally but preferably, about 96 lbs. of recycle liquid naphtha at a temperature of 100° F. are introduced into the top of gas-liquid separation vessel 36 by way of line 38. The naphtha flows down over the packing and scrubs any remaining H₂S from the up-flowing hydrogen-containing gases which have been separated from the naphtha and hydrocarbon oil in separator 36. The scrubbed hydrogen-containing gas stream leaves at the top of separation vessel 36 through line 39 and is recycled through lines 5, 6, 4 and also 14 to the front end of the process for reuse. Periodically, to prevent the buildup of impurities, a portion of the hydrogen-containing gas stream in line 39 is vented through line 40, valve 41, and line 42.

The hydrogen-rich gas departing from the top of gas-liquid separation vessel 36, has the following composition in mole percent:

H ₂	86.71
CO	.28
N ₂ +A	3.13
H ₂ S	.25
CH ₄	7.98
C ₂	.84
C ₃	.37
C ₄ +	.43

A mixture of liquid naphtha and hydrotreated oil is removed through line 43 at the bottom of separator 36 and is introduced into fractionator 44, which operates at a pressure of 100 p.s.i.g. Desulfurized product liquid at a temperature of 260° F. is removed through lines 45-46, valve 47 and line 48 of the bottom of fractionator 44. The product liquid has the following properties: ° API gravity, 30; viscosity, SSU at 122° F., 40; sulfur, wt. per-

cent .02; Conradson carbon residue, wt. percent .10; vanadium, p.p.m. nil; nickel, p.p.m. .04; distillation range, vol. percent recovered, IBP-400° F., 12.1; 400-500° F., 9.2; 500-700° F., 43.5; 700° F., balance. The yield is greater than 92 volume percent.

A stream of vaporized naphtha and normally gaseous materials is removed from the upper portion of fractionator 44 at a temperature of 475° F. by way of line 49 and is cooled in heat exchanger 50 to a temperature of 150° F. to liquefy the naphtha. The cooled stream passes through line 51 and into a gas-liquid separation vessel or disengager 52. By means of pump 53, liquid naphtha is recycled through lines 54, 55 and 38 into gas-liquid separator 36 to scrub H₂S from the hydrogen-containing gas-liquid separator 36 to scrub H₂S from the hydrogen-containing gas as previously described. About 930 lbs. of liquid naphtha at a temperature of 150° F. are pumped through line 12 to the front end of the process and mixed with hydrogen-containing gas, as previously described.

From line 56 at the top of disengager 52, about 3,526 cubic feet of tail gas mixture at a temperature of 150° F. are removed having the following composition in volume percent: H₂, 27.36; H₂S, 19.37; C₂+, 28.69; CH₄, 24.74; and CO₂, .05. The tail gas may be processed by conventional downstream units which separate the components for production of sulfur, e.g. by means of a Claus unit; and the tail gas may be processed further and burned as fuel gas.

At the bottom of disengager 52, any accumulated water may be separated by way of line 60, valve 61, and line 62.

Example II

Example II illustrates the effect of increasing the ratio of total pounds of supplemental naphtha which are introduced into stripper vessel 9 per pound of recycle hydrogen-containing gas. The data shown in Table 2 below indicates that for the process described in Example I, an increased rate of addition of supplemental naphtha produces a decrease in the concentration of H₂S, CH₄, and CO₂ in the hydrogen-containing recycle gas stream. The comparison is based on maximum H₂S, CH₄, and CO₂ in the recycle hydrogen-containing gas when no supplemental naphtha from an external source is introduced into the system.

TABLE 2

	Percent of no naphtha value		
	H ₂ S	CH ₄	CO ₂
Lbs. naphtha per lb. recycle gas:			
0.4.....	62	86	76
0.9.....	35	80	72
1.2.....	22	61	67
1.5.....	18	54	65
2.0.....	10	49	62

Example III

The purpose of Example III is to demonstrate the advantages of operating the subject process with additions of supplemental naphtha from an external source in the manner described in Example I, in comparison with operating without additions of supplemental naphtha from an external source. Accordingly, in Example III no supplemental naphtha from an external source is passed through stripper vessel 9, catalytic reactor 27, or gas-liquid separator 36. All other operating conditions and flow rates are substantially the same as described previously in Example I.

The composition in mole percent of the hydrogen-containing gas in line 39 is as follows:

H ₂	77.80
CO.....	.25
5 N ₂ +A.....	2.81
H ₂ S.....	1.42
CO ₂02
CH ₄	14.69
C ₂	1.53
10 C ₃67
C ₄ +.....	.77

The product liquid has the following properties: ° API gravity, 29.5; viscosity, SSU at 122° F., 54.9; sulfur, wt. percent 0.17; distillation range, vol. percent recovered, IBP-400° F., 10.9; 400-500° F., 9.3; 500-700° F., 43.0; 700° F., balance.

From the aforesaid data and that reported in Example I it may be concluded that by means of the subject invention the amounts of sulfur in the product liquid may be decreased more than 80% and the amount of H₂S in the tail gas mixture may be increased about 5%.

The process of the invention has been described generally and by example with reference to hydrocarbonaceous feedstocks and naphtha scrubbing fluids of particular compositions for purposes of clarity and illustration only. It will be apparent to those skilled in the art from the foregoing that the various modifications of the process and the materials disclosed herein can be made without departure from the spirit of the invention.

We claim:

1. A process for desulfurizing hydrocarbonaceous fuels comprising:

- (1) passing a first stream comprising a mixture of hydrogen-containing gas and said hydrocarbonaceous fuel through a tubular heater under conditions of turbulent flow, heating said mixture to a temperature in the range of about 600 to 1,000° F. in said tubular heater, and introducing the effluent stream from said tubular heater into a free-flow stripper vessel free from catalyst; simultaneously introducing a second stream comprising a gaseous mixture of hydrogen-containing gas and supplemental naphtha at a temperature in the range of about 600 to 1,000° F. into said stripper vessel in direct contact counter-current flow with said mixture of hydrogen-containing gas and hydrocarbonaceous fuel, simultaneously thermocacking and hydrotreating said hydrocarbonaceous fuel in said stripper vessel, removing an overhead process stream from said stripper vessel, and removing a heavy bottoms stream from said stripper vessel;
 - (2) hydrocracking and hydrotreating said overhead stream from the stripper vessel in (1) while in contact with a hydrocracking catalyst in a hydrocracking zone;
 - (3) cooling the effluent gas stream from (2) to liquefy the naphtha contained in said gas stream;
 - (4) introducing the process stream from (3) into a gas-liquid separating zone, separating a stream of hydrogen-containing gas from said process stream and recycling at least a portion of said separated hydrogen-containing stream to (1) as said hydrogen-containing gas;
 - (5) introducing the remainder of the process stream from (4) into a fractionation and separation zone, and separating said process stream into: a stream of normally gaseous materials selected from the group consisting of H₂S, CO₂, CH₄, and mixtures thereof; a normally liquid product stream substantially free from sulfur; and a stream of naphtha; and
 - (6) recycling at least a portion of the naphtha recovered in (5) to step (1) as said supplemental naphtha.
2. The process of claim 1 wherein steps (1) to (4) are conducted at substantially the same pressure in the

range of about 1,000 to 6,000 p.s.i.g. less ordinary line drop, and the pressure in the fractionation zone in step (5) is in the range of about 0 to 6,000 p.s.i.g.

3. The process of claim 1 wherein the standard cubic feet of hydrogen-containing gas per barrel of hydrocarbonaceous fuel of said first stream in step (1) is in the range of about 4,000 to 18,000.

4. The process of claim 1 where in step (1) the weight ratio of supplemental naphtha to hydrocarbonaceous fuel is in the range of about 0.2 to 5, and in said second stream the ratio of standard cubic feet of hydrogen-containing gas plus supplemental naphtha per barrel of hydrocarbonaceous fuel is in the range of about 1,000 to 57,000.

5. The process of claim 1 wherein the weight ratio of said stripper bottoms in step (1) to said hydrocarbonaceous fuel is in the range of about .05 to .250.

6. The process of claim 1 further provided with the steps of recycling a portion of the naphtha recovered from step (5) in liquid phase to step (4), and scrubbing said stream of separated hydrogen-containing gas in said gas-liquid separating zone with said recycled naphtha.

7. The process of claim 1 further provided with the step of mixing at least a portion of the liquid product stream from step (5) with the overhead process stream from step (1) and introducing said mixed streams into the hydrocracking zone in step (2).

8. The process of claim 1 wherein the gas-liquid separating zone in step (4) comprises at least in part a packed column.

9. The process of claim 1 wherein said hydrocarbonaceous fuel is a liquid hydrocarbon fuel comprising from about .2 to 10 weight percent sulfur and less than about 10 weight percent of naphtha having an initial atmospheric boiling point in the range of about 200 to 800° F.

10. The process of claim 9 wherein said hydrocarbonaceous fuel is selected from the group consisting of petroleum tar and asphalt, petroleum distillates and residua, reduced crude petroleum, crude oil, heavy fuel oil, topped

crude oil, coal tar, coal oil, pitches, crude shale oil, tar-sand oil, and mixtures thereof.

11. The process of claim 1 wherein said hydrogen-containing gas is selected from the group consisting of substantially pure hydrogen e.g. 90-97 volume percent H₂, a recycle hydrogen stream recovered subsequently in the process and containing at least 40 volume percent hydrogen, and hydrogen-rich gas as obtained for example by the partial oxidation of hydrocarbonaceous fuels with or without water-gas shift and CO₂ removal and containing at least 40 volume percent hydrogen, and mixtures thereof.

12. The process of claim 1 further provided with the steps of reacting at least a portion of the heavy bottoms stream from said stripper vessel of step (1) with a free oxygen containing gas in a free-flow partial oxidation synthesis gas generator so as to produce a hydrogen containing gas, and introducing said hydrogen containing gas into said stripper vessel of step (1) as at least a portion of said hydrogen-containing gas.

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